Quantum Mechanics I

Peter S. Riseborough

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1 Principles of Classical Mechanics

Newton’s laws can be reformulated in a variety of different ways. These different formulations provide more powerful and elegant methods for solving problems which involve many different variables and have a natural formulation in non-Cartesian coordinate systems, such as spherical polar coordinates. In non-Cartesian coordinate systems, vector formulations are complicated by the fact that the orthogonal directions associated with the variables depend upon the values of the generalized coordinates. The advantage of the alternate formulation of Newton’s laws is based on the fact that they involve scalar quantities rather than vector quantities, therefore, they do not require transforming the equations of motion between the Cartesian coordinates and the non-Cartesian system.

1.1 Lagrangian Mechanics

The Lagrangian approach to classical mechanics is based on a scalar quantity, the Lagrangian $L$, which depends upon the generalized coordinates and velocities.

For a Cartesian coordinate system, the coordinates are the position of the particle $x$, $y$ and $z$. The generalized velocities are the time derivatives of the coordinates, which we represent by $\dot{x}$, $\dot{y}$ and $\dot{z}$.

For a non-Cartesian coordinate system, such as spherical polar coordinates, the generalized coordinates for one particle are $r$, $\theta$, and $\phi$. The generalized velocities are the time derivatives of the coordinates, which are $\dot{r}$, $\dot{\theta}$, and $\dot{\phi}$.

The Lagrangian is given by the difference of the kinetic energy $T$ and the potential energy $V$,

$$ L = T - V $$

In Cartesian coordinates, we have

$$ L = \frac{m}{2} \dot{x}^2 + \frac{m}{2} \dot{y}^2 + \frac{m}{2} \dot{z}^2 - V(x, y, z) $$

In spherical polar coordinates, we have

$$ L = \frac{m}{2} \dot{r}^2 + \frac{m}{2} \dot{\theta}^2 + \frac{m}{2} \frac{\dot{r}^2 \sin^2 \theta \dot{\phi}^2}{\sin^2 \theta} - V(r, \theta, \phi) $$
1.1.1 Exercise 1
Find the Lagrangian for a particle in terms of spherical polar coordinates.

1.1.2 Solution 1
The Lagrangian for a particle in a potential is given by

\[ L = \frac{m}{2} \dot{r}^2 - V(r) \]  

and with \( \underline{r} \equiv (r, \theta, \phi) \) one has

\[ \dot{\underline{r}} = \frac{\partial r}{\partial \dot{r}} \frac{dr}{dt} + \frac{\partial r}{\partial \dot{\theta}} \frac{d\theta}{dt} + \frac{\partial r}{\partial \dot{\phi}} \frac{d\phi}{dt} \]  

but the three orthogonal unit vectors of spherical polar coordinates \( \hat{e}_r, \hat{e}_\theta \) and \( \hat{e}_\phi \) are defined as the directions of increasing \( r \), increasing \( \theta \) and increasing \( \phi \).
Figure 2: The Spherical Polar Coordinate System. An orthogonal set of unit vectors $\hat{e}_r$, $\hat{e}_\theta$ and $\hat{e}_\varphi$ can be constructed which, respectively, correspond to the directions of increasing $r$, $\theta$ and $\varphi$.

Thus,

\[
\frac{\partial r}{\partial r} = \hat{e}_r, \quad \frac{\partial r}{\partial \theta} = r \hat{e}_\theta, \quad \frac{\partial r}{\partial \varphi} = r \sin \theta \hat{e}_\varphi
\]

(6)

Hence

\[
\dot{\mathbf{r}} = \hat{e}_r \frac{dr}{dt} + r \hat{e}_\theta \frac{d\theta}{dt} + r \sin \theta \hat{e}_\varphi \frac{d\varphi}{dt}
\]

(7)

and as the unit vectors are orthogonal

\[
L = \frac{m}{2} \left[ \left( \frac{dr}{dt} \right)^2 + r^2 \left( \frac{d\theta}{dt} \right)^2 + r^2 \sin^2 \theta \left( \frac{d\varphi}{dt} \right)^2 \right] - V(r)
\]

(8)
For a problem involving $N$ particles, we denote the generalized coordinates by $q_i$, where $i$ runs over the $3N$ values corresponding to the 3 coordinates for each of the $N$ particles, and the generalized velocities by $\dot{q}_i$. The Lagrangian $L$ is a function of the set of $q_i$ and $\dot{q}_i$, and we shall write this as $L(q_i, \dot{q}_i)$ in which only one set of coordinates and velocities appears. However, $L$ depends on all the coordinates and velocities. The Lagrangian is the sum of the kinetic energy of the particles minus the total potential energy, which is the sum of the external potentials acting on each of the particles together with the sum of any interaction potentials acting between pairs of particles.

1.1.3 The Principle of Least Action

The equations of motion originate from an extremum principle, often called the principle of least action. The central quantity in this principle is given by the action $S$ which is a number that depends upon the specific function which is a trajectory $q_i(t')$. These trajectories run from the initial position at $t' = 0$, which is denoted by $q_i(0)$, to a final position at $t' = t$, denoted by $q_i(t)$. These two sets of values are assumed to be known, and they replace the two sets of initial conditions, $q_i(0)$ and $\dot{q}_i(0)$, used in the solution of Newton’s laws. There are infinitely many arbitrary trajectories that run between the initial and final positions. The action for any one of these trajectories, $q_i(t')$ is given by a number which has the value of the integration

$$S = \int_0^t dt' \: L(q_i(t'), \dot{q}_i(t'))$$

(9)

The value of $S$ depends on the particular choice of trajectory $q_i(t')$. The action is an example of a functional $S[q_i(t')]$ as it yields a number that depends upon the choice of a function. The extremum principle asserts that the value of $S$ is an extremum, i.e. a maximum, minimum or saddle point, for the trajectory which satisfies Newton’s laws.

To elucidate the meaning of the extremal principle, we shall consider an arbitrary trajectory $q_i(t')$ that goes between the initial and final position in a time interval of duration $t$. Since this trajectory is arbitrary, it is different from the trajectory that satisfies Newton’s laws, which as we shall show later is an extremal trajectory $q_i^{ex}(t')$. The difference or deviation between the arbitrary trajectory and the extremal trajectory is defined by

$$\delta q_i(t') = q_i(t') - q_i^{ex}(t')$$

(10)

An important fact is that this deviation tends to zero at the end points $t' = 0$ and $t' = t$ since our trajectories are defined to all run through the specific initial $q_i(0)$ and final positions $q_i(t)$ at $t' = 0$ and $t' = t$. Let us consider the variety of the plots of $\delta q_i(t')$ versus $t'$. There are infinitely many different curves. Let us concentrate on a single shape of the curve, then we can generate
Figure 3: Arbitrary trajectories $q_i(t)$ originating from a specific initial point $q_i(t_i)$ at $t = t_i$ and ending up at a specific final point $q_i(t_f)$ at time $t = t_f$.

a whole family of such curves by either increasing or decreasing the magnitude of the deviation by a factor of $\lambda$. The family of trajectories is given by

$$q_i(t') = q^{ex}_i(t') + \lambda \delta q_i(t')$$

(11)

When $\lambda = 0$ the original curve reduces to the extremal curve and when $\lambda = 1$ we recover our initial choice for the arbitrary trajectory.

If we substitute this family of trajectories into the action, we would find a number $S(\lambda)$ that depends on $\lambda$. This function $S(\lambda)$ should be extremal, i.e. either a maximum, minimum, or a saddle point as a function of $\lambda$ at $\lambda = 0$ if the action is an extremum at the extremal trajectory. The condition that the action is extremal is just that

$$\frac{\partial S}{\partial \lambda} = 0$$

(12)

at $\lambda = 0$, or the first order term in the Taylor series expansion of $S(\lambda)$ in $\lambda$ is zero.

Let us first look at a simple example of motion in one dimension, where the Lagrangian is given by

$$L(x, \dot{x}) = \frac{m}{2} \dot{x}^2 - V(x)$$

(13)
Figure 4: Arbitrary trajectories $q_i(t)$ going between specific initial and final points, and the extremal trajectory $q_i^{ex}(t)$. The deviation $\delta q_i(t)$ is defined as $\delta q_i(t) = q_i(t) - q_i^{ex}(t)$.

and let us substitute

$$x(t') = x_{ex}(t') + \lambda \delta x(t')$$

in $S(\lambda)$ and expand in powers of $\lambda$,

$$S(\lambda) = \int_0^t dt' L(x_{ex}(t'), x_{ex}'(t')) + \lambda \delta x(t') + \lambda \delta x'(t')$$

$$= \int_0^t dt' L(x_{ex}(t'), x_{ex}'(t'))$$

$$+ \lambda \int_0^t dt' \left[ \frac{\partial}{\partial x} L(x(t'), \dot{x}(t')) \right]_{\lambda=0} \delta x(t') + \lambda \frac{\partial}{\partial \dot{x}} L(x(t'), \dot{x}(t')) \left[ \lambda=0 \right] \delta \dot{x}(t')$$

$$+ O(\lambda^2)$$

(15)

In the above expression, the partial derivatives of the Lagrangian are evaluated with the extremal trajectory. Since we are only concerned with the condition that $S$ is extremal at $\lambda = 0$, the higher order terms in the Taylor expansion in $\lambda$ are irrelevant. If $S$ is to be extremal, then the extremum condition means that the term linear in $\lambda$ must vanish, no matter what our particular choice of
\( \delta x(t') \) is. Thus, we require that
\[
\int_0^t dt' \left[ \frac{\partial}{\partial x} L(x(t'), \dot{x}(t')) \right]_{\lambda=0} \delta x(t') + \frac{\partial}{\partial \dot{x}} L(x(t'), \dot{x}(t')) \left. \right|_{\lambda=0} \delta \dot{x}(t') = 0
\]
(16)
for any shape of \( \delta x(t') \). Since this expression involves both \( \delta x(t') \) and \( \delta \dot{x}(t') \), we shall eliminate the time derivative of the deviation in the second term. To do this we integrate the second term by parts, that is
\[
\int_0^t dt' \left[ \frac{\partial}{\partial \dot{x}} L(x(t'), \dot{x}(t')) \right]_{\lambda=0} \delta \dot{x}(t') = \left. \int_0^t dt' \left[ \frac{d}{d\ell'} \frac{\partial}{\partial \dot{x}} L(x(t'), \dot{x}(t')) \right]_{\lambda=0} \right|_{\lambda=0} \delta x(t')
\]
(17)
The boundary terms vanish at the beginning and the end of the time interval since the deviations \( \delta x(t') \) vanish at both these times. On substituting the expression (17) back into the term of \( S(\lambda) \) linear in \( \lambda \), one obtains
\[
\int_0^t dt' \left[ \frac{\partial}{\partial x} L(x(t'), \dot{x}(t')) \right]_{\lambda=0} \delta x(t') - \left. \left( \frac{d}{d\ell'} \frac{\partial}{\partial \dot{x}} L(x(t'), \dot{x}(t')) \right) \right|_{\lambda=0} \delta x(t') = 0
\]
(18)
This integral must be zero for all shapes of the deviation \( \delta x(t') \) if \( x_{ex}(t') \) is the extremal trajectory. This can be assured if the term in the square brackets is identically zero. This gives the equation
\[
\left. \frac{\partial}{\partial x} L(x(t'), \dot{x}(t')) \right|_{\lambda=0} = \left. \left( \frac{d}{d\ell'} \frac{\partial}{\partial \dot{x}} L(x(t'), \dot{x}(t')) \right) \right|_{\lambda=0} = 0
\]
(19)
which determines the extremal trajectory. Now using the form of the Lagrangian given in equation 13, one finds
\[
\frac{\partial V(x_{ex}(t'))}{\partial x} + m \frac{d}{d\ell'} \dot{x}(t') = 0
\]
(20)
which is identical to the equations found from Newton’s laws. Thus, the extremal principle reproduces the results obtained from Newton’s laws.

1.1.4 The Euler-Lagrange Equations
Let us now go back to the more general case with \( N \) particles, and arbitrary coordinates \( q_i \) and arbitrary Lagrangian \( L \). It is straightforward to repeat the derivation of the extremal condition and find that the equations of motion for the extremal trajectory \( q_i(t') \) reduce to the 3N equations,
\[
\left. \frac{\partial}{\partial q_i} L(q_j(t'), \dot{q}_j(t')) \right|_{\lambda=0} = \left. \left( \frac{d}{d\ell'} \frac{\partial}{\partial q_i} L(q_j(t'), \dot{q}_j(t')) \right) \right|_{\lambda=0} = 0
\]
(21)
Figure 5: Arbitrary trajectories $x(t)$ going between specific initial and final points, and the extremal trajectory $x_{ex}(t)$. The deviation $\delta x(t)$ is defined as $\delta x(t) = x(t) - x_{ex}(t)$.

where there is one equation for each value of $i$. The value of $j$ is just the dummy variable which reminds us that $L$ depends on all the coordinates and velocities. These equations are the Euler-Lagrange equations, and are a set of second order differential equations which determine the classical trajectory.

1.1.5 Generalized Momentum

The angular momentum is an example of what we call a generalized momentum. We define a generalized momentum in the same way as the components of momentum are defined for a particle in Cartesian coordinates. The generalized momentum $p_i$ conjugate to the generalized coordinate $q_i$ is given by the equation

$$p_i = \left( \frac{\partial L}{\partial \dot{q}_i} \right)$$

Thus, in a Cartesian coordinate system, we find the $x$-component of a particle’s momentum is given by

$$p_x = \left( \frac{\partial L}{\partial \dot{x}} \right) = m\dot{x}$$
Likewise, for the $y$ and $z$ components

$$p_y = \left( \frac{\partial L}{\partial \dot{y}} \right) = m\dot{y} \quad (24)$$

and

$$p_z = \left( \frac{\partial L}{\partial \dot{z}} \right) = m\dot{z} \quad (25)$$

The Euler-Lagrange equations of motion for the general case is re-written in terms of the generalized momentum as

$$\frac{\partial L}{\partial q_i} - \left( \frac{d p_i}{dt} \right) = 0 \quad (26)$$

This equation has the same form as Newton’s laws involving the rate of change of momentum on one side and the derivative of the Lagrangian w.r.t a coordinate on the other side.

### 1.1.6 Exercise 2

Find the classical equations of motion for a particle, in spherical polar coordinates.

### 1.1.7 Solution 2

The generalized momenta are found via

$$p_r = \frac{\partial L}{\partial \dot{r}} = m\dot{r}$$

$$p_{\theta} = \frac{\partial L}{\partial \dot{\theta}} = m r^2 \dot{\theta}$$

$$p_{\phi} = \frac{\partial L}{\partial \dot{\phi}} = m r^2 \sin^2 \theta \dot{\phi} \quad (27)$$
The Euler-Lagrange equations become

\[
\begin{align*}
\frac{dp_r}{dt} &= \frac{\partial L}{\partial r} = m \left( \dot{r}^2 + \sin^2 \theta \dot{\phi}^2 \right) - \frac{\partial V}{\partial r} \\
\frac{dp_\theta}{dt} &= \frac{\partial L}{\partial \theta} = m r \sin \theta \cos \theta \dot{\phi}^2 - \frac{\partial V}{\partial \theta} \\
\frac{dp_\phi}{dt} &= \frac{\partial L}{\partial \phi} = -\frac{\partial V}{\partial \phi}
\end{align*}
\]
1.2 Hamiltonian Mechanics

Hamiltonian Mechanics formulates mechanics not in terms of the generalized coordinates and velocities, but in terms of the generalized coordinates and momenta. The Hamiltonian will turn out to be the equivalent of energy. Since Newton’s laws give rise to a second order differential equation and require two initial conditions, to solve Newton’s laws we need to integrate twice. The first integration can be done with the aid of an integrating factor. For example, with

$$m \ddot{x} = -\frac{\partial V}{\partial x}$$  \hspace{1cm} (29)

the integrating factor is the velocity, $\dot{x}$. On multiplying the equation by the integrating factor and then integrating, one obtains

$$\frac{m}{2} \dot{x}^2 = E - V(x)$$  \hspace{1cm} (30)

where the constant of integration is the energy $E$. Note that the solution is now found to lie on the surface of constant energy in the two-dimensional space formed by $x$ and $\dot{x}$. The solution of the mechanical problem is found by integrating once again. The point is, once we have obtained the energy, we are closer to finding a solution of the equations of motion. Hamiltonian mechanics results in a set of first order differential equations.

The Hamiltonian, $H(q_i, p_i, t)$, is a function of the generalized coordinates $q_i$ and generalized momentum $p_i$. It is defined as a Legendre transformation of the Lagrangian

$$H(q_i, p_i, t) = \sum_i \dot{q}_i \ p_i - L(q_i, \dot{q}_i, t)$$  \hspace{1cm} (31)

The Legendre transformation has the effect of eliminating the velocity $\dot{q}_i$ and replacing it with the momentum $p_i$.

The equations of motion can be determined from the Lagrangian equations of motion. Since the Hamiltonian is considered to be a function of coordinates and momenta alone, an infinitesimal change in $H$ occurs either through an infinitesimal change in the coordinates $dq_i$, momenta $dp_i$ or, if the Lagrangian has any explicit time dependence, through $dt$,

$$dH = \sum_i \left( \frac{\partial H}{\partial q_i} \ dq_i + \frac{\partial H}{\partial p_i} \ dp_i \right) + \frac{\partial H}{\partial t} \ dt$$  \hspace{1cm} (32)

However, from the definition of $H$ one also has

$$dH = \sum_i \left( \dot{q}_i \ dp_i + p_i \ d\dot{q}_i - \frac{\partial L}{\partial \dot{q}_i} \ d\dot{q}_i - \frac{\partial L}{\partial q_i} \ dq_i \right) - \frac{\partial L}{\partial t} \ dt$$  \hspace{1cm} (33)
The terms proportional to $dq_i$ cancel as, by definition, $p_i$ is the same as $\frac{\partial L}{\partial q_i}$. Thus, we have

$$dH = \sum_i \left( \dot{q}_i \ dp_i - \frac{\partial L}{\partial q_i} \ dq_i \right) - \frac{\partial L}{\partial t} \ dt$$

The cancellation of the terms proportional to the infinitesimal change $dq_i$ is a result of the Legendre transformation, and confirms that the Hamiltonian is a function of only the coordinates and momenta. We also can use the Lagrangian equations of motion to express $\frac{\partial L}{\partial q_i}$ as the time derivative of the momentum $\dot{p}_i$.

### 1.2.1 The Hamilton Equations of Motion

We can now compare the specific form of the infinitesimal change in $H$ found above, with the infinitesimal differential found from its dependence on $p_i$ and $q_i$. On equating the coefficients of $dq_i$, $dp_i$ and $dt$, one has

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$
$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$
$$- \frac{\partial L}{\partial t} = \frac{\partial H}{\partial t}$$

The first two equations are the Hamiltonian equations of motion. The Hamiltonian equations are two sets of first order differential equations, rather than the one set of second order differential equations given by the Lagrangian equations of motion.

An example is given by motion in one dimension where

$$L = \frac{m}{2} \dot{x}^2 - V(x)$$

the momentum is given by

$$p = \frac{\partial L}{\partial \dot{x}} = m \dot{x}$$

Then, the Hamiltonian becomes

$$H = p \ \dot{x} - L$$
$$= p \ \dot{x} - \frac{m}{2} \dot{x}^2 + V(x)$$
$$= \frac{p^2}{2m} + V(x)$$
which is the same as the energy.

For a single particle moving in a central potential, we find that the Hamiltonian in spherical polar coordinates has the form

\[ H = \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} + \frac{p_\phi^2}{2mr^2\sin^2\theta} + V(r) \]  

which is the energy of the particle in spherical polar coordinates.

1.2.2 Exercise 3

Find the Hamiltonian and the Hamiltonian equations of motion for a particle in spherical polar coordinates.

1.2.3 Solution 3

Using the expression for the Lagrangian

\[ L = \frac{m}{2} \left[ \left( \frac{dr}{dt} \right)^2 + r^2 \left( \frac{d\theta}{dt} \right)^2 + r^2 \sin^2\theta \left( \frac{d\phi}{dt} \right)^2 \right] - V(r) \]  

one finds the generalized momenta

\[ p_r = \frac{\partial L}{\partial \dot{r}} = m \dot{r} \]
\[ p_\theta = \frac{\partial L}{\partial \dot{\theta}} = m r^2 \dot{\theta} \]
\[ p_\phi = \frac{\partial L}{\partial \dot{\phi}} = m r^2 \sin^2\theta \dot{\phi} \]

The Hamiltonian is given by

\[ H = p_r \dot{r} + p_\theta \dot{\theta} + p_\phi \dot{\phi} - L \]  

which on eliminating \( \dot{r}, \dot{\theta} \) and \( \dot{\phi} \) in terms of the generalized momenta, leads to

\[ H = \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} + \frac{p_\phi^2}{2mr^2\sin^2\theta} + V(r) \]

The equations of motion become

\[ \dot{r} = \frac{p_r}{m} \]
\[ \dot{\theta} = \frac{p_\theta}{mr^2} \]
\[ \dot{\phi} = \frac{p_\phi}{m r^2 \sin^2\theta} \]
and

\[
\begin{align*}
\dot{p}_r &= - \left( \frac{p_\theta^2}{m r^3} + \frac{p_\varphi^2}{m \sin^2 \theta r^3} \right) - \frac{\partial V}{\partial r} \\
\dot{p}_\theta &= - \cos \theta \frac{p_\varphi^2}{m \sin^2 \theta r^2} - \frac{\partial V}{\partial \theta} \\
\dot{p}_\varphi &= - \frac{\partial V}{\partial \varphi}
\end{align*}
\] (45)

1.2.4 Time Evolution of a Physical Quantity

Given any physical quantity \( A \) then it can be represented by a function of the all the coordinates and momenta, and perhaps explicitly on time \( t \), but not on derivatives with respect to time. This quantity \( A \) is denoted by \( A(q_i, p_i, t) \). The rate of change of \( A \) with respect to time is given by the total derivative,

\[
\frac{dA}{dt} = \sum_i \left( \frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i \right) + \frac{\partial A}{\partial t}
\] (46)

where the first two terms originate from the dynamics of the particle’s trajectory, the last term originates from the explicit time dependence of the quantity \( A \).

On substituting the Hamiltonian equations of motion into the total derivative, and eliminating the rate of change of the coordinates and momenta, one finds

\[
\frac{dA}{dt} = \sum_i \left( \frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} \right) + \frac{\partial A}{\partial t}
\] (47)

1.2.5 Poisson Brackets

The Poisson Brackets of two quantities, \( A \) and \( B \), is given by the expression

\[
[A, B]_{PB} = \sum_i \left( \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right)
\] (48)

The equation of motion for \( A \) can be written in terms of the Poisson Bracket,

\[
\frac{dA}{dt} = [A, H]_{PB} + \frac{\partial A}{\partial t}
\] (49)
From the definition, it can be seen that the Poisson Bracket is anti-symmetric
\[
[A, B]_{PB} = - [B, A]_{PB}
\] (50)
The Poisson Bracket of a quantity with itself is identically zero
\[
[A, A]_{PB} = 0
\] (51)
If we apply this to the Hamiltonian we find
\[
\frac{dH}{dt} = [H, H]_{PB} + \frac{\partial H}{\partial t}
\] (52)
\[
\frac{dH}{dt} = \frac{\partial H}{\partial t}
\]
Thus, if the Hamiltonian doesn’t explicitly depend on time, the Hamiltonian is constant. That is, the energy is conserved.

Likewise, if \( A \) doesn’t explicitly depend on time and if the Poisson Bracket between \( H \) and \( A \) is zero,
\[
[A, H]_{PB} = 0
\] (53)
one finds that \( A \) is also a constant of motion
\[
\frac{dA}{dt} = [A, H]_{PB} = 0
\] (54)
Another important Poisson Bracket relation is the Poisson Bracket of the canonically conjugate coordinates and momenta, which is given by
\[
[p_j, q_{j'}]_{PB} = \sum_i \left( \frac{\partial p_j}{\partial q_i} \frac{\partial q_{j'}}{\partial p_i} - \frac{\partial p_j}{\partial p_i} \frac{\partial q_{j'}}{\partial q_i} \right)
\] (55)
The first term is zero as \( q \) and \( p \) are independent. The last term involves the Kronecker delta function. The Kronecker delta function is given by
\[
\delta_{i,j} = 1 \text{ if } i = j
\]
\[
\delta_{i,j} = 0 \text{ if } i \neq j
\] (56)
and is zero unless \( i = j \), where it is unity. Thus, the Poisson Bracket between a generalized coordinate and its conjugate generalized momentum is −1,
\[
[p_j, q_{j'}]_{PB} = - \delta_{j,j'}
\] (57)
while the Poisson Bracket between a coordinate and the momentum conjugate to a different coordinate is zero. We can also show that

\[ [p_j, p_{j'}]_{PB} = [q_j, q_{j'}]_{PB} = 0 \quad (58) \]

These Poisson Brackets shall play an important role in quantum mechanics, and are related to the commutation relations of canonically conjugate coordinate and momentum operators.
1.3 A Charged Particle in an Electromagnetic Field

In the classical approximation, a particle of charge $q$ in an electromagnetic field represented by $E(r, t)$ and $B(r, t)$ is subjected to a Lorentz force

$$F = q \left( E(r, t) + \frac{1}{c} \dot{r} \wedge B(r, t) \right)$$

(59)

The Lorentz force acts as a definition of the electric and magnetic fields, $E(r, t)$ and $B(r, t)$ respectively. In classical mechanics, the fields are observable through the forces they exert on a charged particle.

In general, quantum mechanics is couched in the language of potentials instead of forces, therefore, we shall be replacing the electromagnetic fields by the scalar and vector potentials. The electromagnetic fields are solutions of Maxwell’s equations which not only express the fields in terms of the sources and but also form consistency conditions. The scalar and vector potentials simplify Maxwell’s equations since they automatically satisfy the consistency conditions. However, as their definitions specify that they are solutions of first-order partial differential equations, they are not unique. Despite the ambiguity in the potentials, the physical results that can be derived from them are unique.

1.3.1 The Electromagnetic Field

The electromagnetic field satisfies Maxwell’s eqns.,

$$\nabla \cdot B(r, t) = 0$$

$$\nabla \cdot E(r, t) = \rho(r, t)$$

$$\nabla \wedge E(r, t) + \frac{1}{c} \frac{\partial}{\partial t} B(r, t) = 0$$

$$\nabla \wedge B(r, t) - \frac{1}{c} \frac{\partial}{\partial t} E(r, t) = \frac{1}{c} j(r, t)$$

(60)

where $\rho(r, t)$ and $j(r, t)$ are the charge and current densities. The last two equations describe the relation between the fields and the sources. The first two equations are the source free equations and are automatically satisfied if one introduced a scalar $\phi(r, t)$ and a vector potential $A(r, t)$ such that

$$B(r, t) = \nabla \wedge A(r, t)$$

$$E(r, t) = -\nabla \phi(r, t) - \frac{1}{c} \frac{\partial}{\partial t} A(r, t)$$

(61)

In classical mechanics, the electric and magnetic induction fields, $E$ and $B$, are regarded as the physically measurable fields, and the scalar $\phi(r, t)$ and a vector potential $A(r, t)$ are not physically measurable. There is an arbitrariness in the values of the potentials $\phi(r, t)$ and $A(r, t)$ as they are defined to be the solutions of differential equations which relate them to the physically measurable
\( \mathbf{E}(\mathbf{r}, t) \) and \( \mathbf{B}(\mathbf{r}, t) \) fields. This arbitrariness is formalized in the concept of a
gauge transformation, which means that the potentials are not unique and if one
replaces the potentials by new values which involve derivatives of any arbitrary
scalar function \( \Lambda(\mathbf{r}, t) \)

\[
\phi(\mathbf{r}, t) \rightarrow \phi(\mathbf{r}, t) - \frac{1}{c} \frac{\partial}{\partial t} \Lambda(\mathbf{r}, t)
\]
\[
\mathbf{A}(\mathbf{r}, t) \rightarrow \mathbf{A}(\mathbf{r}, t) + \nabla \Lambda(\mathbf{r}, t)
\]

(62)

the physical fields, \( \mathbf{E}(\mathbf{r}, t) \) and \( \mathbf{B}(\mathbf{r}, t) \), remain the same. This transformation
is called a gauge transformation. Although the laws of physics are formulated
in terms of the gauge fields \( \phi(\mathbf{r}, t) \) and \( \mathbf{A}(\mathbf{r}, t) \), the physical results are gauge-
invariant.

### 1.3.2 The Lagrangian for a Classical Charged Particle

The Lagrangian for a classical particle in an electromagnetic field is expressed
as

\[
L = -m c^2 \sqrt{\left(1 - \frac{\mathbf{v}^2}{c^2}\right)} - q \, \phi(\mathbf{r}, t) + \frac{q}{c} \, \mathbf{A}(\mathbf{r}, t) \cdot \mathbf{\dot{r}}
\]

(63)

The canonical momentum now involves a component originating from the field
as well as the mechanical momentum

\[
P = m \, \frac{\mathbf{v}}{\sqrt{1 - \frac{\mathbf{v}^2}{c^2}}} + \frac{q}{c} \, \mathbf{A}(\mathbf{r}, t)
\]

(64)

The Lagrangian equations of motion for the classical particle are

\[
\frac{d}{dt} \left( m \, \frac{\mathbf{v}}{\sqrt{1 - \frac{\mathbf{v}^2}{c^2}}} + \frac{q}{c} \, \mathbf{A}(\mathbf{r}, t) \right) = -q \, \nabla \phi(\mathbf{r}, t) + \frac{q}{c} \, \nabla \left( \mathbf{\dot{r}} \cdot \mathbf{A}(\mathbf{r}, t) \right)
\]

(65)

where the time derivative is a total derivative. The total derivative of the vector
potential term is written as

\[
\frac{d}{dt} \mathbf{A}(\mathbf{r}, t) = \frac{\partial}{\partial t} \mathbf{A}(\mathbf{r}, t) + \mathbf{\dot{r}} \cdot \nabla \mathbf{A}(\mathbf{r}, t)
\]

(66)

as it relates the change of vector potential experienced by a moving particle.
The change of vector potential may occur due to an explicit time dependence
of \( \mathbf{A}(\mathbf{r}, t) \) at a fixed position, or may occur due to the particle moving to a new
position in a non-uniform field \( \mathbf{A}(\mathbf{r}, t) \).
1.3.3 Exercise 4

Show that these equations reduce to the relativistic version of the equations of motion with the Lorentz force law

\[ \frac{d}{dt} \left( m \dot{r} \frac{1}{\sqrt{1 - \frac{\dot{r}^2}{c^2}}} \right) = q \left( E(r, t) + \frac{1}{c} \dot{r} \wedge B(r, t) \right) \]  

(67)

1.3.4 Solution 4

The Euler-Lagrange equation is of the form

\[ \frac{d}{dt} \left( m \dot{r} \frac{1}{\sqrt{1 - \frac{\dot{r}^2}{c^2}}} + \frac{q}{c} A(r, t) \right) = -q \nabla \phi(r, t) + \frac{q}{c} \nabla \left( \dot{r} \cdot A(r, t) \right) \]  

(68)

On substituting the expression for the total derivative of the vector potential

\[ \frac{d}{dt} A(r, t) = \frac{\partial}{\partial t} A(r, t) + \dot{r} \cdot \nabla A(r, t) \]  

(69)

one obtains the equation

\[ \frac{d}{dt} \left( m \dot{r} \frac{1}{\sqrt{1 - \frac{\dot{r}^2}{c^2}}} \right) = -q \nabla \phi(r, t) - \frac{q}{c} \frac{\partial}{\partial t} A(r, t) \]

\[ + \frac{q}{c} \nabla \left( \dot{r} \cdot A(r, t) \right) - \frac{q}{c} \left( \dot{r} \cdot \nabla \right) A(r, t) \]  

(70)

The last two terms can be combined to yield

\[ \frac{d}{dt} \left( m \dot{r} \frac{1}{\sqrt{1 - \frac{\dot{r}^2}{c^2}}} \right) = -q \nabla \phi(r, t) - \frac{q}{c} \frac{\partial}{\partial t} A(r, t) \]

\[ + \frac{q}{c} \dot{r} \wedge \left( \nabla \wedge A(r, t) \right) \]  

(71)

The first two terms on the right hand side are identifiable as the expression for the electric field \( E(r, t) \) and the last term involving the curl \( A(r, t) \) is recognized as involving the magnetic induction field \( B(r, t) \) and, therefore, comprises the magnetic component of the Lorentz Force Law.
Despite the fact that the Lagrangian of a charged particle depends on the
gauge fields and, therefore, changes form under a gauge transformation, the
classical equations of motion are gauge invariant. The equations of motion are
gauge invariant since they only dependent on the electromagnetic fields $E(r, t)$
and $B(r, t)$. The gauge invariance of the equations of motion can be seen in a
different way, that is by directly applying a gauge transformation to the action $S$. Under a gauge transformation

$$\phi(r, t) \rightarrow \phi(r, t) - \frac{1}{c} \frac{\partial}{\partial t} \Lambda(r, t)$$

$$A(r, t) \rightarrow A(r, t) + \nabla \Lambda(r, t)$$

(72)

the Lagrangian $L$ of a particle with charge $q$

$$L = \frac{m}{2} \dot{r}^2 - q \phi(r, t) + \frac{q}{c} A(r, t) \cdot \dot{r}$$

(73)

transforms to

$$L \rightarrow L' = L + \frac{q}{c} \left( \frac{\partial}{\partial t} \Lambda(r, t) + \nabla \Lambda(r, t) \cdot \dot{r} \right)$$

(74)

However, the term proportional to $q$ is recognized as being a total derivative
with respect to time. That is, if one considers $r$ to have the time-dependence $r(t)$ of any trajectory connecting the initial and final position of the particle, then

$$L \rightarrow L' = L + \frac{q}{c} \frac{d}{dt} \Lambda(r(t), t)$$

(75)

where the derivative is evaluated over a trajectory of the particle. Hence, under
a gauge transformation, the action changes from $S$ to $S'$, where

$$S' = \int_{t_i}^{t_f} L(r, \dot{r}) + \frac{q}{c} \int_{t_i}^{t_f} dt \frac{d}{dt} \Lambda(r(t), t)$$

$$= S + \frac{q}{c} \left( \Lambda(r_{tf}, t_f) - \Lambda(r_{ti}, t_i) \right)$$

(76)

which only depends on the end-points and not on the path that was chosen.
Thus, the gauge transformation only adds a constant term to the action and
the trajectory identified by extremal principle is unaffected by the gauge transform-

### 1.3.5 The Hamiltonian of a Classical Charged Particle

The Hamiltonian for a charged particle is found from

$$H = p \cdot \dot{r} - L$$

(77)
which, with the relation between the momentum and the mechanical momentum,

\[ p - \frac{q}{c} A(r, t) = m \frac{\hat{r}}{\sqrt{1 - \frac{\hat{r}^2}{c^2}}} \quad (78) \]

leads to

\[ H = \sqrt{\left( c^2 \left( p - \frac{q}{c} A(r, t) \right) \right)^2 + m^2 c^4} + q \phi(r, t) \quad (79) \]

The presence of the electromagnetic field results in the two replacements

\[ \begin{align*}
  p & \rightarrow p - \frac{q}{c} A(r, t) \\
  H & \rightarrow H - q \phi(r, t)
\end{align*} \quad (80) \]

An electromagnetic field is often incorporated in a Hamiltonian describing free charged particles through these two replacements. These replacements retain relativistic invariance as both the pairs \( E \) and \( p \) and \( \phi(r, t) \) and \( A(r, t) \) form four vectors. This procedure of including an electromagnetic field is based on what is called the minimal coupling assumption. The non-relativistic limit of the Hamiltonian is found by expanding the square root in powers of \( \frac{p^2}{m^2 c^2} \) and neglecting the rest mass energy \( m c^2 \) results in the expression

\[ H = \frac{1}{2m} \left( p - \frac{q}{c} A(r, t) \right)^2 + q \phi(r, t) \quad (81) \]

which forms the basis of the Hamiltonian used in the Schrödinger equation.

---

### 1.3.6 Exercise 5

Derive the Hamiltonian for a charged particle in an electromagnetic field.

### 1.3.7 Solution 5

The Lagrangian is given by

\[ L = -m c^2 \sqrt{1 - \frac{\hat{r}^2}{c^2}} - q \phi(r, t) + \frac{q}{c} \hat{r} \cdot A(r, t) \quad (82) \]

so the generalized momentum \( p \) is given by

\[ p - \frac{q}{c} A(r, t) = \frac{m \hat{r}}{\sqrt{1 - \frac{\hat{r}^2}{c^2}}} \quad (83) \]
and so on inverting this one finds

\[ \frac{\mathbf{\hat{r}}}{c} = \frac{\left( \mathbf{p} - \frac{q}{c} A(\mathbf{r}, t) \right)}{\sqrt{m^2 c^2 + \left( \mathbf{p} - \frac{q}{c} A(\mathbf{r}, t) \right)^2}} \quad (84) \]

and

\[ 1 - \frac{\mathbf{\hat{r}}^2}{c^2} = \frac{m^2 c^2}{m^2 c^2 + \left( \mathbf{p} - \frac{q}{c} A(\mathbf{r}, t) \right)^2} \quad (85) \]

The Hamiltonian is then found from the Legendre transformation

\[
H = \mathbf{p} \cdot \mathbf{\hat{r}} - L \\
= \left( \mathbf{p} - \frac{q}{c} A(\mathbf{r}, t) \right) \cdot \mathbf{\hat{r}} + m c^2 \sqrt{1 - \frac{\mathbf{\hat{r}}^2}{c^2} + q \phi(\mathbf{r}, t)} \\
= c \sqrt{m^2 c^2 + \left( \mathbf{p} - \frac{q}{c} A(\mathbf{r}, t) \right)^2} + q \phi(\mathbf{r}, t) \quad (86)
\]

On expanding the quadratic kinetic energy term, one finds the Hamiltonian has the form of a sum of the unperturbed Hamiltonian and an interaction Hamiltonian \( H_{\text{int}} \),

\[
H = \left( \frac{\mathbf{p}^2}{2m} + q \phi(\mathbf{r}, t) \right) + H_{\text{int}} \quad (87)
\]

The interaction \( H_{\text{int}} \) couples the particle to the vector potential

\[
H_{\text{int}} = -\frac{q}{2mc} \left( \mathbf{p} \cdot A(\mathbf{r}, t) + A(\mathbf{r}, t) \cdot \mathbf{p} \right) + \frac{q^2}{2mc^2} A^2(\mathbf{r}, t) \quad (88)
\]

where the first term linear in \( A \) is the paramagnetic coupling and the last term quadratic in \( A^2 \) is known as the diamagnetic interaction. For a uniform static magnetic field \( B(\mathbf{r}, t) = B \), one possible form of the vector potential is

\[
A(\mathbf{r}) = -\frac{1}{2} \mathbf{r} \wedge B \quad (89)
\]

The interaction Hamiltonian has the form

\[
H_{\text{int}} = +\frac{q}{2mc} \left( \mathbf{r} \wedge B \right) \cdot \mathbf{p} + \frac{q^2}{8mc^2} \left( \mathbf{r} \wedge B \right)^2 \quad (90)
\]
The first term can be written as the ordinary Zeeman interaction between the orbital magnetic moment and the magnetic field

\[ H_{int} = -\frac{q}{2 mc} (B \cdot L) + \frac{q^2}{8 m c^2} (r \wedge B)^2 \]  

(91)

where the orbital magnetic moment \( \mathbf{M} \) is related to the orbital angular momentum via

\[ \mathbf{M} = +\frac{q}{2 mc} L \]  

(92)

Hence, the ordinary Zeeman interaction has the form of a dipole interaction

\[ H_{\text{Zeeman}} = -\mathbf{M} \cdot \mathbf{B} \]  

(93)

Figure 6: A particle with charge \( q \) and angular momentum \( L \), possesses a magnetic dipole moment \( \mathbf{M} \) given by \( \mathbf{M} = +\frac{q}{2 mc} L \).

Elementary particles such as electrons have another form of magnetic moment and angular momentum which is intrinsic to the particle, and is not connected to any physical motion of the particle. The intrinsic angular momentum of elementary particles is known as spin.

There are two general approaches that can be taken to Quantum Mechanics. One is the path integral approach which was first developed by Dirac and then...
popularized by Feynmann. This approach is based on the use of the Lagrangian formulation of classical mechanics. The other approach which is more common, and is the one that we shall follow exclusively, is based on the Hamiltonian formulation of classical mechanics.
2 Failure of Classical Mechanics

Classical Mechanics fails to correctly describe some physical phenomena. This first became apparent at the atomic level. Historically, the failure of classical mechanics was first manifested after Rutherford’s discovery of the structure of the atom. Classically, an electron orbiting around a charged nucleus should continuously radiate energy according to Maxwell’s Electromagnetic Theory. The radiation leads to the electron experiencing a loss of energy, and thereby continuously reducing the radius of the electrons orbit. Thus, the atom becomes unstable as the electron spirals into the nucleus. However, it is a well established experimental fact that atoms are stable and that the atomic energy levels have discrete values for the energy. The quantization of the energy levels is seen through the Franck-Hertz experiment, which involves inelastic collisions between atoms. Other experimental evidence for the quantization of atomic energy levels is given by the emission and absorption of electromagnetic radiation. For example, the series of dark lines seen in the transmitted spectrum when light, with a continuous spectrum of wavelengths, falls incident on hydrogen gas is evidence that the excitation spectrum consists of discrete energies. Niels Bohr discovered that the excitation energy $\Delta E$ and the angular frequency of the light $\omega$ are related via

$$\Delta E = \hbar \omega$$

The quantity $\hbar$ is known as Planck’s constant and has the value of

$$\hbar = 1.0545 \times 10^{-34} \text{ J s}$$

$$= 0.65829 \times 10^{-15} \text{ eV s}$$

The Balmer, Lyman and Paschen series of electromagnetic absorption by hydrogen atoms establishes that $\Delta E$ takes on discrete values.

Another step in the development of quantum mechanics occurred when Louis de Broglie postulated wave particle duality, namely that entities which have the attributes of particles also possess attributes of waves. This is formalized by the relationships

$$E = \hbar \omega$$

$$p = \hbar k$$

The de Broglie relations were verified by Davisson and Germer in their experiments in which a beam of electrons were placed incident on the surface of a crystalline solid, and the reflected beam showed a diffraction pattern indicative of the fact that the electrons have a wave length $\lambda$. The diffraction condition relates the angle of the diffracted beam to the ratio of the separation between the planes of atoms and the wavelength $\lambda$. Furthermore, the diffraction condition showed a variation with the particle’s energies which is consistent with the wavelength momentum relation.
2.1 Semi-Classical Quantization

The first insight into quantum phenomena came from Niels Bohr, who imposed an additional condition on Classical Mechanics\(^1\). This condition, when imposed on systems where particles undergo periodic orbits, reduces the continuous values of allowed energies to a set of discrete energies. This semi-classical quantization condition is written as

\[
\oint p_i \, dq_i = n_i \, h
\]

where \(p_i\) and \(q_i\) are the canonically conjugate momentum and coordinates of Lagrangian or Hamiltonian Mechanics, and \(n_i\) is an integer from the set \((0,1,2,3,4,\ldots,\infty)\) and \(h\) is a universal constant. The integration is over one period of the particle’s orbit in phase space\(^2\). The discrete values of the excitation energies found for the hydrogen atom produces reasonably good agreement with the excitation energies found for the absorption or emission of light from hydrogen gas.

2.1.1 Exercise 6

Assuming that electrons move in circular orbits in the Coulomb potential due to a positively charged nucleus, (of charge \(Z \, e\)), find the allowed values of the energy when the semi-classical quantization condition is imposed.

2.1.2 Solution 6

The Lagrangian \(L\) is given in terms of the kinetic energy \(T\) and the scalar electrostatic potential \(V\) by \(L = T - V\). Then in spherical polar coordinates \((r,\theta,\varphi)\), one finds the Lagrangian

\[
L = \frac{m \, r^2}{2} + \frac{m \, r^2 \, \dot{\theta}^2}{2} + \frac{m \, r^2 \, \sin^2 \theta \, \dot{\varphi}^2}{2} + \frac{Z \, e^2}{r}
\]

The Euler-Lagrange equation for the radius \(r\) is given by

\[
\frac{\partial L}{\partial r} = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{r}} \right)
\]
\[ m r \dot{\theta}^2 + m r \sin^2 \theta \dot{\phi}^2 - \frac{Z e^2}{r^2} = m \ddot{r} \]  

while the equation of motion for the polar angle \( \theta \) is given by

\[
\frac{\partial L}{\partial \dot{\theta}} = \frac{d}{dt} \left( \frac{\partial L}{\partial \theta} \right)
= \frac{m r^2}{2} \sin 2 \theta \dot{\phi}^2 = m \frac{d}{dt} \left( r^2 \dot{\theta} \right)
\]

and finally we find

\[
\frac{\partial L}{\partial \phi} = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\phi}} \right)
0 = m \frac{d}{dt} \left( r^2 \sin^2 \theta \dot{\phi} \right)
\]

According to the assumption, the motion is circular, which we choose to be in the equatorial plane \( r = a, \theta = \frac{\pi}{2} \). Thus, one has

\[
\frac{Z e^2}{a^2} = m a \dot{\phi}^2
0 = m a^2 \ddot{\phi}
\]

Hence, we find that the angular velocity is a constant, \( \dot{\phi} = \omega \).

To impose the semi-classical quantization condition we need the canonical momentum. The canonical momenta are given

\[
p_r = \frac{\partial L}{\partial \dot{r}} = 0
p_\theta = \frac{\partial L}{\partial \dot{\theta}} = 0
p_\phi = \frac{\partial L}{\partial \dot{\phi}} = m r^2 \sin^2 \theta \dot{\phi} = m a^2 \omega
\]

The semi-classical quantization condition becomes

\[
\oint p_\phi \, d\phi = m a^2 \omega 2\pi = n_\phi \hbar
\]

From the above one has the two equations

\[
m a^2 \omega = n_\phi \hbar
\frac{Z e^2}{a^2} = m a \omega^2
\]

On solving these for the Bohr radius \( a \) and angular frequency \( \omega \), one finds

\[
\omega = \frac{Z^2 e^4}{n_\phi^3 \hbar^3}
a = \frac{n_\phi^2 \hbar^2}{Z e^2 m}
\]
Substituting these equations in the expression for the energy $E$, one finds the expression first found by Bohr

$$ E = \frac{m a^2 \omega^2}{2} - \frac{Z e^2}{a} $$

$$ E = -\frac{Z e^2}{2a} $$

$$ E = -\frac{m Z^2 e^4}{2 n_p^2 \hbar^2} $$

This agrees with the exact (non-relativistic) quantum mechanical expression for the energy levels of electrons bound to a $H$ ion.

2.1.3 Exercise 7

Find the energy of a one-dimensional simple Harmonic oscillator, of mass $m$ and frequency $\omega$, when the semi-classical quantization condition is imposed.

2.1.4 Solution 7

The Hamiltonian is given by

$$ H(p, q) = \frac{p^2}{2m} + \frac{m \omega^2 q^2}{2} $$

Hamilton’s equations of motions are

$$ \dot{p} = -\frac{\partial H}{\partial q} = -m \omega^2 q $$

$$ \dot{q} = +\frac{\partial H}{\partial p} = \frac{p}{m} $$

Thus, we have the equation of motion

$$ \ddot{q} + \omega^2 q = 0 $$

which has the solution in the form

$$ q(t) = A \sin(\omega t + \phi) $$

$$ p(t) = m \omega A \cos(\omega t + \phi) $$
The semi-classical quantization condition becomes
\[
\oint p(t) \, dq(t) = m \, \omega \, A^2 \int_0^{2\pi} d\varphi \, \cos^2 \varphi
\]
\[
= m \, \omega \, A^2 \, 2 \pi = n \, \hbar
\]

Thus, we find \( A^2 = \frac{2 \, n \hbar}{m \, \omega} \) where \( \hbar = \frac{\hbar}{2\pi} \) and the energy becomes
\[
E = H(p, q) = \frac{m \, \omega^2 \, A^2}{2} = n \, \hbar \, \omega
\]

This should be compared with the exact quantum mechanical result \( E = \hbar \omega \, (n + \frac{1}{2}) \). The difference between these results become negligible for large \( n \). That is for a fixed Energy \( E \), the results approach each other in the limit of large \( n \) or equivalently for small \( \hbar \). This is example is illustrative of the correspondence principle, which states that Quantum Mechanics, should closely approximate Classical Mechanics where Classical Mechanics is known to provide an accurate description of nature, and that this in this limit \( \hbar \) can be considered to be small.
3 Principles of Quantum Mechanics

The Schrödinger approach to Quantum Mechanics is known as wave mechanics. The Schrödinger formulation is in terms of states of a system which are represented by complex functions defined in Euclidean space, $\Psi(r)$ known as wave functions and measurements are represented by linear differential operators. The Schrödinger approach, though most common is not unique. An alternate approach was pursued by Heisenberg, in which the state of the system are represented by column matrices and measurements are represented by square matrices. This second approach is known as Heisenberg’s matrix mechanics. These two approaches were shown to be equivalent by Dirac, who developed an abstract formulation of Quantum Mechanics using an abstract representation of states and operators.

We shall first consider the system at a fixed time $t$, say $t = 0$. The wave function, $\Psi(r)$, represents a state of a single particle at that instant of time, and has a probabilistic interpretation. Consider an ensemble of $N$ identical and non-interacting systems, each of which contains a measurement apparatus and a single particle. Each measurement apparatus has its own internal reference frame with its own origin. A measurement of the position $r$ (referenced to the coordinate system attached to the measurement apparatus) is to be made on each particle in the ensemble. Just before the measurements are made, each particle is in a state represented by $\Psi(r)$. Measurements of the positions of each particle in the ensemble will result in a set of values of $r$ that represents points in space, referenced w.r.t. the internal coordinate system. The probability that a measurement of the position $r$ of a particle will give a value in the infinitesimal volume $d^3r$ containing the point $r$, is given by

$$P(r) \ d^3r = |\Psi(r)|^2 \ d^3r \quad (114)$$

Thus, $P(r) \ d^3r$ is the probability of finding the particle in the infinitesimal volume $d^3r$ located at $r$. The probability is directly proportional to the size of the volume $d^3r$, and $P(r) = |\Psi(r)|^2$ is the probability density. Since the particle is somewhere in three-dimensional space, the probability is normalized such that

$$\int |\Psi(r)|^2 \ d^3r = 1 \quad (115)$$

This normalization condition will have to be enforced on the wave function if it is to represent a single-particle state. The normalization condition must be true for all times, if the particle number is conserved.\(^4\)

\(^3\)Alternatively, instead of considering an ensemble of identical systems, one could consider performing $N$ successive measurements on a single system. However, before each successive measurement is made, one would have to reset the initial condition. That is, the system should be prepared so that, just before each measurement is made, the particle is in the state described by $\Psi(r)$.

\(^4\)For well-behaved functions, the normalization condition implies that $|\Psi(r)|^2$ vanishes as $|r| \to \infty$. 

38
Given two states, $\Psi(r)$ and $\Phi(r)$, one can define an inner product or overlap matrix element as the complex constant given by

$$\int d^3r \, \Phi^*(r) \, \Psi(r)$$

where the integration runs over all volume of three-dimensional space. It should be noted that inner product of two wave functions depends on the order that the wave functions are specified. If the inner product is taken in the opposite order, one finds

$$\int d^3r \, \Psi^*(r) \, \Phi(r) = \left( \int d^3r \, \Phi^*(r) \, \Psi(r) \right)^*$$

which is the complex conjugate of the original inner product. The normalization of the wave function $\Psi(r)$ just consists of the inner product of the wave function with itself. The interpretation of the squared modulus of the wave function as a probability density requires that the normalization of a state is unity.

We should note that if all observable quantities for a state always involve the wave function times its complex conjugate, then the absolute phase of the wave function is not observable. Only phase differences are measurable. Therefore, it is always possible to transform a wave function by changing its phase

$$\Psi(r) \to \Psi'(r) = \exp \left[ \frac{i \Lambda(r)}{\hbar} \right] \Psi(r)$$

where $\Lambda(r)$ is an arbitrary real function.
3.1 The Principle of Linear Superposition

In quantum mechanics, a measurement of a physical quantity of a single particle which is in a unique state will result in a value of the measured quantity that is one of a set of possible results \( a_n \). Repetition of the measurement on a particle in exactly the same initial state may yield other values of the measured quantity (such as \( a_m \)). The probability distribution for the various results \( a_n \) is governed by the particular state of the system that the measurement is being performed on.

This suggests that a state of a quantum mechanical system, at any instant, can be represented as a superposition of states corresponding to the different possible results of the measurement. Let \( \Phi_n(\vec{r}) \) be a state such that a measurement of \( A \) on the state will definitely give the result \( a_n \). The simplest way of making a superposition of states is by linearly adding multiples of the wave functions \( \Phi_n(\vec{r}) \) corresponding to the possible results.

Thus, the principle of linear superposition can be stated as

\[
\Psi(\vec{r}) = \sum_n C_n \Phi_n(\vec{r})
\]

where the expansion coefficients \( C_n \) are complex numbers. The expansion coefficients can be determined from a knowledge of the wave function of the state \( \Psi(\vec{r}) \) and the set of functions, \( \Phi_n(\vec{r}) \), representing the states in which a measurement of \( A \) is known to yield the result \( a_n \). The expansion coefficients \( C_n \) are related to the probability that the measurement on the state \( \Psi(\vec{r}) \) results in the value \( a_n \).

The principle of linear superposition of the wave function can lead to interference in the results of measurements. For example, the results of a measurement of the position of the particle \( \vec{r} \), leads to a probability distribution \( P(\vec{r}) \) according to

\[
P(\vec{r}) \; d^3\vec{r} = |\Psi(\vec{r})|^2 \; d^3\vec{r} = \sum_{n,m} C^*_m C_n \Phi^*_m(\vec{r}) \Phi_n(\vec{r}) \; d^3\vec{r}
\]

On isolating the terms with \( n = m \), one finds terms in which the phases of the wave functions \( \Phi_n(\vec{r}) \) and the phases of the complex numbers \( C_n \) separately cancel. The remaining terms, in which \( n \neq m \), represent the interference terms. Thus

\[
P(\vec{r}) \; d^3\vec{r} = \sum_n |C_n|^2 \; |\Phi_n(\vec{r})|^2 + \sum_{n \neq m} C^*_m C_n \Phi^*_m(\vec{r}) \Phi_n(\vec{r}) \; d^3\vec{r}
\]

The coefficient \( |C_n|^2 \) is the probability that the state represented by \( \Psi(\vec{r}) \) is in the state \( n \).
As an example, consider a state which is in a superposition of two states each of which represents a state of definite momentum, \( \mathbf{p} = \hbar \mathbf{k} \) and \( \mathbf{p} = -\hbar \mathbf{k} \).

The forward and backward travelling states are

\[
\Phi_k(r) = C_k \exp \left[ + i \frac{\mathbf{k} \cdot \mathbf{r}}{2} \right] \\
\Phi_{-k}(r) = C_{-k} \exp \left[ - i \frac{\mathbf{k} \cdot \mathbf{r}}{2} \right]
\]

These states are not normalizable and, therefore, each state must represent beams of particles with definite momentum in which the particles are uniformly distributed over all space. Since the integral \( \int |\Psi(r)|^2 d^3r \to \infty \), the beam must be considered to contain an infinite number of particles.

The probability densities or intensities of the two independent beams are given by

\[
P_k(r) = |\Phi_k(r)|^2 = |C_k|^2 \\
P_{-k}(r) = |\Phi_{-k}(r)|^2 = |C_{-k}|^2
\]

We shall assume that these beams have the same intensities, that is \( |C_{-k}|^2 = |C_{+k}|^2 \). Then, in this case the wave function can be expressed in terms of the phases of \( C_{\pm} = |C| \exp[i \delta_{\pm}] \). When the beams are superimposed, the state is described by the wave function

\[
\Psi(r) = |C| \exp \left[ i \frac{(\delta_+ + \delta_-)}{2} \right] \\
\times \left( \exp \left[ + i \left( \mathbf{k} \cdot \mathbf{r} + \frac{(\delta_+ - \delta_-)}{2} \right) \right] + \exp \left[ - i \left( \mathbf{k} \cdot \mathbf{r} + \frac{(\delta_+ - \delta_-)}{2} \right) \right] \right)
\]

This state is a linear superposition and has a probability density for finding the particle at \( \mathbf{r} \) given by \( P(r) \) where

\[
P(r) = 4 |C|^2 \cos^2 \left( \frac{\mathbf{k} \cdot \mathbf{r} + (\delta_+ - \delta_-)}{2} \right)
\]

Thus, the backward and forward travelling beam interfere, the superposition gives rise to consecutive planes of maxima and minima. The maxima are located at

\[
\mathbf{k} \cdot \mathbf{r} + \frac{(\delta_+ - \delta_-)}{2} = \pi n
\]

and the minima are located at

\[
\mathbf{k} \cdot \mathbf{r} + \frac{(\delta_+ - \delta_-)}{2} = \frac{\pi}{2} \left( 2n + 1 \right)
\]
There is a strong analogy between Quantum Mechanics and Optics. The wave function $\Psi(r, t)$ plays the role corresponding to the electric field $E(r, t)$. Both the wave function and the electric field obey the principle of linear superposition. The probability density of finding the particle at point $r$, $|\Psi(r, t)|^2$, plays the role of the intensity of light, $I$, which is proportional to $|E(r, t)|^2$. In fact, the intensity of light is just proportional to the probability density of finding a photon at the point $r$. The phenomenon of interference occurs in Quantum Mechanics and also in Optics. The analogy between Quantum Mechanics and Optics is not accidental, as Maxwell’s equations are intimately related to the “Schrödinger equation” for a massless particle with intrinsic spin $S = 1$. 
3.2 Wave Packets

By combining momentum states with many different values of the momentum, one can obtain states in which the particle is essentially localized in a finite volume. These localized states are defined to be wave packets. Wave packets are the closest one can get to a classical state of a free particle, which has a well defined position and momentum. For a quantum mechanical wave packet, the distribution of results for measurements of the position and momentum are sharply peaked around the classical values. The wave function can be expressed as a Fourier transform

\[ \Psi(r) = \left( \frac{1}{2\pi} \right)^{3/2} \int d^3k \, \Phi(k) \exp \left[ + i \cdot k \cdot r \right] \]  \hspace{1cm} (128)

where \( \Phi(k) \) is related to the momentum probability distribution function. Since the exponential factor represents states of different momenta, this relation is an example of how a wave function can be expanded in terms of states corresponding to the various possible results of a physical measurement. The momentum

\footnote{This is an example of the principle of linear superposition, in which the discrete variable \( n \) has been replaced by a Riemann sum over the continuous variable \( k \) and the expansion coefficients \( C_n \) are proportional to \( \Phi(k) \).}
probability distribution function is related to the wave vector probability distribution function \( P_k(k) \), defined by

\[
P_k(k) \, d^3k = |\Phi(k)|^2 \, d^3k
\]  

The function \( \Phi(k) \) can be determined from knowledge of \( \Psi(r) \) from the inverse relation

\[
\Phi(k) = \left( \frac{1}{2\pi} \right)^3 \int d^3r \, \Psi(r) \, \exp \left[ -i \, k \cdot r \right]
\]  

These results are from the mathematical theory of Fourier Transformations. The consistency of the Fourier Transform with the Inverse Fourier Transform can be seen by combining them via

\[
\Psi(r) = \left( \frac{1}{2\pi} \right)^3 \int d^3k \, \Phi(k) \, \exp \left[ +i \, k \cdot r \right]
\]  

(131)

together with the representation of the three-dimensional Dirac delta function

\[
\delta^3(r - r') = \left( \frac{1}{2\pi} \right)^3 \int d^3k \, \exp \left[ i \, k \cdot (r - r') \right]
\]  

(132)

On inserting the integral representation of the Dirac delta function eqn(132) into eqn(131), one finds an equation which is the formal definition of the Dirac delta function

\[
\Psi(r) = \int d^3r' \, \Psi(r') \, \delta^3(r - r')
\]  

(133)

That equation (132) provides a representation of the three-dimensional Dirac delta function can by seen directly by factorizing it into the product of three independent one-dimensional delta functions as

\[
\delta^3(r - r') = \delta(x - x') \, \delta(y - y') \, \delta(z - z')
\]  

(134)

and then comparing with the right hand side which can also be factorized into three independent one-dimensional integrals. Each factor in the three-dimensional delta function of eqn(132) can be replaced by the representation of the one-dimensional delta function as a limit of a sequence of Lorentzian functions of width \( \epsilon \),

\[
\delta(x - x') = \lim_{\epsilon \to 0} \frac{1}{\pi} \frac{\epsilon}{(x - x')^2 + \epsilon^2}
\]  

(135)

The sequence of function is shown in fig(8). Then on evaluating the integrations over each of the one-dimensional variables in the right hand side of eqn(132)
and using the replacement \((x - x') \rightarrow (x - x') \pm i \epsilon\) needed to keep the integral convergent, one finds that each of the three factors have the same form

\[
\begin{align*}
\frac{1}{2 \pi} \lim_{L \to \infty} \int_{-L}^{+L} dk \exp \left[ i k (x - x') \right] &= \frac{1}{2 \pi} \lim_{L \to \infty} \left( \int_{0}^{+L} dk \exp \left[ i k (x - x') - \epsilon k \right] + \int_{-L}^{0} dk \exp \left[ i k (x - x') + \epsilon k \right] \right) \\
&= \frac{1}{2 \pi} \left( - \frac{1}{i (x - x') - \epsilon} + \frac{1}{i (x - x') + \epsilon} \right) \\
&= \lim_{\epsilon \to 0} \frac{1}{\pi} \frac{\epsilon}{(x - x')^2 + \epsilon^2}
\end{align*}
\]

which equals the corresponding representation of the delta function on the left hand side. This completes the identification, and proves that the inverse Fourier transform of the Fourier transform is the original function. It has also proved that any square integrable function, i.e. normalizable function, can be expanded as a sum of momentum eigenfunctions. The momentum eigenstates interfere destructively almost everywhere, except at the position where the wave packet is
In general, the $d$-dimensional momentum distribution is related to the distribution of $\mathbf{k}$ vectors, $|\Phi(\mathbf{k})|^2$ by the relation

$$ P_p(p) = \int d^d k \, \delta^d(p - \hbar \mathbf{k}) \left| \Phi(\mathbf{k}) \right|^2 $$

$$ = \frac{1}{\hbar^d} \left| \Phi\left(\frac{p}{\hbar}\right) \right|^2 $$

(137)

In future, we shall find it convenient to include factors of $\hbar^{-\frac{d}{2}}$ into the definition of the $d$-dimensional Fourier transform so that, on squaring the modulus, they give the properly normalized momentum distribution function.

---

### 3.2.1 Exercise 8

Given a wave function $\Psi(x)$ where

$$ \Psi(x) = C \exp\left[ -\frac{(x - x_0)^2}{4 \delta x^2} \right] \exp\left[ + i k_0 x \right] $$

(138)

determine $C$, up to an arbitrary phase factor, and determine $\Phi(k_x)$. Later, we shall see that $|\Phi(k_x)|^2$ is proportional to the probability distribution of the $x$ component of momentum of the system. In three dimensions $|\Phi(\mathbf{k})|^2 \, d^3k$ is the probability of finding the system with a wave vector $\mathbf{k}$ in an infinitesimal volume $d^3k$ around the point $\mathbf{k}$.

---

### 3.2.2 Solution 8

The magnitude of the coefficient $C$ is determined from the normalization condition

$$ \int_{-\infty}^{+\infty} dx \, |\Psi(x)|^2 = 1 $$

(139)

which is evaluated as

$$ |C|^2 \int_{-\infty}^{+\infty} dx \, \exp\left[ -\frac{(x - x_0)^2}{2 \delta x^2} \right] = 1 $$

(140)

On changing the variable of integration from $x$ to $y$ where

$$ y = \frac{x - x_0}{\sqrt{2} \delta x} $$

(141)
the normalization condition becomes
\[ 1 = |C|^2 \sqrt{2} \delta x \int_{-\infty}^{+\infty} dy \exp \left[ -y^2 \right] \]
\[ 1 = |C|^2 \sqrt{2 \pi} \delta x \]
Hence, the magnitude of \( C \) is found as
\[ |C| = \frac{1}{(2 \pi)^{\frac{1}{4}} \delta x^{\frac{1}{2}}} \]  
\[ (143) \]

The \( k \)-space wave function is found from
\[ \Phi(k_x) = \frac{1}{\sqrt{2 \pi}} \int_{-\infty}^{+\infty} dx \Psi(x) \exp[-i k_x x] \]
\[ = \frac{1}{(2 \pi)^{\frac{1}{2}} \delta x^{\frac{1}{2}}} \int_{-\infty}^{+\infty} dx \exp \left[ -\frac{(x - x_0)^2}{4 \delta x^2} \right] \exp[i k_0 x] \exp[-i k_x x] \]
\[ (144) \]

Combining the exponential factors and completing the square by changing variable from \( x \) to \( z \) where
\[ z = x - x_0 + 2 i (k_x - k_0) \delta x^2 \]  
\[ (145) \]
one finds that

\[ \Phi(k_x) = \frac{1}{(2 \pi)^{\frac{3}{4}} \delta x^{\frac{1}{2}}} \int_{-\infty}^{+ \infty} dz \exp \left[ - \frac{(z)^2}{4 \delta x^2} \right] \times \exp \left[ - (k_0 - k_x)^2 \delta x^2 \right] \exp \left[ - i (k_x - k_0) x_0 \right] \]

\[ = \delta x^{\frac{1}{2}} \left( \frac{2}{\pi} \right)^{\frac{1}{4}} \exp \left[ - (k_0 - k_x)^2 \delta x^2 \right] \exp \left[ - i (k_x - k_0) x_0 \right] \]

Thus, we see that in \( k_x \) space the modulus squared wave function \( |\Phi(k_x)|^2 \) is centered around \( k_0 \) and has a \( k \) width which is proportional to \( \delta x^{-1} \).

Figure 10: The momentum space distribution function \( |\Phi(p)|^2 \). The momentum distribution is centered about \( p_0 \).

### 3.2.3 Exercise 9

Given the wave function

\[ \Psi(x) = C \exp \left[ - \lambda \, |x| \right] \]

(147)
where \( \lambda \) is a positive real number, find \( C \) and the properly normalized momentum distribution function.

Figure 11: The real space distribution function \( | \Psi(x) |^2 \).

### 3.2.4 Solution 9

The normalization condition is given by

\[
\int_{-\infty}^{+\infty} dx \ | \Psi(x) |^2 = 1
\]  

(148)

which is evaluated as

\[
| C |^2 \int_{-\infty}^{+\infty} dx \ \exp \left[ -2 \lambda | x | \right] = 1
\]  

(149)

The integration can be broken up into two parts, one over the range \((-\infty, 0)\) and the second over the range \((0, +\infty)\). On replacing \( | x | \) by \( \pm x \) in the appropriate interval, we have

\[
1 = | C |^2 \left( \int_{-\infty}^{0} dx \ \exp \left[ +2 \lambda x \right] + \int_{0}^{+\infty} dx \ \exp \left[ -2 \lambda x \right] \right)
\]
1 = \left| C \right|^2 \left( \frac{1}{2\lambda} + \frac{1}{2\lambda} \right) \quad \quad (150)

Thus, the normalization is given by

\left| C \right| = \sqrt{\lambda} \quad \quad (151)

Figure 12: The momentum space distribution function \( |\Phi(p)|^2 \).

The \( k \)-space wave function is given by

\begin{align*}
\Phi(k_x) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \: \Psi(x) \exp \left[ -i k_x x \right] \\
&= \sqrt{\frac{\lambda}{2\pi}} \int_{-\infty}^{+\infty} dx \: \exp \left[ -\lambda |x| \right] \exp \left[ -i k_x x \right]
\end{align*} \quad \quad (152)

This is evaluated, as before, by breaking up the integral into two intervals. The first interval is an integration over the range \((-\infty, 0)\) and the second interval has \( x \) in the range \((0, +\infty)\). Thus, we find

\begin{align*}
\Phi(k_x) &= \sqrt{\frac{\lambda}{2\pi}} \left( \frac{1}{\lambda - i k_x} + \frac{1}{\lambda + i k_x} \right)
\end{align*}
\[
= \sqrt{\frac{\lambda}{2\pi}} \frac{2 \lambda}{\lambda^2 + k_x^2}
\]

(153)

The width of the \(k_x\) distribution is proportional to \(\lambda\). The momentum distribution \(P_p(p_x)\) is given by

\[
P_p(p_x) \, dp_x = \left| \Phi \left( \frac{p_x}{\hbar} \right) \right|^2 \frac{dp_x}{\hbar}
\]

(154)

Thus, we find that the momentum distribution function is given by

\[
P_p(p_x) = \frac{2}{\pi} \frac{\hbar^3 \lambda^3}{(\hbar^2 \lambda^2 + p_x^2)^2}
\]

(155)

which is properly normalized to unity.
3.3 Probability, Mean and Deviations

In Quantum Mechanics one often deals with systems in a well defined state, however, the result of a particular measurement is indeterminate. That is, usually, the result of the measurement cannot be predicted with absolute certainty. Therefore, we shall review some aspects of probabilities and averages.

Figure 13: The set of results of $N$ sequential measurements of $A$. The average value $\langle A \rangle$ and the magnitude of the root mean squared deviation $\Delta A_{rms}$ of this set of measurements are indicated in red. Also shown are $\Delta A_i$ which represent the deviations of some individual data points from the average value.

The average or mean value of a measured quantity $A$, denoted by $\overline{A}$, is expressed as an integral (and/or a sum) over all the possible values of the measurement $A$, weighted with the probability distribution function $P(A)$ via

$$\overline{A} = \int dA \; P(A) \; A$$

(156)

The integration runs over all possible (real) values of $A$. The higher moments $A^m$ have averages, $\overline{A^m}$, which are given by

$$\overline{A^m} = \int dA \; P(A) \; A^m$$

(157)
Figure 14: The probability distribution $P(A)$ is defined as the relative frequency of the occurrence of result $A$, in the limit $N \to \infty$ where $N$ is the number of measurements.

The deviation of the variable $A$ from its mean value is defined by

$$\Delta A = A - \overline{A}$$  \hspace{1cm} (158)

The average value of $\Delta A$ is zero, as can be seen from

$$\overline{\Delta A} = \overline{A} - \overline{A} = 0$$  \hspace{1cm} (159)

which just reflects the fact that the variable $A$ fluctuates equally on both sides of the average value $\overline{A}$. A measure of the size of the fluctuations can be found from the mean squared deviation $\overline{\Delta A^2}$ via

$$\overline{\Delta A^2} = \int dA P(A) (A - \overline{A})^2$$

$$= \int dA P(A) (A^2 - 2A \overline{A} + \overline{A}^2)$$

$$= \overline{A^2} - \overline{A}^2$$  \hspace{1cm} (160)

The mean squared deviation is non-zero as $\Delta A^2$ is always positive definite. The variance or root mean squared (r.m.s.) deviation $\Delta A_{rms}$ provides a measure of the fluctuations in $A$.

$$\Delta A_{rms} = \sqrt{\overline{\Delta A^2}}$$
\[= \sqrt{(A - \bar{A})^2} \]
\[= \sqrt{(\bar{A}^2 - \bar{A}^2)} \]  
(161)

The r.m.s. deviation is a measure of the uncertainty in the value of \( A \).

From the examples of wave packets given in exercise 4, it can be found that the uncertainty in the \( i \)-th component of the momentum and the \( i \)-th component of the particle’s position satisfies the inequality

\[\Delta r_{i} \text{ rms} \cdot \Delta p_{i} \text{ rms} \geq \frac{\hbar}{2} \]  
(162)

This is an example of the Heisenberg uncertainty relation, applied to the variables \( r \) and \( p \).

### 3.3.1 Exercise 10

Given \( P(x) \) where

\[P(x) = \left( \frac{1}{2\pi} \right)^\frac{1}{2} \delta x^{-1} \exp \left[ - \frac{(x - x_0)^2}{2 \delta x^2} \right] \]  
(163)

find \( \bar{x}, \overline{x^2}, \Delta x^2 \) and \( \Delta x^4 \).

### 3.3.2 Solution 10

The average value of \( x \), denoted as \( \bar{x} \) is given by

\[\bar{x} = \int_{-\infty}^{+\infty} dx \, P(x) \, x \]
\[= \int_{-\infty}^{+\infty} dx \, |\Psi(x)|^2 \, x \]
\[= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \, \delta x^{-1} \exp \left[ - \frac{(x - x_0)^2}{2 \delta x^2} \right] \, x \]  
(164)

Changing variable to \( y = x - x_0 \), one has

\[\bar{x} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} \exp \left[ - \frac{y^2}{2 \delta x^2} \right] \, (y + x_0) \]  
(165)
The term linear in $y$ is odd and, therefore, vanishes. The term proportional to $x_0$ factors out of the integral to yield
\[
\pi = x_0 \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} \exp \left[ - \frac{y^2}{2 \delta x^2} \right] = x_0 \int_{-\infty}^{+\infty} dx \, P(x) = x_0
\]
as $P(x)$ is normalized to unity. Thus, the average value of $x$ is $x_0$.

The average value of $x^2$ is given by
\[
\langle x^2 \rangle = \int_{-\infty}^{+\infty} dx \, P(x) \, x^2
\]
\[
= \int_{-\infty}^{+\infty} dx \, |\Psi(x)|^2 \, x^2
\]
\[
= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \, \delta x^{-1} \exp \left[ - \frac{(x - x_0)^2}{2 \delta x^2} \right] \, x^2
\]
(167)

Changing variable to $y = x - x_0$ one has
\[
\langle x^2 \rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} \exp \left[ - \frac{y^2}{2 \delta x^2} \right] \left( y^2 + 2y \, x_0 + x_0^2 \right)
\]
(168)

The term linear in $y$ is odd and, therefore, vanishes. The term proportional to $x_0^2$ factors out of the integral to yield
\[
\langle x^2 \rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} \, y^2 \exp \left[ - \frac{y^2}{2 \delta x^2} \right] + \frac{x_0^2}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} \exp \left[ - \frac{y^2}{2 \delta x^2} \right]
\]
\[
= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} \, y^2 \exp \left[ - \frac{y^2}{2 \delta x^2} \right] + x_0^2 \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} \exp \left[ - \frac{y^2}{2 \delta x^2} \right]
\]
\[
= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} \, y^2 \exp \left[ - \frac{y^2}{2 \delta x^2} \right] + x_0^2 \int_{-\infty}^{+\infty} dx \, P(x)
\]
\[
= x_0^2 + \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} \, y^2 \exp \left[ - \frac{y^2}{2 \delta x^2} \right]
\]
(169)
as $P(x)$ is normalized to unity. Since we have
\[
\frac{1}{\sqrt{\alpha}} \int_{-\infty}^{+\infty} dy \, \exp \left[ - \alpha y^2 \right] = \frac{1}{\sqrt{\alpha}}
\]
(170)
then by differentiating with respect to $\alpha$ we find

$$
\frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} dy \ y^2 \exp \left[ -\alpha \ y^2 \right] = - \frac{\partial}{\partial \alpha} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} dy \ exp \left[ -\alpha \ y^2 \right]
$$

$$
= - \frac{\partial}{\partial \alpha} \frac{1}{\sqrt{\alpha}}
$$

$$
= + \frac{1}{2} \frac{1}{\sqrt{\alpha^3}} \quad (171)
$$

Hence

$$
\bar{x}^2 = x_0^2 + \delta x^2 \quad (172)
$$

Thus, the average value of $x^2$ is $x_0^2 + \delta x^2$.

The mean squared deviation is then found as

$$
\Delta x_{rms}^2 = \Delta x^2 = \int_{-\infty}^{+\infty} dx \ \delta x \ P(x) (x - x_0)^2
$$

$$
= \frac{1}{\sqrt{2} \ \pi} \int_{-\infty}^{+\infty} dy \ \delta x^{-1} y^2 \exp \left[ -\frac{y^2}{2 \ \delta x^2} \right] \quad (173)
$$

The integration was previously evaluated, and yields

$$
\Delta x_{rms}^2 = \delta x^2 \quad (174)
$$

Finally, we can show that

$$
\Delta x^4 = \int_{-\infty}^{+\infty} dx \ \delta x \ P(x) (x - x_0)^4
$$

$$
= \frac{1}{\sqrt{2} \ \pi} \int_{-\infty}^{+\infty} dy \ \delta x^{-1} y^4 \exp \left[ -\frac{y^2}{2 \ \delta x^2} \right] \quad (175)
$$

The integration can be performed by taking the second derivative with respect to $\alpha$ of

$$
\frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} dy \ \exp \left[ -\alpha \ y^2 \right] = \frac{1}{\sqrt{\alpha}} \quad (176)
$$

Then, by differentiating with respect to $\alpha$, we find

$$
\frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} dy \ y^4 \exp \left[ -\alpha \ y^2 \right] = + \frac{\partial^2}{\partial \alpha^2} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} dy \ \exp \left[ -\alpha \ y^2 \right]
$$

$$
= + \frac{\partial^2}{\partial \alpha^2} \frac{1}{\sqrt{\alpha}}
$$

$$
= + \frac{3}{4} \frac{1}{\sqrt{\alpha^5}} \quad (177)
$$
Thus, we have

\[ \Delta x^4 = \int_{-\infty}^{+\infty} dx \, P(x) \, (x - x_0)^4 \]

\[ = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, \delta x^{-1} y^4 \exp \left[ -\frac{y^2}{2 \delta x^2} \right] \]

\[ = 3 \delta x^4 \]

(178)

3.3.3 Exercise 11

Find the r.m.s. deviation in the particle's position \( \Delta x_{\text{rms}} \) and momentum \( \Delta p_{x\text{rms}} \) for the wave packet

\[ \Psi(x) = \left( \frac{1}{2\pi} \right)^{\frac{1}{4}} \delta x^{-\frac{1}{2}} \exp \left[ -\frac{(x - x_0)^2}{4 \delta x^2} \right] \exp \left[ + i k_0 x \right] \]

(179)

3.3.4 Solution 11

From the results of Exercise 10 we immediately find that \( \Delta x_{\text{rms}} = \delta x \).

The \( k_x \) space wave function is given by

\[ \Phi(k_x) = \delta x^{\frac{1}{2}} \left( \frac{2}{\pi} \right)^{\frac{1}{4}} \exp \left[ -\frac{(k_0 - k_x)^2 \delta x^2}{2} \right] \exp \left[ - i (k_x - k_0) x_0 \right] \]

(180)

Thus, with \( p_x = h k_x \) one has the momentum probability distribution \( P(p_x) \) given by

\[ P(p_x) \, dp_x = \left| \Phi \left( \frac{p_x}{\hbar} \right) \right|^2 \frac{dp_x}{\hbar} \]

\[ = \left( \frac{2}{\pi} \right)^{\frac{1}{4}} \exp \left[ - 2 \left( \frac{k_0 - k_x}{\delta x} \right)^2 \right] \frac{\delta x}{\hbar} \, dp_x \]

(181)

Hence, this is a Gaussian distribution centered at \( p_x = h k_0 \), so the average value of the momentum is \( h k_0 \). The width of the Gaussian is \( \hbar^{\frac{1}{2}} \delta x \), so

\[ \Delta p_{x\text{rms}} \Delta x_{\text{rms}} = \frac{\hbar}{2} \]

(182)
which is an example of the Heisenberg uncertainty principle in which the equality holds.

### 3.3.5 Exercise 12

Given that a particle moving in one dimension is in a state given by

\[
\Psi(x) = \begin{cases} \left( \frac{1}{x^L} \right)^{\frac{1}{2}} & \text{if } |x| < L \\ 0 & \text{otherwise} \end{cases}
\]

find the probability that it is found in a momentum eigenstate, and verify that

![Figure 15: The wavefunction \( \Psi(x) \) given in Exercise 12.](image)

the probability distribution is properly normalized.
3.3.6 Solution 12

The real space wave function is expressed in terms of the momentum space wave function via

$$\Psi(x) = \int \frac{dp}{\sqrt{2\pi\bar{h}}} \exp \left[ + i \frac{p x}{\bar{h}} \right] \Phi(p)$$  \hspace{1cm} (184)

and the inverse relation is

$$\Phi(p) = \int \frac{dx}{\sqrt{2\pi\bar{h}}} \exp \left[ - i \frac{p x}{\bar{h}} \right] \Psi(x)$$  \hspace{1cm} (185)

The properly normalized momentum space wave function $\Phi(p)$ is evaluated as

$$\Phi(p) = \int_{-L}^{+L} \frac{dx}{\sqrt{2\pi\bar{h}}} \frac{1}{\sqrt{2L}} \exp \left[ - i \frac{p x}{\bar{h}} \right]$$

$$= \frac{1}{\sqrt{4\pi\bar{h}L}} \int_{-L}^{+L} \frac{1}{\sqrt{2L}} \exp \left[ - i \frac{p x}{\bar{h}} \right]$$

$$= \sqrt{\frac{L}{\pi\bar{h}}} \sin \left( \frac{pL}{\bar{h}} \right)$$  \hspace{1cm} (186)

The normalized momentum probability density $P(p)$ is given by the modulus squared of the momentum space wave function

$$P(p) = \left| \Phi(p) \right|^2 = \frac{L}{\pi\bar{h}} \sin^2 \left( \frac{pL}{\bar{h}} \right)$$  \hspace{1cm} (187)

The distribution $P(p)$ is properly normalized since

$$\int_{-\infty}^{+\infty} dx \frac{\sin^2 x}{x^2} = \pi$$  \hspace{1cm} (188)
3.4 Operators and Measurements

In Schrödinger’s wave mechanics, a physical or measurable quantity is represented by a (linear) differential operator $\hat{A}$. An operator $\hat{A}$ is defined by its action on the states represented by arbitrary wave functions $\Psi(r)$. The operator $\hat{A}$ transforms the state $\Psi(r)$ into another state $\Phi(r)$ via

$$\hat{A} \Psi(r) = \Phi(r)$$  \hspace{1cm} (189)

A measurement on a quantum mechanical system generally disturbs the system thereby causing a change in the state of the system. As the measurement results in a change in the state of a system, the measurement is represented by an operator.

A linear operator $\hat{A}$ is defined by its action on a state $\Psi(r)$ that is a linear superposition,

$$\Psi(r) = \sum_n C_n \Phi_n(r)$$  \hspace{1cm} (190)

An operator $\hat{A}$ acting on a state $\Psi(r)$ formed as a linear superposition is defined
to be a linear operator if, and only if, it produces the result
\[ \hat{A} \sum_n C_n \Phi_n(\mathbf{r}) = \sum_n C_n \hat{A} \Phi_n(\mathbf{r}) \] (191)

That is, the resulting state must be equivalent to the superposition of the states formed by \( \hat{A} \) acting on the components \( \Phi_n(\mathbf{r}) \).

The position operator \( \hat{r} \) is given by the vector \( \mathbf{r} \). Its operation on the state \( \Psi(\mathbf{r}) \) is just that of multiplication by \( \mathbf{r} \).

\[ \hat{r} \Psi(\mathbf{r}) = \mathbf{r} \Psi(\mathbf{r}) \] (192)

The momentum operator \( \hat{p} \) is given by \( -i \hbar \nabla \). The operator \( \nabla \) is given in Cartesian coordinates as
\[ \nabla = \hat{e}_x \frac{\partial}{\partial x} + \hat{e}_y \frac{\partial}{\partial y} + \hat{e}_z \frac{\partial}{\partial z} \] (193)
where \( \hat{e}_x, \hat{e}_y \) and \( \hat{e}_z \) are the three orthogonal unit vectors used to define a Cartesian coordinate system. The action of the momentum operator on a state \( \Psi(\mathbf{r}) \) is given by
\[ \hat{p} \Psi(\mathbf{r}) = -i \hbar \nabla \Psi(\mathbf{r}) \] (194)

The kinetic energy operator is given by \( \hat{T} = -\frac{\hbar^2}{2m} \nabla^2 \). Its action on a state \( \Psi(\mathbf{r}) \) is given by
\[ \hat{T} \Psi(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}) \] (195)
where the Laplacian is given in Cartesian coordinates as
\[ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \] (196)
The operators have no mathematical meaning except when they act upon a wave function.

### 3.4.1 Operator Equations

Just as in Hamiltonian Mechanics, the operators corresponding to physically measurable quantities can be expressed in terms of the momentum and position operators. This requires compounding operators, via addition and multiplication. The results of compounding operators can lead to operator equations. Operator equations, if valid, must be true if the same expression results when the operators on both side of the equality sign act on the same arbitrary wave function. Usually in writing an operator equation the wave function is suppressed, but it is implicitly assumed to be present.
3.4.2 Operator Addition

Given two differential operators \( \hat{A} \) and \( \hat{B} \), each defined by their action on every wave function \( \Psi(r) \) by

\[
\begin{align*}
\hat{A} \Psi(r) &= \Phi_A(r) \\
\hat{B} \Psi(r) &= \Phi_B(r)
\end{align*}
\] (197)

where the final wave functions \( \Phi_X(r) \) are dependent on the particular choice of the wave function \( \Psi(r) \). The sum of two operators is defined as \(( \hat{A} + \hat{B} )\) and is given by the linear sum

\[
( \hat{A} + \hat{B} ) \Psi(r) = \Phi_A(r) + \Phi_B(r)
= \hat{A} \Psi(r) + \hat{B} \Psi(r)
\] (198)

An example is given by the differential operator

\[
\frac{\partial^2}{\partial x^2} + 3 \frac{\partial}{\partial x} + x^4
\] (199)

Another example is given by the kinetic energy operator for a particle in Cartesian coordinates

\[
\hat{T} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)
\] (200)

where the kinetic energies for motion along the \( x, y \) and \( z \) axis add.

3.4.3 Operator Multiplication

Given two differential operators \( \hat{A} \) and \( \hat{B} \), each defined by their action on every conceivable wave function \( \Psi(r) \) by

\[
\begin{align*}
\hat{A} \Psi(r) &= \Phi_A(r) \\
\hat{B} \Phi_A(r) &= \Phi_{BA}(r)
\end{align*}
\] (201)

then the product of two operators is defined by their successive actions.

\[
\hat{B} \hat{A} \Psi(r) = \hat{B} \Phi_A(r)
= \Phi_{BA}(r)
\] (202)
Two examples are given by multiplying two operators $\frac{\partial^n}{\partial x^n}$ and $\frac{\partial^m}{\partial x^m}$ which yields the compound operator $\frac{\partial^{n+m}}{\partial x^{n+m}}$ and similarly by multiplying the operators $x^n$ and $x^m$ yields $x^{n+m}$.

Important examples of the multiplication of two operators are given by:

**The kinetic energy for motion in one dimension.**

The kinetic energy operator is derived from the classical expression

$$\hat{T_x} = \frac{\hat{p}_x^2}{2\,m}$$

$$= \frac{\hat{p}_x \cdot \hat{p}_x}{2\,m}$$

$$= \frac{1}{2\,m} \left( -i\,\hbar\,\frac{\partial}{\partial x} \right) \left( -i\,\hbar\,\frac{\partial}{\partial x} \right)$$

$$= -\frac{\hbar^2}{2\,m} \frac{\partial^2}{\partial x^2}$$

(203)

**The kinetic energy for motion in three dimensions.**

The kinetic energy operator is derived as

$$\hat{T} = \frac{\hat{p}^2}{2\,m}$$

$$= \frac{\hat{p} \cdot \hat{p}}{2\,m}$$

$$= \frac{1}{2\,m} \left( -i\,\hbar\,\hat{e}_x \frac{\partial}{\partial x} - i\,\hbar\,\hat{e}_y \frac{\partial}{\partial y} - i\,\hbar\,\hat{e}_z \frac{\partial}{\partial z} \right)^2$$

$$= -\frac{\hbar^2}{2\,m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

(204)

where we have used the representation of the vector momentum $\hat{p}$ in terms of its components and the unit vectors $\hat{e}_x$, $\hat{e}_y$ and $\hat{e}_z$.

The (vector) orbital angular momentum operator $\hat{L}$ is given by the vector product of two vector operators

$$\hat{L} = \hat{\mathbf{r}} \wedge \hat{\mathbf{p}}$$

(205)

and is expressed as

$$\hat{L} = \hat{\mathbf{r}} \hat{L}_x + \hat{\mathbf{e}}_y \hat{L}_y + \hat{\mathbf{e}}_z \hat{L}_z$$

(206)
where

\[
\hat{L}_z = -i \hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)
\]

\[
\hat{L}_y = -i \hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)
\]

\[
\hat{L}_x = -i \hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)
\]

This is actually a pseudo-vector, as it transforms like a vector under every symmetry operation except inversion.

It should be noted that in general, unlike in the previous two examples, the product of two operators depends on the order in which they act on the wave function. If two operators have the effect

\[
\hat{B} \Psi(r) = \Phi_B(r)
\]

\[
\hat{A} \Phi_B(r) = \Phi_{AB}(r)
\]

then the product of the two operators is defined by their successive actions

\[
\hat{A} \hat{B} \Psi(r) = \hat{A} \Phi_B(r)
\]

\[
= \Phi_{AB}(r)
\]

\[
\neq \Phi_{BA}(r)
\]

For example, in multiplying \( \hat{A} = \frac{\partial}{\partial x} \) and \( \hat{B} = x^m \) one has

\[
\hat{A} \hat{B} \Psi(x) = \frac{\partial}{\partial x} \left( x^m \Psi(x) \right)
\]

\[
= m x^{m-1} \Psi(x) + x^m \frac{\partial}{\partial x} \Psi(x)
\]

whereas on taking the product in the opposite order one obtains a different result

\[
\hat{B} \hat{A} \Psi(x) = x^m \frac{\partial}{\partial x} \left( \Psi(x) \right)
\]

### 3.4.4 Commutators

The commutator of two operators \( \hat{A} \) and \( \hat{B} \) is defined as the difference of the products of two operators taken in different orders

\[
[ \hat{A}, \hat{B} ] = \hat{A} \hat{B} - \hat{B} \hat{A}
\]
In this equation, like other operator equations, it should always be remembered that the operators are assumed to act on an arbitrary wave function. Note that the commutator is anti-symmetric

\[
[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]
\]  

(213)

From the previous example, where \(\hat{A} = \frac{\partial}{\partial x}\) and \(\hat{B} = x^m\), one has

\[
[\hat{A}, \hat{B}] \Psi(x) = \hat{A} \hat{B} \Psi(x) - \hat{B} \hat{A} \Psi(x) = \frac{\partial}{\partial x} \left(x^m \Psi(x)\right) - x^m \frac{\partial}{\partial x} \left(\Psi(x)\right) = m x^{m-1} \Psi(x)
\]

(214)

Since the above equation is true for every arbitrary \(\Psi(x)\), one has the operator equation

\[
\frac{\partial}{\partial x} x^m - x^m \frac{\partial}{\partial x} = m x^{m-1}
\]

(215)

where the presence of the wave function is implicitly assumed. An important example is given by the commutator of \(\hat{x} = x\) and \(\hat{p}_y = -i \hbar \frac{\partial}{\partial y}\) then

\[
[\hat{x}, \hat{p}_x] = [x, -i \hbar \frac{\partial}{\partial x}] = i \hbar
\]

(216)

The commutators of the \(x, y,\) and \(z\) components of the momentum and position operators are given by

\[
[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i \hbar
\]

(217)

If the commutator of two operators is zero, then the two operators are said to commute. An example of two commuting operators is given by \(\hat{x} = x\) and \(\hat{p}_y = -i \hbar \frac{\partial}{\partial y}\). In general, the commutators between different components of the particle’s coordinates and momenta are zero.

\[
[\hat{x}, \hat{p}_y] = [\hat{y}, \hat{p}_x] = 0
\]

\[
[\hat{y}, \hat{p}_z] = [\hat{z}, \hat{p}_y] = 0
\]

\[
[\hat{x}, \hat{p}_z] = [\hat{z}, \hat{p}_x] = 0
\]

(218)

The commutator of an operator \(\hat{A}\) and the sum of two operators \(\hat{B}\) and \(\hat{C}\) is given by

\[
[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]
\]

(219)
whereas the commutator of an operator and a product of two operators \( \hat{B} \) and \( \hat{C} \) is given by

\[
[\hat{A}, \hat{B} \hat{C}] = [\hat{A}, \hat{B}] \hat{C} + \hat{B} [\hat{A}, \hat{C}] \tag{220}
\]

and

\[
[\hat{A} \hat{B}, \hat{C}] = \hat{A} [\hat{B}, \hat{C}] + [\hat{A}, \hat{C}] \hat{B} \tag{221}
\]

Repeated application of the above relations allows one to express the commutator of \([\hat{A}, \hat{B}^n]\) as

\[
[\hat{A}, \hat{B}^n] = [\hat{A}, \hat{B}] \hat{B}^{n-1} + \hat{B} [\hat{A}, \hat{B}] \hat{B}^{n-2} + \hat{B}^2 [\hat{A}, \hat{B}] \hat{B}^{n-3} + \ldots + \hat{B}^{n-1} [\hat{A}, \hat{B}] + \hat{B}^{n-1} [\hat{A}, \hat{B}] \tag{222}
\]

which involves the sum of \(n\) commutators.

If the commutator \([\hat{A}, \hat{B}]\) is not an operator but is a constant instead, the above expression simplifies to

\[
[\hat{A}, \hat{B}^n] = n [\hat{A}, \hat{B}] \hat{B}^{n-1} \tag{223}
\]

This can be used to prove that if the commutator \([\hat{A}, \hat{B}]\) is a constant then, for any function \(f(\hat{B})\) which has a power series expansion, one has

\[
[\hat{A}, f(\hat{B})] = [\hat{A}, \hat{B}] f'(\hat{B}) \tag{224}
\]

where \(f'(x)\) is the derivative of \(f(x)\), that is \(f'(x) = \frac{\partial f}{\partial x}\). Examination of this operator equation gives justification for representing any pair of operators that have a constant commutator as a pair which consists of the variable and the commutation constant times a derivative w.r.t. the variable.

3.4.5 Exercise 13

Determine the commutator \([\hat{p}, V(\hat{x})]\). This expression occurs in the equation which determines the time derivative of the average value of the momentum, \(\hat{p}\).

3.4.6 Solution 13

The commutators between the components of momentum and the components of the position are given by

\[
[\hat{p}_i, x_j] = -i \hbar \delta_{i,j} \tag{225}
\]
These commutators are constants. Thus, on defining the potential as a Taylor series expansion in $\mathbf{r}$ one has

$$[ \hat{p}_i, V(\mathbf{r}) ] = -i \hbar \frac{\partial V(\mathbf{r})}{\partial x_i}$$ (226)

which is the $i$-th component of the commutator

$$[ \hat{p}, V(\mathbf{r}) ] = -i \hbar \nabla V(\mathbf{r})$$ (227)

The commutator of the momentum and the potential is related to the gradient of the potential and thus is related to the force.

### 3.4.7 Exercise 14

Determine the three commutators $[ \hat{x}, \hat{L}_z ]$, $[ \hat{y}, \hat{L}_z ]$ and $[ \hat{z}, \hat{L}_z ]$ of the components of the position vector and the $z$ component of the angular momentum operator.

Also find the commutator of $\hat{L}_z$ with the components of the momentum $\hat{p}$, $[ \hat{p}_x, \hat{L}_z ]$, $[ \hat{p}_y, \hat{L}_z ]$ and $[ \hat{p}_z, \hat{L}_z ]$.

### 3.4.8 Solution 14

The $z$ component of the angular momentum is given by

$$\hat{L}_z = \hat{x} \hat{p}_y - \hat{y} \hat{p}_x$$ (228)

Then, the commutator with the $x$ component of the position is given by

$$[ \hat{x}, \hat{L}_z ] = [ \hat{x}, \hat{x} \hat{p}_y ] - [ \hat{x}, \hat{y} \hat{p}_x ]$$
$$= -\hat{y} [ \hat{x}, \hat{p}_x ]$$
$$= -i \hbar \hat{y}$$ (229)

The commutator with the $y$ component of the position is given by

$$[ \hat{y}, \hat{L}_z ] = [ \hat{y}, \hat{x} \hat{p}_y ] - [ \hat{y}, \hat{y} \hat{p}_x ]$$
$$= +\hat{x} [ \hat{y}, \hat{p}_y ]$$
$$= +i \hbar \hat{x}$$ (230)

The third commutator is given by

$$[ \hat{z}, \hat{L}_z ] = [ \hat{z}, \hat{x} \hat{p}_y ] - [ \hat{x}, \hat{y} \hat{p}_x ]$$
$$= 0$$ (231)
Hence, we obtain
\[
\begin{align*}
[ \hat{x} , \hat{L}_z ] &= -i \hbar \hat{y} \\
[ \hat{y} , \hat{L}_z ] &= +i \hbar \hat{x} \\
[ \hat{z} , \hat{L}_z ] &= 0
\end{align*}
\]
(232)

The remaining commutators can be obtained from the two non-zero commutators by cyclically permuting \(x, y\) and \(z\).

Similarly, the commutation relations between the components of the angular momentum and the components of the momentum are evaluated from
\[
\begin{align*}
[ \hat{p}_x , \hat{L}_z ] &= [ \hat{p}_x , \hat{x} \hat{p}_y ] - [ \hat{p}_x , \hat{y} \hat{p}_x ] \\
&= [ \hat{p}_x , \hat{x} ] \hat{p}_y \\
&= -i \hbar \hat{p}_y
\end{align*}
\]
(233)

Hence, the commutators of the \(z\) component of angular momentum with the components of the momentum are found as
\[
\begin{align*}
[ \hat{p}_x , \hat{L}_z ] &= -i \hbar \hat{p}_y \\
[ \hat{p}_y , \hat{L}_z ] &= +i \hbar \hat{p}_x \\
[ \hat{p}_z , \hat{L}_z ] &= 0
\end{align*}
\]
(234)

The other commutators can be found by cyclic permutation of the subscripts \(x, y\) and \(z\).

---

### 3.4.9 Exercise 15

Determine the double commutator \([ x , [ x , \hat{H} ] ]\), where the Hamiltonian is given by \(\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r})\). This commutator forms the basis of the Thomas-Reiche-Kuhn Sum rule for the intensity of optical absorption by atoms.

---

### 3.4.10 Solution 15

The commutator between the \(x\) component of the position and the Hamiltonian \(\hat{H}\) can be decomposed into the sum of the commutators between \(x\) and the potential \(V(\hat{r})\) and the commutator of \(x\) with the potential energy \(\frac{\hat{p}^2}{2m}\)
\[
[ x , \hat{H} ] = [ x , V(\hat{r}) ] + [ x , \frac{\hat{p}^2}{2m} ]
\]
(235)
The commutator between the $x$ component of the position and the potential vanishes
\[ [x, V(r)] = 0 \quad (236) \]

The only non-zero part of the commutator is the commutator between the $x$ component of the kinetic energy and the position. This non-zero commutator is evaluated as
\[ [x, \hat{p}_x^2 \frac{2}{m}] = \frac{1}{2m} \left( [x, \hat{p}_x] \hat{p}_x + \hat{p}_x [x, \hat{p}_x] \right) \]
\[ = \frac{i\hbar}{2m} \hat{p}_x \quad (237) \]

Hence, the double commutator is given by
\[ [x, [x, \hat{H}]] = -\frac{\hbar^2}{m} \quad (238) \]

Another special example of an operator equation that we shall extensively use is in the definition of an exponential of an operator
\[ \exp \left[ \lambda \hat{A} \right] = \sum_n \frac{\lambda^n \hat{A}^n}{n!} \quad (239) \]

where $\lambda$ is any complex number.

Consider the operator which is a function of $\lambda$ and defined via,
\[ \hat{f}(\lambda) = e^{\lambda \hat{A}} \hat{B} e^{-\lambda \hat{A}} \quad (240) \]

then it is easy to prove that the derivatives are given by the series of expressions,
\[ \left( \frac{d\hat{f}}{d\lambda} \right) = \hat{A} \hat{f}(\lambda) - \hat{f}(\lambda) \hat{A} \]
\[ = [\hat{A}, \hat{f}(\lambda)] \]
\[ \left( \frac{d^2\hat{f}}{d\lambda^2} \right) = [\hat{A}, \frac{d\hat{f}}{d\lambda}] \]
\[ = [\hat{A}, [\hat{A}, \hat{f}(\lambda)]] \quad (241) \]

This infinite set of equations can be used in the Taylor expansion of $\hat{f}(\lambda)$ to yield
\[ e^{\lambda \hat{A}} \hat{B} e^{-\lambda \hat{A}} = \hat{B} + \lambda [\hat{A}, \hat{B}] + \frac{\lambda^2}{2!} [\hat{A}, [\hat{A}, \hat{B}]] \]
\[ + \frac{\lambda^3}{3!} [\hat{A}, [\hat{A}, [\hat{A}, \hat{B}]]) + \ldots \quad (242) \]
where we have used the fact that $\hat{f}(0) = \hat{B}$.

### 3.4.11 Exercise 16

Given the first order differential equation

$$i \hbar \frac{d\hat{U}(t)}{dt} = \hat{H} \hat{U}(t)$$

and $\hat{U}(0) = 1$, find an expression for $\hat{U}(t)$. This equation and operator is usually seen in the context of the time evolution of a wave function, and the initial condition expresses the fact that the wave function is continuous at $t = 0$.

### 3.4.12 Solution 16

The solution for the time evolution operator is found by integrating the equation

$$\hat{U}(t) = \hat{U}(0) - i \frac{\hbar}{\hbar} \int_0^t dt' \hat{H} \hat{U}(t')$$

and then iterating

$$\hat{U}(t) = \hat{U}(0) - i \frac{\hbar}{\hbar} \int_0^t dt' \hat{H} \hat{U}(0) - \frac{1}{\hbar^2} \int_0^t dt' \int_t^0 dt'' \hat{H} \hat{H} \hat{U}(t'') + \ldots$$

$$= \hat{U}(0) - i \frac{\hbar}{\hbar} t \hat{H} \hat{U}(0) - \frac{1}{\hbar^2} \frac{t^2}{2} \hat{H} \hat{H} \hat{U}(0) + \ldots$$

$$= \exp \left[ -i \frac{\hbar}{\hbar} \hat{H} \right] \hat{U}(0)$$

In the last line the series is recognized as the expansion of the exponential. Since the initial condition corresponds to $\hat{U}(0) = 1$, we obtain the solution as

$$\hat{U}(t) = \exp \left[ -i \frac{\hbar}{\hbar} \hat{H} \right]$$
3.4.13 Exercise 17

Given the first order linear differential operator equation
\[
\frac{d\hat{B}(\lambda)}{d\lambda} = \left[ \hat{A}, \hat{B}(\lambda) \right] \tag{247}
\]
with the boundary condition $\hat{B}(0) = \hat{C}$, find an expression for $\hat{B}(\lambda)$.

---

3.4.14 Solution 17

Since
\[
\frac{\partial \hat{B}(\lambda)}{\partial \lambda} = \left[ \hat{A}, \hat{B}(\lambda) \right] \tag{248}
\]
one can integrate the equation to yield
\[
\hat{B}(\lambda) - \hat{B}(0) = \int_0^\lambda d\lambda' \left[ \hat{A}, \hat{B}(\lambda') \right]
\]
This equation can be iterated to yield
\[
\hat{B}(\lambda) = \hat{C} + \int_0^\lambda d\lambda' \left[ \hat{A}, \hat{C} \right] + \int_0^\lambda d\lambda' \int_0^{\lambda'} d\lambda'' \left[ \hat{A}, \left[ \hat{A}, \hat{B}(\lambda'') \right] \right] + \ldots
\]
which can be evaluated as
\[
\hat{B}(\lambda) = \hat{C} + \lambda \left[ \hat{A}, \hat{C} \right] + \frac{\lambda^2}{2!} \left[ \hat{A}, \left[ \hat{A}, \hat{C} \right] \right] + \ldots \tag{251}
\]
which is the Taylor series of $\hat{B}(\lambda)$.

From eqn(242) of the previous example, the Taylor series can be recognized as the expansion of
\[
\hat{B}(\lambda) = \exp \left[ + \lambda \hat{A} \right] \hat{C} \exp \left[ - \lambda \hat{A} \right] \tag{252}
\]
Alternatively, the series can be re-arranged as
\[
\hat{B}(\lambda) = \left( 1 + \lambda \hat{A} + \frac{\lambda^2}{2!} \hat{A}^2 + \ldots \right) \hat{C} \left( 1 - \lambda \hat{A} + \frac{\lambda^2}{2!} \hat{A}^2 + \ldots \right)
\]
\[
= \exp \left[ + \lambda \hat{A} \right] \hat{C} \exp \left[ - \lambda \hat{A} \right] \tag{253}
\]
giving the same result.

### 3.4.15 Exercise 18

The Baker - Campbell - Hausdorff relation

\[
\exp\left[\hat{A}\right]\exp\left[\hat{B}\right] = \exp\left[(\hat{A} + \hat{B})\right]\exp\left[\frac{1}{2}\left[\hat{A},\hat{B}\right]\right]
\]

(254)

is only valid for operators \(\hat{A}\) and \(\hat{B}\) that have commutator which is a constant, i.e.

\[
[\hat{A},\hat{B}] = \text{Const.}
\]

(255)

Derive the Baker - Cambell - Hausdorff relation.

### 3.4.16 Solution 18

First we note that, from the series expansion of the exponential, one can show

\[
\left[\exp\left[\lambda \hat{B}\right],\hat{A}\right] = \lambda \exp\left[\lambda \hat{B}\right]\left[\hat{B},\hat{A}\right]
\]

(256)

Now let us consider the operator function \(\hat{f}(\lambda)\) defined by

\[
\hat{f}(\lambda) = \exp\left[\lambda \hat{A}\right]\exp\left[\lambda \hat{B}\right]\exp\left[-\lambda (\hat{A} + \hat{B})\right]
\]

(257)

Then the derivative with respect to \(\lambda\) is given by

\[
\frac{\partial \hat{f}}{\partial \lambda} = \exp\left[\lambda \hat{A}\right]\hat{A}\exp\left[\lambda \hat{B}\right]\exp\left[-\lambda (\hat{A} + \hat{B})\right]
\]

\[
+ \exp\left[\lambda \hat{A}\right]\exp\left[\lambda \hat{B}\right]\hat{B}\exp\left[-\lambda (\hat{A} + \hat{B})\right]
\]

\[
- \exp\left[\lambda \hat{A}\right]\exp\left[\lambda \hat{B}\right](\hat{A} + \hat{B})\exp\left[-\lambda (\hat{A} + \hat{B})\right]
\]

(258)

---


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On commuting \( \exp[\lambda \hat{B}] \) with \( \hat{A} \) in the first term, we find

\[
\frac{\partial \hat{f}}{\partial \lambda} = \lambda \exp[\lambda \hat{A}] \exp[\lambda \hat{B}] [\hat{A}, \hat{B}] \exp\left[-\lambda (\hat{A} + \hat{B})\right]
\] (259)

as the other terms cancel identically. Furthermore as the commutator is a constant it may be factored out, thus we have

\[
\frac{\partial \hat{f}}{\partial \lambda} = \lambda [\hat{A}, \hat{B}]
\] (260)

which on integrating and re-arranging yields

\[
\exp[\lambda \hat{A}] \exp[\lambda \hat{B}] = \exp[\lambda (\hat{A} + \hat{B})] \exp\left[\frac{\lambda^2}{2} [\hat{A}, \hat{B}]\right]
\] (261)

and on setting \( \lambda = 1 \) we have proved the relationship.

The Taylor-MacLaurin expansion of a function \( f(x) \) is given by

\[
f(x + a) = \exp\left[a \frac{\partial}{\partial x}\right] f(x)
\] (262)

which has the three-dimensional analogue

\[
f(r + a) = \exp\left[a \cdot \nabla\right] f(r)
\] (263)

This is equivalent to a shift of the origin by \( +a \), or a shift of the function by \( -a \).

### 3.4.17 Eigenvalue Equations

Given a differential operator \( \hat{A} \) one can find eigenfunctions \( \varphi_a(r) \) and eigenvalues \( a \). The eigenfunctions and eigenvalues are determined from the eigenvalue equation,

\[
\hat{A} \varphi_a(r) = a \varphi_a(r)
\] (264)

An example is given by the eigenfunctions of the \( x \) component of the momentum, \( \hat{p}_x \), defined on the interval \((-\infty, \infty)\). The eigenvalue equation is

\[
\hat{p}_x \varphi_p(r) = p_x \varphi_p(r)
\]

\[- i \hbar \frac{\partial}{\partial x} \varphi_p(r) = p_x \varphi_p(r)
\] (265)
The eigenfunctions are of the form

$$\varphi_p(r) \propto \exp \left[ i \frac{p_x x}{\hbar} \right]$$

and the eigenvalue $p_x$ is any real number. Thus, the eigenvalues form a continuous spectra with values in the interval $(-\infty, \infty)$. The momentum eigenfunctions are also eigenfunctions of the kinetic energy operator $\hat{T}_x$, since $\hat{T}_x = \frac{\hat{p}_x^2}{2m}$. We should note that two eigenfunctions correspond to the same eigenvalue of $\hat{T}_x$. These two eigenfunctions are those which correspond to the momentum eigenvalues $+p_x$ and $-p_x$. When an eigenvalue corresponds to more than one eigenfunction, the eigenvalue is said to be degenerate. The above eigenfunctions of $\hat{T}_x$ are doubly degenerate. The degeneracy is the number of linearly independent\(^7\) eigenfunctions corresponding to the same eigenvalue, and this depends on the space of the functions being considered. For example, if the wave functions depend on $x, y$ and $z$, one can find eigenfunctions of $\hat{p}_x$ of the form

$$\Psi(x, y, z) = \left( \frac{1}{2\pi\hbar} \right)^{\frac{3}{2}} \exp \left[ i \frac{p_x x}{\hbar} \right] \exp \left[ i \frac{p_y y}{\hbar} \right] \exp \left[ i \frac{p_z z}{\hbar} \right]$$

the eigenvalue $p_x$ is infinitely degenerate.

Note that a factor of $\hbar^{-\frac{d}{2}}$ has been introduced into the normalization of the $d$-dimensional momentum eigenstates, or equivalently the $d$-dimensional Fourier transform. This factor was introduced in order that the momentum distribution function is properly normalized.

In general, given an eigenfunction $\Psi_a(r)$ of an operator $\hat{A}$ with eigenvalue $a$, then any function of the operator $f(\hat{A})$ satisfies the eigenvalue equation

$$f(\hat{A}) \Psi_a(r) = f(a) \Psi_a(r)$$

where the eigenvalue is $f(a)$.

Another example is given by the energy eigenfunctions of the one-dimensional harmonic oscillator, which has the Hamiltonian operator $\hat{H}$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{m\omega^2}{2} x^2$$

\(^7\)A set of functions $\phi_n$ is said to be linearly independent if any function of the set cannot be expressed as a linear superposition of the other members of the set. That is, if the set of $\phi_n$ is linearly independent, the only solution of the equation

$$\sum_n C_n \phi_n = 0$$

is the trivial solution in which all the coefficients are zero $C_n = 0$. 

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The energy eigenvalue equation for the harmonic oscillator is

\[
\hat{H} \Psi_n(x) = \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{m \omega^2}{2} x^2 \right) \Psi_n(x) = E_n \Psi_n(x)
\] (270)

which has the energy eigenvalues \( E_n = \hbar \omega \left( n + \frac{1}{2} \right) \) where \( n \) is any positive integer (including 0). The energy eigenfunctions are \( \Psi_n(x) \), where

\[
\Psi_n(x) = \frac{(-1)^n}{\sqrt{2^n n!}} \left( \frac{m \omega}{\hbar \pi} \right)^{\frac{1}{4}} \exp\left[ + \frac{m \omega}{2 \hbar} x^2 \right] \left( \frac{\hbar}{m \omega} \right)^{\frac{n}{2}} \frac{d^n}{dx^n} \exp\left[ - \frac{m \omega}{\hbar} x^2 \right]
\] (271)

In this case the eigenvalues are in the form of a discrete set of numbers, and the eigenfunctions are localized about the origin. The harmonic oscillator, classically, corresponds to a situation in which a particle would be bound to the origin by the quadratic potential, for any value of the energy \( E \).

### 3.4.18 Exercise 19

Show that if

\[
\Psi(r) = \exp\left[ - \phi(r) \right]
\] (272)

satisfies appropriate boundary conditions then it represents a bound state wave function with energy eigenvalue \( E \) for a particle moving in the potential

\[
V(r) = \frac{\hbar^2}{2m} \left[ (\nabla \phi(r))^2 - \nabla^2 \phi(r) \right] + E
\] (273)

### 3.4.19 Exercise 20

An electron is moving in one dimension and is constrained to the region outside a perfect conductor \( x > 0 \), where the potential is given by the image potential

\[
V(x) = -\frac{e^2}{2x}
\] (274)

where \( e \) is the charge of the electron. Find a bound state energy eigenfunction \( \phi(x) \) and the average value of \( x \).
Figure 17: The one-dimensional image potential $V(x)$ which confines an electron close to the surface of a metal. The bound state energy is marked by a horizontal line.

Hint: Try a wave function of the form $x \exp[-\alpha x]$ for $x > 0$.

### 3.4.20 Solution 20

The trial wave function is chosen as

$$\phi(x) = A x \exp\left[ - \alpha x \right]$$

for $x > 0$ and is zero for negative values of $x$, and is shown in fig(18). Thus, the wave function is localized as $x \to \infty$ and vanishes at the surface at $x = 0$, representing a particle trapped in the attractive image potential. The electron does not penetrate into the metal. On substituting the wave function into the energy eigenvalue equation

$$\left[ - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{e^2}{2x} \right] \phi(x) = E \phi(x)$$

and on noting that

$$\frac{\partial \phi}{\partial x} = \left( \frac{1}{x} - \alpha \right) \phi(x)$$
and the second derivative is given by

\[ \frac{\partial^2 \phi}{\partial x^2} = -\left( \frac{2}{x} - \alpha \right) \alpha \phi(x) \]  

(278)

one finds that the eigenvalue equation reduces to

\[ \left[ -\frac{\hbar^2}{2m} \left( \alpha^2 - 2\frac{\alpha}{x} \right) - \frac{e^2}{2x} \right] \phi(x) = E \phi(x) \]  

(279)

This is an algebraic equation, which is solved by choosing \( \alpha \) such that

\[ \alpha = \frac{m e^2}{2 \hbar^2} \]  

(280)

and the energy eigenvalue \( E \) is then given by

\[ E = -\frac{m e^4}{8 \hbar^2} \]  

(281)

The eigenvalue \( E \) is negative, corresponding to the fact that classically the electron is trapped in the potential well and does not have enough energy to reach \( x \to \infty \). The threshold energy for the particle to reach infinity is \( E = 0 \), and hence the particle must have a negative energy.

Figure 18: The wave function \( \Psi(x) \) of an electron bound to the surface of a metal.
3.4.21 Exercise 21

A particle of mass $m$ is confined to the region $x > 0$ and is subjected to a potential $V(x)$ given by

$$V(x) = V_0 \left[ \frac{a^2}{x^2} - \frac{a}{x} \right]$$

(282)

where $V_0$ and $a$ are constants. The potential is sketched in fig(19). Derive the bound state energy and wave function.

Hint: Try a wave function of the form $x^s \exp[-\alpha x]$ for $x > 0$.

3.4.22 Solution 21

We shall consider the trial wave function

$$\phi(x) = C x^s \exp[-\alpha x]$$

(283)
which has the second derivative given by
\[
\frac{\partial^2}{\partial x^2} \phi(x) = \left( \frac{s(s - 1)}{x^2} - 2 \alpha \frac{s}{x} + \alpha^2 \right) \phi(x) \tag{284}
\]
On substituting into the energy eigenvalue equation one finds the consistency equations
\[
s(s - 1) = \frac{2mV_0}{\hbar^2} a^2
\]
\[
2s\alpha = \frac{2mV_0}{\hbar^2} a
\]
\[
\alpha^2 = -\frac{2mE}{\hbar^2} \tag{285}
\]
Thus, we find the exponent \( s \) as
\[
s = \frac{1}{2} \pm \sqrt{\frac{1}{4} + \frac{2mV_0}{\hbar^2} a^2} \tag{286}
\]
Since the wave function should be square integrable we take the positive root. Then from the second equation we find
\[
\alpha = \frac{2mV_0}{\hbar^2} a \sqrt{1 + \frac{8mV_0}{\hbar^2} a^2} \tag{287}
\]
from which one can find the energy \( E \).

### 3.4.23 Exercise 22

Prove that the energy eigenfunctions of the harmonic oscillator are given by \( \Psi_n(x) \) given above.

### 3.4.24 Solution 22

The wave function \( \Psi_n(x) \) should satisfy the energy eigenvalue equation,
\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{m\omega^2}{2} x^2 \right] \Psi_n(x) = \hbar\omega \left( n + \frac{1}{2} \right) \Psi_n(x) \tag{288}
\]
First let us transform to the dimensionless variable \( y \) where
\[
y = \sqrt{\frac{m\omega}{\hbar}} x \tag{289}
\]
Then, the energy eigenvalue equation can be simplified to

\[
- \frac{\partial^2}{\partial y^2} + y^2 \Phi_n(y) = (2n + 1) \Phi_n(y) \tag{290}
\]

We have to show that \( \Phi_n(y) \) given by

\[
\Phi_n(y) = \exp \left[ + \frac{y^2}{2} \right] \left( \frac{\partial}{\partial y} \right)^n \exp \left[ - y^2 \right] \tag{291}
\]
satisfies the above dimensionless eigenvalue equation. We shall prove this by induction.

We first note that the above trial wave function with \( n = 0 \) satisfies the eigenvalue equation as

\[
- \frac{\partial^2}{\partial y^2} + y^2 \exp \left[ - \frac{y^2}{2} \right] = \exp \left[ - \frac{y^2}{2} \right] \tag{292}
\]

So the trial wave function satisfies the equation for \( n = 0 \), and is thus a solution for this particular \( n \).

Then we shall prove that, if the trial wave function satisfies the eigenvalue equation for an arbitrary \( n \), then the function also satisfies the equation for \( n + 1 \).

Let us first note that

\[
\exp \left[ + \frac{y^2}{2} \right] \left( \frac{\partial}{\partial y} \right)^n \exp \left[ - \frac{y^2}{2} \right] = \left( \exp \left[ + \frac{y^2}{2} \right] \left( \frac{\partial}{\partial y} \right) \exp \left[ - \frac{y^2}{2} \right] \right)^n = \left( + \frac{\partial}{\partial y} - y \right)^n \tag{293}
\]

The trial wave function is assumed to satisfy the equation

\[
- \frac{\partial^2}{\partial y^2} + y^2 \left( + \frac{\partial}{\partial y} - y \right)^n \exp \left[ - \frac{y^2}{2} \right] = (2n + 1) \left( + \frac{\partial}{\partial y} - y \right)^n \exp \left[ - \frac{y^2}{2} \right] \tag{294}
\]

and we aim to show that if the above equation is true then the equation with \( n + 1 \)

\[
- \frac{\partial^2}{\partial y^2} + y^2 \left( + \frac{\partial}{\partial y} - y \right)^{n+1} \exp \left[ - \frac{y^2}{2} \right] = (2n + 3) \left( + \frac{\partial}{\partial y} - y \right)^{n+1} \exp \left[ - \frac{y^2}{2} \right] \tag{295}
\]
is also true. We note that the operator identity
\[
\left[ - \frac{\partial^2}{\partial y^2} + y^2 \right] \left( + \frac{\partial}{\partial y} - y \right) = \left( + \frac{\partial}{\partial y} - y \right) \left[ - \frac{\partial^2}{\partial y^2} + y^2 + 2 \right]
\]

is always valid. On substituting this identity into the eigenvalue equation with the \(n+1\)th trial function, we have
\[
\left( + \frac{\partial}{\partial y} - y \right) \left[ - \frac{\partial^2}{\partial y^2} + y^2 + 2 \right] \left( + \frac{\partial}{\partial y} - y \right)^n \exp \left[ - \frac{y^2}{2} \right] = \left( + \frac{\partial}{\partial y} - y \right) \left( 2n + 3 \right) \left( + \frac{\partial}{\partial y} - y \right)^n \exp \left[ - \frac{y^2}{2} \right]
\]

and on cancelling the term
\[
\left( + \frac{\partial}{\partial y} - y \right) 2 \left( + \frac{\partial}{\partial y} - y \right)^n \exp \left[ - \frac{y^2}{2} \right]
\]

from both sides of the equation, we obtain
\[
\left( + \frac{\partial}{\partial y} - y \right) \left[ - \frac{\partial^2}{\partial y^2} + y^2 \right] \left( + \frac{\partial}{\partial y} - y \right)^n \exp \left[ - \frac{y^2}{2} \right] = \left( + \frac{\partial}{\partial y} - y \right) \left( 2n + 1 \right) \left( + \frac{\partial}{\partial y} - y \right)^n \exp \left[ - \frac{y^2}{2} \right]
\]

This is true if eqn(294) holds true, as we are only taking a derivative of eqn(294). Equation(294) is true for \(n = 0\) and so from the above we have shown that it is true for \(n = 1\). By induction this equation is also true for all higher integer values of \(n\).

3.4.25 Adjoint or Hermitean Conjugate Operators

Given an operator, \(\hat{A}\), which corresponds to a physical measurement \(A\) and a system that has a wave function that is an eigenfunction of the operator corresponding to the eigenvalue \(a\) then a measurement of that physical quantity \(A\) definitely results in the value \(a\).

The adjoint operator or Hermitian conjugate operator is defined by the matrix elements between two arbitrary wave functions
\[
\int d^3r \Phi^*(r) \hat{A} \Psi(r) = \left( \int d^3r \Psi^*(r) \hat{A}^\dagger \Phi(r) \right)^*
\]

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This definition involves the inner product of the wave function \( \hat{A} \Psi(r) \), which is the state \( \Psi(r) \) after it is transformed by the operator \( \hat{A} \), and \( \Phi(r) \). The definition relates this inner product to the complex conjugate of the inner product of the state \( \hat{A}^\dagger \Phi(r) \) with \( \Psi(r) \).

From the definition of the adjoint or Hermitean conjugate, it is easy to prove that the Hermitean conjugate of the Hermitean conjugate of an operator \( \hat{A} \) is the same as the original operator \( \hat{A} \),

\[
\left( \hat{A}^\dagger \right)^\dagger = \hat{A}
\] (301)

This is proved by using the definition of the adjoint twice

\[
\int d^3r \, \Phi^*(r) \, \hat{A} \, \Psi(r) = \left( \int d^3r \, \Phi^*(r) \, \hat{A}^\dagger \, \Phi(r) \right)^*
\]

\[
= \left( \left( \int d^3r \, \Phi^*(r) \, \left( \hat{A}^\dagger \right)^\dagger \, \Psi(r) \right)^* \right)^*
\] (302)

which, since \((z^*)^* = z\) for any complex number, yields the identification \((\hat{A}^\dagger)^\dagger = \hat{A}\).

Also a complex constant \( a \), when regarded as an operator, has a Hermitean conjugate which is just its complex conjugate \( a^* \).

An example of finding the Hermitean conjugate of an operator is given by considering the differential operator in one dimension.

\[
\hat{A} = \frac{\partial}{\partial x}
\] (303)

The Hermitean conjugate or self adjoint operator, \( \hat{A}^\dagger \), is found from

\[
\int_{-\infty}^{+\infty} dx \, \Phi^*(x) \frac{\partial}{\partial x} \Psi(x) =
\]

\[
= \Phi^*(x) \Psi(x) \bigg|_{-\infty}^{\infty} - \int_{-\infty}^{+\infty} dx \, \frac{\partial}{\partial x} \left( \Phi^*(x) \right) \Psi(x)
\]

\[
= - \int_{-\infty}^{+\infty} dx \, \frac{\partial}{\partial x} \left( \Phi^*(x) \right) \Psi(x)
\] (304)

where the second line involves integration by parts and the third line utilizes the boundary conditions on the wave functions

\[
\lim_{|x| \to \infty} \Psi(x) = 0
\] (305)

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which are implied by the normalization condition. From this, one identifies the Hermitean conjugate operator as

$$\hat{A}^\dagger = -\frac{\partial}{\partial x}$$  \hspace{1cm} (306)

Another example of a Hermitean conjugate of an operator is given by translation operator, which translates the wave function by the vector $\mathbf{a}$.

$$\hat{S}(\mathbf{a}) = \exp\left[-\mathbf{a} \cdot \nabla \right]$$  \hspace{1cm} (307)

This, when acting on a wave function $\Psi(\mathbf{r})$ generates the Taylor MacLaurin series expansion of the function $\Psi(\mathbf{r} - \mathbf{a})$. The Hermitean conjugate is found from the series expansion of the exponential operator, and integrating by parts to yield

$$\hat{S}^\dagger(\mathbf{a}) = \exp\left[+\mathbf{a} \cdot \nabla \right]$$  \hspace{1cm} (308)

which coincides with the inverse of $\hat{S}(\mathbf{a})$, as

$$\hat{S}^\dagger(\mathbf{a}) \hat{S}(\mathbf{a}) = \hat{S}(\mathbf{a}) \hat{S}^\dagger(\mathbf{a}) = 1$$  \hspace{1cm} (309)

Thus, we have

$$\hat{S}^\dagger(\mathbf{a}) = \hat{S}^{-1}(\mathbf{a})$$  \hspace{1cm} (310)

Operators that have their Hermitean conjugate operators equal to their inverses are called unitary operators. Thus, an operator $\hat{A}$ is a unitary operator if

$$\hat{A}^\dagger = \hat{A}^{-1}$$  \hspace{1cm} (311)

Hence, $\hat{S}(\mathbf{a})$ is a unitary operator.

Another unitary operator is given by the time translation operator $\hat{U}(t)$ which is found to be

$$\hat{U}(t) = \exp\left[-i \frac{\hat{H} t}{\hbar} \right]$$  \hspace{1cm} (312)

where $\hat{H}$ is the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$  \hspace{1cm} (313)

and $V(x)$ is a real function. Then it can be shown that the Hermitean conjugate of $\hat{U}$ is given by

$$\hat{U}^\dagger(t) = \exp\left[i \frac{\hat{H} t}{\hbar} \right]$$  \hspace{1cm} (314)
Figure 20: The unitary operator $\hat{S}(a)$ produces a translation of the wave function by $a$. The translation operator $\hat{T}$ acts on the coordinates and transforms the point $x$ to the point $x' = x + a$, i.e. $x' = \hat{T} x$. Under the translation, the wave function $\phi(x)$ is transformed to $\phi'(x)$, such that the value of $\phi'$ at $x'$ is the same as the value of $\phi$ at the point $x$. Therefore, $\phi'(x') = \phi(x)$ so, $\phi'(x) = \phi(\hat{T}^{-1}x)$. The unitary operator which transforms the wave function is then specified as $\phi'(x) = \hat{S}(a) \phi(x) = \phi(\hat{T}^{-1}x)$.

In this case, the Hermitean conjugate is just the complex conjugate of the operator. Also we have that the Hermitean conjugate coincides with the inverse operator

$$\hat{U}^\dagger(t) \hat{U}(t) = \hat{U}(t) \hat{U}^\dagger(t) = 1 \quad (315)$$

This is the condition that has to be satisfied for an operator to be a unitary operator. The unitary condition for the time evolution operator ensures that the normalization of the states is independent of time.

The Hermitean conjugate of a product of two operators ($\hat{A} \hat{B}$)$^\dagger$ is given by the product of the Hermitean conjugates taken in reverse order, ($\hat{B}^\dagger \hat{A}^\dagger$). This can be proved by starting with the definition of the Hermitean conjugate of the product

$$\left( \int d^3x \; \Psi^*(x) \left( \hat{A} \hat{B} \right) \Phi(x) \right)^* = \int d^3x \; \Phi^*(x) \left( \hat{A} \hat{B} \right)^\dagger \Psi(x) \quad (316)$$

The product operator is defined in terms of the state which results when the
operator \( \hat{A} \) acts on the state \( \hat{B} \Phi(\mathbf{r}) \). On using the definition of the Hermitean conjugate twice, successively, one finds

\[
\begin{align*}
&= \left( \int d^3 r \, \Psi^*(\mathbf{r}) \, \hat{A} \left( \hat{B} \Phi(\mathbf{r}) \right) \right)^* \\
&= \int d^3 r \left( \hat{B} \Phi(\mathbf{r}) \right)^* \left( \hat{A}^\dagger \Psi(\mathbf{r}) \right) \\
&= \left( \int d^3 r \left( \hat{A}^\dagger \Psi(\mathbf{r}) \right)^* \left( \hat{B} \Phi(\mathbf{r}) \right) \right)^* \\
&= \int d^3 r \, \Phi^*(\mathbf{r}) \, \hat{B}^\dagger \left( \hat{A}^\dagger \Psi(\mathbf{r}) \right) \\
&= \int d^3 r \, \Phi^*(\mathbf{r}) \, \hat{B}^\dagger \hat{A}^\dagger \Psi(\mathbf{r})
\end{align*}
\]

which completes the proof.

3.4.26 Hermitean Operators

A Hermitean operator (or self Adjoint operator) is any operator that satisfies the condition

\[ \hat{A}^\dagger = \hat{A} \] (318)

That is, if an operator is Hermitean, the Hermitean conjugate of the operator is equal to the operator.

Examples of Hermitean operators are given by, the components of the momentum operators \( \hat{p}_x = -i \hbar \frac{\partial}{\partial x} \), \( \hat{p}_y = -i \hbar \frac{\partial}{\partial y} \) and \( \hat{p}_z = -i \hbar \frac{\partial}{\partial z} \), and also the single-particle Hamiltonian defined by

\[ \hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\mathbf{r}) \] (319)

is Hermitean.

In spherical polar coordinates \((r, \theta, \phi)\), the canonical generalized momenta could correspond to the Hermitean operators

\[
\begin{align*}
\hat{p}_r &= -i \hbar \frac{\partial}{\partial r} \, r \\
\hat{p}_\theta &= -i \hbar \frac{1}{\sin \frac{1}{2} \theta} \frac{\partial}{\partial \theta} \, \sin \frac{1}{2} \theta \\
\hat{p}_\phi &= -i \hbar \frac{\partial}{\partial \phi}
\end{align*}
\]

(320)

These operators are Hermitean operators. Note that when these operators are taken between two wave functions, and integrated over the volume \( r^2 \, dr \, \sin \theta \, d\theta \, d\phi \)
the resulting factors of \( r \) and \( \sin \theta \) in the expressions are symmetrically placed with respect to the differential operator.

3.4.27 Exercise 23

Prove that the canonical momenta in spherical polar coordinates given in eqn(320) are Hermitean operators.

3.4.28 Exercise 24

The expression for the kinetic energy in the Hamiltonian of eqn(39) when quantized involves the sum of the three operators

\[
\begin{align*}
\hat{p}_r^2 &= -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \\
\hat{p}_\theta^2 &= -\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \\
\hat{p}_\varphi^2 &= -\hbar^2 \frac{\partial^2}{\partial \varphi^2}
\end{align*}
\]  

Show that these three operators are Hermitean.

3.4.29 Solution 24

The Hermitian conjugate of \( \hat{p}_r^2 \) is calculated from the matrix elements

\[
\begin{align*}
\int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta \int_0^\infty dr \ r^2 \ \Phi^*(r, \theta, \varphi) \ \hat{p}_r^2 \ \Psi(r, \theta, \varphi)
\end{align*}
\]

by integrating by parts twice with respect to \( \varphi \). On integrating by parts for the first time, one obtains

\[
\begin{align*}
-\int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta \int_0^\infty dr \ r^2 \ \Phi^*(r, \theta, \varphi) \ \frac{\partial^2}{\partial \varphi^2} \Psi(r, \theta, \varphi)
\end{align*}
\]  

(322)
\[
\begin{align*}
\hbar^2 \int_0^\pi d\theta \sin \theta \int_0^\infty dr \ r^2 \ \Phi^*(r, \theta, \varphi) \left( \frac{\partial}{\partial \varphi} \Psi(r, \theta, \varphi) \right) \\
+ \hbar^2 \int_0^2 \pi d\varphi \int_0^\pi d\theta \ \sin \theta \int_0^\infty dr \ r^2 \ \left( \frac{\partial}{\partial \varphi} \Phi^*(r, \theta, \varphi) \right) \left( \frac{\partial}{\partial \varphi} \Psi(r, \theta, \varphi) \right) \\
\end{align*}
\]

(323)

The boundary term vanishes since the wave functions are \(2\pi\) periodic in \(\varphi\), i.e., \(\Psi(r, \theta, \varphi) = \Psi(r, \theta, \varphi + 2\pi)\). On integrating by parts once again, one obtains

\[
\begin{align*}
\hbar^2 \int_0^2 \pi d\varphi \int_0^\pi d\theta \ \sin \theta \int_0^\infty dr \ r^2 \ \Phi^*(r, \theta, \varphi) \left( \frac{\partial^2}{\partial \varphi^2} \Phi(r, \theta, \varphi) \right) \\
\end{align*}
\]

(324)

where the boundary terms have vanished once again. Thus, we have found that

\[
\left( \hat{p}_\varphi^2 \right)^\dagger = -\hbar^2 \frac{\partial^2}{\partial \varphi^2}
\]

(325)

Hence, \(\hat{p}_\varphi^2\) is Hermitean.

The Hermitean conjugate of \(\hat{p}_\theta^2\) is calculated from the matrix elements

\[
\begin{align*}
\int_0^\pi d\varphi \int_0^\pi d\theta \ \sin \theta \int_0^\infty dr \ r^2 \ \Phi^*(r, \theta, \varphi) \ \hat{p}_\theta^2 \ \Psi(r, \theta, \varphi) \\
= -\hbar^2 \left( \int_0^\pi d\varphi \int_0^\pi d\theta \ \sin \theta \int_0^\infty dr \ r^2 \ \Phi^*(r, \theta, \varphi) \ \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \Psi(r, \theta, \varphi) \right) \right)
\end{align*}
\]

(326)

by integrating by parts twice with respect to \(\theta\). Note that the factor \(\sin \theta\) in the metric for the volume integral has cancelled with a factor from the component of the kinetic energy. On integrating by parts for the first time, one obtains

\[
\begin{align*}
\hbar^2 \int_0^\pi d\varphi \int_0^\pi d\theta \ \sin \theta \int_0^\infty dr \ r^2 \ \Phi^*(r, \theta, \varphi) \left( \frac{\partial}{\partial \theta} \Psi(r, \theta, \varphi) \right) \\
+ \hbar^2 \left( \int_0^\pi d\varphi \int_0^\pi d\theta \ \sin \theta \int_0^\infty dr \ r^2 \ \Phi^*(r, \theta, \varphi) \left( \frac{\partial}{\partial \theta} \Psi(r, \theta, \varphi) \right) \right) \\
\end{align*}
\]

(327)

The boundary term vanishes since the wave functions are finite at the poles where \(\sin \theta = 0\). On integrating by parts once again, one obtains

\[
\begin{align*}
\hbar^2 \int_0^\pi d\varphi \int_0^\pi d\theta \ \sin \theta \int_0^\infty dr \ r^2 \ \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \Phi^*(r, \theta, \varphi) \right) \Psi(r, \theta, \varphi)
\end{align*}
\]

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\[-\hbar^2 \left( \int_0^\pi d\varphi \int_0^\pi d\theta \int_0^\infty dr \, r^2 \Psi^\ast(r,\theta,\varphi) \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \Phi(r,\theta,\varphi) \right) \right)^\ast \tag{328}\]

where the boundary terms have vanished once again. Thus, we have found that

\[
\left( \hat{p}_r^2 \right)^\dagger = -\hbar^2 \frac{1}{\sin \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \tag{329}\]

Hence, \( \hat{p}_r^2 \) is Hermitean. Note that the weight factor \( \sin \theta \) in the integral over the solid angle played a crucial role in the proof of Hermiticity.

The radial component of the kinetic energy have the matrix elements

\[
\int_0^\pi d\varphi \int_0^\pi d\theta \int_0^\infty dr \, r^2 \Phi^\ast(r,\theta,\varphi) \hat{p}_r^2 \Psi(r,\theta,\varphi)
= -\hbar^2 \int_0^\pi d\varphi \int_0^\pi d\theta \sin \theta \int_0^\infty dr \, r^2 \Phi^\ast(r,\theta,\varphi) \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \Psi(r,\theta,\varphi) \right) \tag{330}\]

by integrating by parts twice with respect to \( r \). On integrating by parts for the first time, one obtains

\[
\begin{align*}
&\int_0^\pi d\varphi \int_0^\pi d\theta \sin \theta \int_0^\infty dr \, \Phi^\ast(r,\theta,\varphi) \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \Psi(r,\theta,\varphi) \right) \\
&= -\hbar^2 \int_0^\pi d\varphi \int_0^\pi d\theta \sin \theta \int_0^\infty dr \, r^2 \Phi^\ast(r,\theta,\varphi) \left( \frac{\partial}{\partial r} \Psi(r,\theta,\varphi) \right) \bigg|_0^\infty \\
&\quad + \hbar^2 \int_0^\pi d\varphi \int_0^\pi d\theta \sin \theta \int_0^\infty dr \, \left( \frac{\partial}{\partial r} \Phi^\ast(r,\theta,\varphi) \right) \left( \frac{\partial}{\partial r} \Psi(r,\theta,\varphi) \right) \\
&= -\hbar^2 \int_0^\pi d\varphi \int_0^\pi d\theta \sin \theta \int_0^\infty dr \, r^2 \Phi^\ast(r,\theta,\varphi) \left( \frac{\partial}{\partial r} \Psi(r,\theta,\varphi) \right) \left( \frac{\partial}{\partial r} \Phi^\ast(r,\theta,\varphi) \right) \tag{331}\end{align*}
\]

The boundary term vanishes since the wave function vanishes as \( r \to \infty \), i.e., \( \lim_{r \to \infty} \Psi(r,\theta,\varphi) = 0 \) and the weight function vanishes at \( r = 0 \). On integrating by parts once again, one obtains

\[
\begin{align*}
&\int_0^\pi d\varphi \int_0^\pi d\theta \sin \theta \int_0^\infty dr \, \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \Phi^\ast(r,\theta,\varphi) \right) \Psi(r,\theta,\varphi) \\
&= -\hbar^2 \int_0^\pi d\varphi \int_0^\pi d\theta \sin \theta \int_0^\infty dr \, \Psi^\ast(r,\theta,\varphi) \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \Phi(r,\theta,\varphi) \right) \tag{332}\end{align*}
\]

where the boundary terms have vanished once again. Thus, we have found that

\[
\left( \hat{p}_r^2 \right)^\dagger = -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \tag{333}\]

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is Hermitean. In the proof, the weight factor \( r^2 \) played a crucial role in showing the radial part of the kinetic energy is Hermitean.

---

3.4.30 Exercise 25

Using the expression for the momentum operator \( \mathbf{p} = -i \hbar \nabla \) in spherical polar coordinates

\[
\mathbf{p} = -i \hbar \left( \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \tag{334}
\]

where the unit vectors are given in terms of the Cartesian unit vectors via

\[
\hat{e}_r = \sin \theta \cos \varphi \hat{e}_x + \sin \theta \sin \varphi \hat{e}_y + \cos \theta \hat{e}_z \\
\hat{e}_\theta = \cos \theta \cos \varphi \hat{e}_x + \cos \theta \sin \varphi \hat{e}_y - \sin \theta \hat{e}_z \\
\hat{e}_\varphi = -\sin \varphi \hat{e}_x + \cos \varphi \hat{e}_y \tag{335}
\]

show that the resulting expression for the kinetic energy agrees with the expression inferred from the previous exercise.

---

3.4.31 Solution 25

First we shall note that the unit vectors are independent of \( r \) and are only functions of the angles, so

\[
\begin{align*}
\frac{\partial \hat{e}_x}{\partial \theta} &= \hat{e}_\theta \\
\frac{\partial \hat{e}_r}{\partial \varphi} &= \sin \theta \hat{e}_\varphi \\
\frac{\partial \hat{e}_\theta}{\partial \theta} &= -\hat{e}_r \\
\frac{\partial \hat{e}_\theta}{\partial \varphi} &= \cos \theta \hat{e}_\varphi \\
\frac{\partial \hat{e}_\varphi}{\partial \theta} &= 0 \\
\frac{\partial \hat{e}_\varphi}{\partial \varphi} &= -\left( \sin \theta \hat{e}_r + \cos \theta \hat{e}_\theta \right) \tag{336}
\end{align*}
\]

Then, we have

\[
\hat{p}^2 = -\hbar^2 \left[ \hat{e}_r \frac{\partial}{\partial r} \cdot \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_r \frac{\partial}{\partial r} \cdot \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \right]
\]
\[ + \hat{e}_r \frac{\partial}{\partial r} \cdot \hat{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \cdot \hat{e}_r \frac{\partial}{\partial r} \]

\[ + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \cdot \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} \cdot \hat{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \]

\[ + \hat{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \cdot \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \cdot \hat{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \]

which on evaluating the derivatives and evaluating the scalar products of the orthogonal unit vectors becomes

\[ \hat{p}^2 = -\hbar^2 \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right. \]

\[ + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \]

\[ + \left. \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \]  

(338)

The terms containing the first derivatives come from the change in the unit vectors of the fourth, seventh and eight terms of the previous equation. Then this can be simplified to yield

\[ \hat{p}^2 = -\hbar^2 \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \]

(339)

which involves the appropriate expression for the Laplacian in spherical polar coordinates.

---

Given an arbitrary operator \( \hat{B} \) which is not Hermitian, i.e. \( \hat{B} \neq \hat{B}^\dagger \), then one can always construct a Hermitian operator \( \hat{A} \) as

\[ \hat{A} = \frac{1}{2} \left( \hat{B} + \hat{B}^\dagger \right) \]

(340)

since

\[ \hat{A}^\dagger = \frac{1}{2} \left( \hat{B}^\dagger + (\hat{B}^\dagger)^\dagger \right) \]

\[ = \frac{1}{2} \left( \hat{B}^\dagger + \hat{B} \right) \]

\[ = \hat{A} \]

(341)

The operator \( \hat{A} \) is the Hermitian part of the arbitrary operator \( \hat{B} \).
3.4.32 Exercise 26

Construct the Hermitean operators corresponding to the operators \( \hat{B}_r = -i \frac{\partial}{\partial r} \) and \( \hat{B}_\theta = -i \frac{\partial}{\partial \theta} \), expressed in spherical polar coordinates \( r, \theta \) and \( \varphi \).

3.4.33 Solution 26

The Hermitean conjugate of \( \hat{B}_r \) is found by considering the matrix elements and by integrating by parts with respect to \( r \),

\[
- i \int_0^\infty dr \ r^2 \int_0^\pi d\theta \ \sin \theta \int_0^{2\pi} d\varphi \ \Phi^*(r, \theta, \varphi) \frac{\partial}{\partial r} \Psi(r, \theta, \varphi)
= + \left( i \int_0^\infty dr \ r^2 \int_0^\pi d\theta \ \sin \theta \int_0^{2\pi} d\varphi \ \Psi^*(r, \theta, \varphi) \frac{\partial}{\partial r} r^2 \Phi(r, \theta, \varphi) \right)^*
\]

where we have assumed that the wave function satisfies the boundary conditions

\[
\lim_{r \to \infty} \Psi(r, \theta, \varphi) \to 0
\]

Thus, the Hermitean conjugate, \( \hat{B}_r^\dagger \), is given by

\[
\hat{B}_r^\dagger = -i \ \frac{1}{r^2} \frac{\partial}{\partial r} r^2
\]

From this we can construct a Hermitean operator as the Hermitean part of \( \hat{B} \), via

\[
\hat{A}_r = -i \ \frac{1}{2} \left( \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \right)
= -i \ \frac{1}{r} \frac{\partial}{\partial r}
= -i \ \frac{1}{r} \left( \frac{\partial}{\partial r} \frac{r}{\varphi} \right)
\]

Similarly, the Hermitean conjugate of \( \hat{B}_\theta \) is found from

\[
- i \int_0^\infty dr \ r^2 \int_0^\pi d\theta \ \sin \theta \int_0^{2\pi} d\varphi \ \Phi^*(r, \theta, \varphi) \frac{\partial}{\partial \theta} \Psi(r, \theta, \varphi)
= + \left( i \int_0^\infty dr \ r^2 \int_0^\pi d\theta \ \int_0^{2\pi} d\varphi \ \Psi^*(r, \theta, \varphi) \frac{\partial}{\partial \theta} \sin \theta \Phi(r, \theta, \varphi) \right)^*
\]
The boundary term vanishes at \( \theta = 0 \) and \( \theta = \pi \) due to the presence of the \( \sin \theta \) term. Thus, \( \hat{B}_\theta^\dagger \) is given by

\[
\hat{B}_\theta^\dagger = -i \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta
\]

(347)

From this we can construct a Hermitean operator \( \hat{A}_\theta \) via

\[
\hat{A}_\theta = -i \left( \frac{\partial}{\partial \theta} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \right)
\]

\[
= -i \left( \frac{\partial}{\partial \theta} + \frac{\cos \theta}{2 \sin \theta} \right)
\]

\[
= -i \frac{1}{\sin^2 \theta} \left( \frac{\partial}{\partial \theta} \sin^2 \theta \right)
\]

(348)

### 3.4.34 Eigenvalues and Eigenfunctions of Hermitean Operators

Hermitean operators have eigenvalues and eigenfunctions that have three important properties. These are:

(i) The eigenvalues are real numbers.

(ii) Any two eigenfunctions corresponding to different eigenvalues have matrix elements which are zero. Wavefunctions that have this property are said to be orthogonal.

(iii) Any wave function can be expanded in terms of a complete set of the eigenfunctions of a Hermitean operator.

We shall now prove the first two statements. Consider a set of eigenfunctions of the operator \( \hat{A} \). These satisfy the eigenvalue equation

\[
\hat{A} \phi_a(\mathbf{r}) = a \phi_a(\mathbf{r})
\]

(349)

Then take the matrix elements with an eigenfunction corresponding to the eigenvalue \( b \),

\[
\int d^3 \mathbf{r} \phi_b^*(\mathbf{r}) \hat{A} \phi_a(\mathbf{r}) = a \int d^3 \mathbf{r} \phi_b^*(\mathbf{r}) \phi_a(\mathbf{r})
\]

(350)

but since \( \hat{A} \) is Hermitean

\[
= \left( \int d^3 \mathbf{r} \phi_b^*(\mathbf{r}) \hat{A} \phi_a(\mathbf{r}) \right)^*
\]

\[
= \left( \int d^3 \mathbf{r} \phi_a(\mathbf{r}) \hat{A} \phi_b(\mathbf{r}) \right)^*
\]

(351)
However, $\phi_b(r)$ is an eigenstate of $\hat{A}$ with eigenvalue $b$, so
\[
\phi_b^*(r) b \phi_b(r) = b^* \int d^3r \phi_b^*(r) \phi_b(r)
\]
Thus, we find the equality
\[
( a - b^* ) \left( \int d^3r \phi_b^*(r) \phi_b(r) \right) = 0
\]  
(353)

Thus, if the two eigenvalues are the same, $b = a$, and $\phi_a(r)$ is normalized to unity, one must have $a = b^* = a^*$. Hence, we have proved that the eigenvalues of a Hermitian operator are real.

If the eigenvalues are different, $b \neq a$, one then has
\[
\int d^3r \phi_b^*(r) \phi_a(r) = 0
\]  
(354)
Thus, eigenfunctions of the Hermitian operator corresponding to different eigenvalues are orthogonal.

If an eigenvalue is degenerate, then the eigenfunctions corresponding to this eigenvalue are not necessarily orthogonal. However, by choosing appropriate linear combinations of these eigenfunctions one can construct a set of eigenfunctions which are orthogonal. This procedure is known as Gram-Schmidt orthogonalization. We shall implicitly assume that this procedure has always been performed on any set of eigenfunctions.

We shall delay the proof of the expansion of an arbitrary wave function till later. However, we shall show how the orthonormality properties of the eigenfunctions allow a simple evaluation of the expansion coefficients $C_n$ of an arbitrary wave function
\[
\Psi(r) = \sum_n C_n \phi_n(r)
\]
(355)
Taking the matrix elements with the eigenfunction $\phi_m(r)$, one finds
\[
\int d^3r \phi_m^*(r) \Psi(r) = \sum_n C_n \int d^3r \phi_m^*(r) \phi_n(r) = \sum_n C_n \delta_{n,m} = C_m
\]
(356)
Therefore, the expansion of an arbitrary wave function $\Psi(r)$ can be written in the form

$$\Psi(r) = \sum_n \int d^3 r' \phi_n^*(r') \Psi(r') \phi_n(r)$$  (357)

After re-arranging, one recognizes that the sum over the eigenfunctions has the same property as the Dirac delta function. Thus, we have found the completeness condition

$$\sum_n \phi_n^*(r') \phi_n(r) = \delta^3(r - r')$$  (358)

This condition has to be satisfied if any wave function can be expanded in terms of a complete set of eigenfunctions. On going back to the example of momentum eigenfunctions and wave packets, one recognizes that the sum over the eigenvalues $n$ is to be replaced by an integral over the continuous eigenvalues $k$. Furthermore, the completeness condition is just the representation of the Dirac delta function given by eqn(132). In the case of degenerate eigenvalues, an appropriate orthonormal set of eigenfunctions should be constructed.

### 3.4.35 Exercise 27

Express the $x$, $y$ and $z$ components of the orbital angular momentum operator $\hat{L}$ in terms of the spherical polar coordinate variables $(r, \theta, \phi)$. Find all the eigenfunctions and eigenvalues of the $z$ component of the (Hermitian) orbital angular momentum operator $\hat{L}_z$. Show that they form an orthonormal set.

By using the theorems of discrete Fourier transforms for fixed $r$ and $\theta$, show that any wave function can be expanded in terms of the complete set of eigenfunctions of $\hat{L}_z$, $\phi_m(\varphi)$ as

$$\Psi(r, \theta, \varphi) = \sum_m \Phi_m(r, \theta) \phi_m(\varphi)$$  (359)

where the expansion coefficients $\Phi_m(r, \theta)$ are functions of $r$ and $\theta$.

### 3.4.36 Solution 27

Since the momentum is given by

$$\hat{p} = -i \hbar \left( \hat{\epsilon}_r \frac{\partial}{\partial r} + \hat{\epsilon}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\epsilon}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \right)$$  (360)
and \( r = r \hat{e}_r \) then with \( \hat{L} = r \wedge \hat{p} \), one finds that the angular momentum solely has \( \hat{e}_\theta \) and \( \hat{e}_\varphi \) components. The total orbital angular momentum can then be resolved into the Cartesian components as

\[
\begin{align*}
L_x &= -i \hbar \left( -\sin \varphi \frac{\partial}{\partial \theta} - \cos \varphi \cot \theta \frac{\partial}{\partial \varphi} \right), \\
L_y &= -i \hbar \left( +\cos \varphi \frac{\partial}{\partial \theta} - \sin \varphi \cot \theta \frac{\partial}{\partial \varphi} \right), \\
L_z &= -i \hbar \frac{\partial}{\partial \varphi}
\end{align*}
\]

The eigenfunctions of the \( z \) component of the orbital angular momentum operator are

\[
\phi_m(\varphi) = \left( \frac{1}{2 \pi} \right)^{\frac{1}{2}} \exp \left[ i m \varphi \right]
\]

where, because of the condition that \( \phi_m(\varphi) \) is single valued

\[
\phi_m(\varphi) = \phi_m(\varphi + 2 \pi)
\]

then one finds \( \exp[ i m 2 \pi ] = 1 \) which implies that \( m \) can only have integer values. Since these eigenfunctions only involve \( \varphi \), and not \( r \) and \( \theta \), the normalization is only due to the integration over \( \varphi \) between \( 0 \) and \( 2 \pi \). Any function of \( \varphi \) which has period \( 2 \pi \) can be expanded in terms of this set of orthonormal eigenfunctions.

---

### 3.4.37 Exercise 28

Find the expectation value of the nested commutation relation \( [ \hat{x} , [ \hat{x} , \hat{H} ] ] \) between the Hermitean operators \( \hat{x} \) and the energy \( \hat{H} \) between the lowest energy eigenfunctions \( \phi_0 \), i.e., evaluate

\[
\int d^3r \phi_0^*(r) [ x , [ x , \hat{H} ] ] \phi_0(r)
\]

and then use the completeness relation to prove the Thomas-Reiche-Kuhn sum rule

\[
\sum_n \left| \int d^3r \phi_n^*(r) x \phi_n(r) \right|^2 (E_n - E_0) = + \frac{\hbar^2}{2m}
\]

which relates the intensities of optical dipole allowed transitions \( \left| \int d^3r \phi_n^*(r) x \phi_n(r) \right|^2 \) and the energies of the photon involved in the transitions \( (E_n - E_0) \). If all these quantities are measured experimentally, multiplied and summed over all possible transitions, one should obtain unity. If the sum is different from unity
the experiment has failed to identify some transitions or the experimental apparatus has not been calibrated correctly.

3.4.38 Solution 28

Starting from the commutation relation

\[ [ x, [ x, \hat{H} ] ] = - \frac{\hbar^2}{m} \]

\[ \left( x^2 \hat{H} + \hat{H} x^2 - 2 x \hat{H} x \right) = - \frac{\hbar^2}{m} \]  \hspace{1cm} (366)

and taking the matrix elements between \( \Psi_0^*(x) \) and \( \Psi_0(x) \), one has

\[ \int_{-\infty}^{+ \infty} dx \, \Psi_0^*(x) \left( x^2 \hat{H} + \hat{H} x^2 - 2 x \hat{H} x \right) \Psi_0(x) \]

\[ = - \frac{\hbar^2}{m} \int_{-\infty}^{+ \infty} dx \, \Psi_0^*(x) \Psi_0(x) \]

\[ = - \frac{\hbar^2}{m} \]  \hspace{1cm} (367)

since the wave functions are normalized to unity. The right hand side of the commutator consists of four terms. The first and second term will turn out to be identical, although it may not seem obvious at first. The third and fourth are obviously identical and have already been combined and these give rise to the term which contains a factor of 2.

We shall now examine the first term which is given by

\[ \int_{-\infty}^{+ \infty} dx \, \Psi_0^*(x) \ x \ x \ x \ \hat{H} \ \Psi_0(x) \]  \hspace{1cm} (368)

and introduce a factor of 1 between the two \( x \)'s. This 1 can be written as an integral over a Dirac delta function \( \delta(x - x') \) with respect to \( x' \). Thus, we have

\[ \int_{-\infty}^{+ \infty} dx \int_{-\infty}^{+ \infty} dx' \, \Psi_0^*(x) \ x \ \delta(x - x') \ x' \ \hat{H} \ \Psi_0(x') \]  \hspace{1cm} (369)

where everything to the right of the delta function has been expressed in terms of the primed variable \( x' \). Since \( \Psi_0(x') \) is an energy eigenfunction it satisfies

\[ \hat{H} \ \Psi_0(x') = E_0 \ \Psi_0(x') \]  \hspace{1cm} (370)
This can be substituted in the expression for the term we are trying to evaluate, to yield
\[ = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dx' \, \Psi_{0}^*(x) \, x \, \delta(x - x') \, x' \, E_{0} \, \Psi_{0}(x') \] (371)

On writing the delta function in terms of the completeness relation
\[ \delta(x - x') = \sum_{n} \Psi_{n}(x) \, \Psi_{n}^*(x') \] (372)
one obtains
\[ = E_{0} \sum_{n} \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dx' \, \Psi_{0}^*(x) \, x \, \Psi_{n}(x) \, \Psi_{n}^*(x') \, x' \, \Psi_{0}(x') \]
\[ = E_{0} \sum_{n} \left( \int_{-\infty}^{+\infty} dx \, \Psi_{0}^*(x) \, x \, \Psi_{n}(x) \right) \left( \int_{-\infty}^{+\infty} dx' \, \Psi_{n}^*(x') \, x' \, \Psi_{0}(x') \right) \]
\[ = E_{0} \sum_{n} \left| \int_{-\infty}^{+\infty} dx \, \Psi_{0}^*(x) \, x \, \Psi_{n}(x) \right|^2 \] (373)
where we have interchanged the order of summation and integrations.

The second term can be immediately relate it to the first term. The second term is given by
\[ \int_{-\infty}^{+\infty} dx \, \Psi_{0}(x) \, \hat{H} \, x \, \Psi_{0}(x) \] (374)
Let us note that the Hermitean conjugate of the operator \( \hat{H} \, x \) is just \( x \, x \, \hat{H} \). Using the definition of the Hermitean conjugate of an operator, one finds
\[ \int_{-\infty}^{+\infty} dx \, \Psi_{0}^*(x) \, \hat{H} \, x \, \Psi_{0}(x) = \left( \int_{-\infty}^{+\infty} dx \, \Psi_{0}^*(x) \, x \, \Psi_{0}(x) \right)^* \] (375)
Thus, the second term is just the complex conjugate of the first term, which we have seen is real. The first two terms are thus identical.

The remaining terms are evaluated in the same way as the first term. We start with the expression
\[ \int_{-\infty}^{+\infty} dx \, \Psi_{0}^*(x) \, x \, \hat{H} \, x \, \Psi_{0}(x) \] (376)
and introduce a factor of 1 between the $\hat{H}$ and an $x$. This 1 can be written as an integral over a Dirac delta function $\delta(x - x')$ with respect to $x'$. Thus, we have

$$\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dx' \Psi_0^*(x) x \hat{H} \delta(x - x') x' \Psi_0(x')$$

(377)

where everything to the right of the delta function has been expressed in terms of the primed variable $x'$. On writing the delta function in terms of the completeness relation

$$\delta(x - x') = \sum_n \Psi_n(x) \Psi_n^*(x')$$

(378)

one obtains

$$= \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dx' \Psi_0^*(x) x \hat{H} \sum_n \Psi_n(x) \Psi_n^*(x') x' \Psi_0(x')$$

(379)

Since $\Psi_n(x')$ is an energy eigenfunction it satisfies

$$\hat{H} \Psi_n(x') = E_n \Psi_n(x')$$

(380)

This can be substituted in the expression for the term we are trying to evaluate, to yield

$$= \sum_n E_n \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dx' \Psi_0^*(x) x \Psi_n(x) \Psi_n^*(x') x' \Psi_0(x')$$

$$= \sum_n E_n \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dx' \Psi_0^*(x) x \Psi_n(x) \Psi_n^*(x') x' \Psi_0(x')$$

$$= \sum_n E_n \left( \int_{-\infty}^{+\infty} dx \Psi_0^*(x) x \Psi_n(x) \right) \left( \int_{-\infty}^{+\infty} dx' \Psi_n^*(x') x' \Psi_0(x') \right)$$

$$= \sum_n E_n \left| \int_{-\infty}^{+\infty} dx \Psi_0^*(x) x \Psi_n(x) \right|^2$$

(381)

where we have interchanged the order of summation and integrations.

Combining the four term leads to the equation

$$2 \sum_n (E_0 - E_n) \left| \int_{-\infty}^{+\infty} dx \Psi_0^*(x) x \Psi_n(x) \right|^2 = -\frac{\hbar^2}{m}$$

(382)

which was to be proved.
3.4.39 Exercise 29

Evaluate all the 6 commutation relations between the various pairs of the different Cartesian components of the orbital angular momentum operators $\hat{L}$.

3.4.40 Solution 29

The components of the angular momentum are given by

\[
\begin{align*}
\hat{L}_x &= y \hat{p}_z - z \hat{p}_y \\
\hat{L}_y &= z \hat{p}_x - x \hat{p}_z \\
\hat{L}_z &= x \hat{p}_y - y \hat{p}_x
\end{align*}
\]

(383)

The commutators can be evaluated by expanding them

\[
\begin{align*}
[ \hat{L}_x , \hat{L}_y ] &= [ y \hat{p}_z , \hat{L}_y ] - [ z \hat{p}_y , \hat{L}_y ] \\
&= [ y \hat{p}_z , z \hat{p}_x ] + [ z \hat{p}_y , x \hat{p}_z ] \\
&= -i \hbar y \hat{p}_x + i \hbar x \hat{p}_y \\
&= +i \hbar \hat{L}_z
\end{align*}
\]

(384)

so one has the result

\[
[ \hat{L}_x , \hat{L}_y ] = i \hbar \hat{L}_z
\]

(385)

The set of commutators can be summarized as

\[
[ \hat{L}_i , \hat{L}_j ] = i \hbar \epsilon_{i,j,k} \hat{L}_k
\]

(386)

where $\epsilon_{i,j,k}$ is the antisymmetric Levi-Civita symbol, defined as

\[
\epsilon_{i,j,k} = 1
\]

(387)

if $(i, j, k)$ is an even permutation of $(x, y, z)$, and

\[
\epsilon_{i,j,k} = -1
\]

(388)

if $(i, j, k)$ is an odd permutation of $(x, y, z)$ or $\epsilon_{i,j,k}$ is zero otherwise.

3.4.41 Exercise 30

In our discussion of the classical mechanics of a charged particle in an electromagnetic field, we have seen that the momentum of the particle is changed due
to the presence of the vector potential \( \mathbf{A}(r, t) \) and that the Hamiltonian is of the form

\[
H = \frac{p^2}{2m} - \frac{q}{mc} \mathbf{p} \cdot \mathbf{A}(r, t) + \frac{q^2}{2mc^2} \mathbf{A}^2(r, t) + q \phi(r, t)
\]  (389)

In the radiation or Coulomb gauge, defined by the condition \( \nabla \cdot \mathbf{A}(r, t) = 0 \), electromagnetic waves are solely represented by the vector potential. Thus, to lowest order in \( \mathbf{A} \), light couples to the particle via the interaction \( \hat{H}_{\text{int}} \)

\[
\hat{H}_{\text{int}} = -\frac{q}{2mc} \left( \hat{\mathbf{p}} \cdot \mathbf{A}(\hat{r}, t) + \mathbf{A}(\hat{r}, t) \cdot \hat{\mathbf{p}} \right)
\]  (390)

Show that the momentum operator can be expressed as a commutator of the position operator and the Hamiltonian for a charged particle in the scalar potential represented by the Hamiltonian \( \hat{H}_0 \),

\[
-\frac{i\hbar}{m} \hat{\mathbf{p}} = [\hat{H}_0, \hat{\mathbf{r}}]
\]  (391)

Hence, by using the energy eigenfunctions \( \Psi_n(r) \) and eigenvalues \( E_n \) of the unperturbed Hamiltonian \( \hat{H}_0 \), show that if \( \mathbf{A}(r, t) \) only varies over long length scales, i.e. \( \mathbf{A}(r, t) \approx \mathbf{A}(t) \), then

\[
\int d^3r \Psi_n^*(r) \hat{\mathbf{p}} \cdot \mathbf{A}(r, t) \Psi_m(r) = \frac{i\hbar}{m} \left( E_n - E_m \right) \int d^3r \Psi_n^*(r) \hat{\mathbf{r}} \cdot \mathbf{A}(r, t) \Psi_m(r)
\]  (392)

This provides the usual basis for discussing optical transitions involving the absorption or emission of light in terms of dipole transitions, when the wave length of light is much longer than the scale associated with the atomic or electronic structure.

3.4.42 Solution 30

The matrix elements of the interaction term can be expressed as

\[
-\frac{q}{mc} \int d^3r \phi_n^*(r) \hat{\mathbf{p}} \cdot \mathbf{A}(r, t) \phi_m(r)
\]  (393)

where we are using the radiation gauge

\[
\nabla \cdot \mathbf{A} = 0
\]  (394)

in which the vector potential is transverse to the direction of propagation. We can substitute the expression for \( \hat{\mathbf{p}} \) given by

\[
\hat{\mathbf{p}} = -\frac{im}{\hbar} [\mathbf{r}, \hat{H}_0]
\]  (395)
in the matrix elements, to find

\[ i \frac{q}{\hbar c} \int d^3r \phi_m^*(r) \mathbf{A} \cdot \{ r, \hat{H}_0 \} \phi_n(r) \]  

(396)

The matrix elements of the commutator can be expanded as two terms

\[ + i \frac{q}{\hbar c} \int d^3r \phi_m^*(r) \mathbf{A} \cdot \{ r, \hat{H}_0 \} \phi_n(r) \]

\[ - i \frac{q}{\hbar c} \int d^3r \phi_m^*(r) \hat{H}_0 \mathbf{A} \cdot \{ r, \phi_n(r) \} \]  

(397)

Now on using the energy eigenvalue equation

\[ \hat{H}_0 \phi_n(r) = E_n \phi_n(r) \]  

(398)

and the approximate \( r \) independence of the vector potential \( \mathbf{A} \), the first term can be evaluated, yielding

\[ + i \frac{q}{\hbar c} E_n \mathbf{A} \cdot \left( \int d^3r \phi_m^*(r) r \phi_n(r) \right) \]

\[ - i \frac{q}{\hbar c} \mathbf{A} \cdot \left( \int d^3r \phi_m^*(r) \hat{H}_0 r \phi_n(r) \right) \]  

(399)

The matrix elements of \( r \hat{H}_0 \) are related to the complex conjugate of its Hermitian conjugate \( \hat{H}_0 r \), thus

\[ \left( \int d^3r \phi_m^*(r) \hat{H}_0 r \phi_n(r) \right) \]

\[ = \left( \int d^3r \phi_m^*(r) r \hat{H}_0 \phi_n(r) \right)^* \]

\[ = E_m \left( \int d^3r \phi_n^*(r) r \phi_m(r) \right)^* \]  

(400)

Hence, we find

\[ + i \frac{q}{\hbar c} \left( E_n - E_m \right) \mathbf{A} \cdot \left( \int d^3r \phi_m^*(r) r \phi_n(r) \right) \]  

(401)

which can be re-written as

\[ + i \frac{q}{c} \omega_{n,m} \mathbf{A} \cdot \left( \int d^3r \phi_m^*(r) r \phi_n(r) \right) \]  

(402)

where \( E_n - E_m = \hbar \omega_{n,m} \) is related to the frequency of the photon involved in the transition. The matrix elements of \( r \) can be considered to provide an electric dipole for the transition, and hence the approximation that \( \mathbf{A} \) is almost \( r \) independent is called the dipole approximation.
3.4.43 Exercise 31

Extend the proof of the Thomas-Reiche-Kuhn sum rule to show

\[ \sum_n (E_n - E_m) \left| \int d^3 \mathbf{r} \phi_n^*(\mathbf{r}) \exp \left[ i \mathbf{k} \cdot \mathbf{r} \right] \phi_m(\mathbf{r}) \right|^2 = \frac{\hbar^2 k^2}{2m} \]  

(403)

3.4.44 Exercise 32

The scattering of light is encapsulated by the Kramers - Heisenberg formula. This involves the square of matrix elements of the interaction between a charged particle and the field, which is of the order of the fourth power of the vector potential \( \mathbf{A} \). The contributions to the matrix elements for this process are second order in the vector potential, and occurs as a combination of processes involving the paramagnetic interaction squared and the lowest order diamagnetic interaction. At low frequencies, one has Rayleigh scattering of light, which involves a partial cancellation between the contribution of the diamagnetic interaction and the process involving the paramagnetic interaction. In this exercise, we shall express the matrix elements of the diamagnetic interaction in a form similar to that of the second order process involving the paramagnetic interaction, as needed to demonstrate the partial cancellation.

The diamagnetic interaction term can be written as

\[ H_{\text{dia}} = + \frac{q^2}{2mc^2} \mathbf{A}(\mathbf{r}, t) \cdot \mathbf{A}(\mathbf{r}, t) \]  

(404)

The matrix elements of this interaction can be related to the scalar product of two unit vectors

\[ \hat{\mathbf{e}}_\alpha \cdot \hat{\mathbf{e}}_\beta \]  

(405)

Show that,

\[ \hat{\mathbf{e}}_\alpha \cdot \hat{\mathbf{e}}_\beta = \frac{1}{m} \sum_m \frac{1}{E_m - E_n} \times \]

\[ \left[ \int d^3 \mathbf{r} \phi_m^*(\mathbf{r}) \left( \hat{\mathbf{p}} \cdot \hat{\mathbf{e}}_\alpha \right) \phi_n(\mathbf{r}) \int d^3 \mathbf{r} ' \phi_n^*(\mathbf{r} ') \left( \hat{\mathbf{p}} \cdot \hat{\mathbf{e}}_\beta \right) \phi_m(\mathbf{r} ') \right. \]

\[ + \left. \int d^3 \mathbf{r} \phi_m^*(\mathbf{r}) \left( \hat{\mathbf{p}} \cdot \hat{\mathbf{e}}_\beta \right) \phi_n(\mathbf{r}) \int d^3 \mathbf{r} ' \phi_n^*(\mathbf{r} ') \left( \hat{\mathbf{p}} \cdot \hat{\mathbf{e}}_\alpha \right) \phi_m(\mathbf{r} ') \right] \]  

(406)

where \( \phi_m(\mathbf{r}) \) are energy eigenstates with eigenvalues \( E_m \).
We shall first write
\[
\hat{e}_\alpha \cdot \hat{e}_\beta = \sum_{i,j} ( \hat{e}_\alpha \cdot \hat{e}_i ) \delta_{i,j} ( \hat{e}_j \cdot \hat{e}_\beta )
\]
\[
= \sum_{i,j} ( \hat{e}_\alpha \cdot \hat{e}_i ) \left[ \frac{\hat{p}_i \cdot x_j}{i \hbar} \right] ( \hat{e}_j \cdot \hat{e}_\beta )
\]
\[
= \hat{e}_\alpha \cdot \left[ \frac{\hat{p} \cdot \tau}{i \hbar} \right] \cdot \hat{e}_\beta
\]  
(407)

It shall be understood that the scalar product of the operator \( \hat{p} \) is taken with \( \hat{e}_\alpha \), in both terms of the commutator. On taking the matrix elements between \( \phi^*_n(\tau) \) and \( \phi_n(\tau) \) and inserting the completeness relation, we have
\[
\hat{e}_\alpha \cdot \hat{e}_\beta = \hat{e}_\alpha \cdot \int d^3 \tau \phi^*_n(\tau) \left[ \frac{\hat{p} \cdot \tau}{i \hbar} \right] \phi_n(\tau) \cdot \hat{e}_\beta
\]
\[
= \frac{i}{\hbar} \hat{e}_\alpha \cdot \int d^3 \tau \phi^*_n(\tau) \frac{\tau}{i \hbar} \phi_n(\tau) \cdot \hat{e}_\beta
\]
\[
- \frac{i}{\hbar} \hat{e}_\beta \cdot \int d^3 \tau \phi^*_n(\tau) \frac{\tau}{i \hbar} \phi_n(\tau) \cdot \hat{e}_\alpha
\]
\[
= \frac{i}{\hbar} \left[ \hat{e}_\alpha \cdot \int d^3 \tau \phi^*_n(\tau) \frac{\tau}{i \hbar} \phi_m(\tau) \int d^3 \tau' \phi^*_m(\tau') \phi_n(\tau') \cdot \hat{e}_\beta
\]
\[
- \hat{e}_\beta \cdot \int d^3 \tau \phi^*_n(\tau) \frac{\tau}{i \hbar} \phi_m(\tau) \int d^3 \tau' \phi^*_m(\tau') \phi_n(\tau') \cdot \hat{e}_\alpha \right]
\]  
(408)

On using the equality
\[
( E_m - E_n ) \phi^*_m(\tau) \phi_n(\tau) = \phi^*_m(\tau) [ \hat{H}, \tau ] \phi_n(\tau)
\]
\[
= - i \frac{\hbar}{m} \phi^*_m(\tau) \frac{\tau}{i \hbar} \phi_n(\tau)
\]  
(409)

one obtains the result
\[
\hat{e}_\alpha \cdot \hat{e}_\beta = \frac{1}{m} \sum_m \left[ \frac{1}{E_m - E_n} \right] \left[ \int d^3 \tau \phi^*_n(\tau) ( \hat{e}_\alpha \cdot \hat{p} ) \phi^*_m(\tau) \right.
\]
\[
\times \int d^3 \tau' \phi_m(\tau') ( \hat{p} \cdot \hat{e}_\beta ) \phi_n(\tau') \right]
\]
\[
+ \frac{1}{m} \sum_m \left[ \frac{1}{E_m - E_n} \right] \left[ \int d^3 \tau \phi^*_n(\tau) ( \hat{e}_\beta \cdot \hat{p} ) \phi^*_m(\tau) \right.
\]
\[
\times \int d^3 \tau' \phi_m(\tau') ( \hat{p} \cdot \hat{e}_\alpha ) \phi_n(\tau') \right]
\]
\[
\frac{1}{\sqrt{2}\pi}\int d^3r' \phi_m(r') \left( \hat{p}' \cdot \hat{e}_\alpha \right) \phi_n(r')
\]

as was to be proved.

### 3.4.46 Hermitean Operators and Physical Measurements

A physical measurements of a physical quantity \(A\) can result in a set of real numbers \(a\) that are the possible results of the measurement. It is reasonable to represent the operator corresponding to \(A\) as a Hermitean operator \(\hat{A}\), where the eigenvalues correspond to the possible set of results \(a\).

Given a state represented by \(\Psi(r)\) which has the expansion in terms of the eigenfunctions of \(\hat{A}\)

\[
\Psi(r) = \sum_a C_a \phi_a(r)
\]

then the probability of finding a specific result \(a\) in the measurement of \(A\) is given by

\[
P(a) = |C_a|^2
\]

The orthonormality of the set of eigenfunctions ensures that the probability distribution \(P(a)\) is properly normalized.

\[
\int d^3r \left| \Psi(r) \right|^2 = 1
\]

\[
= \int d^3r \left| \sum_a C_a \phi_a(r) \right|^2
\]

\[
= \sum_{a,b} C_b^* C_a \delta_{a,b}
\]

\[
= \sum_a |C_a|^2
\]

Thus, the sum over probabilities \(P(a)\) is also normalized to unity.

The moments of the probability distribution are given by the matrix elements of powers of the operator

\[
\overline{A^n} = \int d^3r \Psi^*(r) \hat{A}^n \Psi(r)
\]

\[
= \int d^3r \sum_{m'} C_{m'}^* \Phi_{m'}^*(r) \hat{A}^n \sum_m C_m \Phi_m(r)
\]

\[
= \int d^3r \sum_{m'} C_{m'}^* \Phi_{m'}^*(r) \sum_m C_m a_m^* \Phi_m(r)
\]

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\[
\sum_{m,m'} C^*_{m'} C_m \delta_{m,m'} a^*_m = \sum_m |C_m|^2 a_m^n \tag{414}
\]

and in particular the average value of \( \mathcal{A} \) is given by the matrix elements

\[
\overline{\mathcal{A}} = \int d^3 \mathbf{r} \, \Psi^*(\mathbf{r}) \, \hat{\mathcal{A}} \, \Psi(\mathbf{r}) \tag{415}
\]

This is often called the expectation value of \( \hat{\mathcal{A}} \) in the state \( \Psi(\mathbf{r}) \).

### 3.4.47 Exercise 33

Find the average values of the energy and the momentum of a particle in the state represented by the wave function

\[
\Psi(\mathbf{r}) = C \exp \left[ -\alpha (\mathbf{r} - \mathbf{r}_0)^2 \right] \tag{416}
\]

where \( \alpha^2 = \frac{m \omega}{\hbar} \), and the Hamiltonian is given by

\[
\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m \omega^2 \mathbf{r}^2}{2} \tag{417}
\]

Also find the mean squared deviation of the (vector) position operator.

### 3.4.48 Solution 33

The magnitude of the normalization constant is found from the condition

\[
1 = |C|^2 \int d^3 \mathbf{r} \, \exp \left[ -2 \alpha (\mathbf{r} - \mathbf{r}_0)^2 \right] \tag{418}
\]

The integral is evaluated to yield

\[
1 = |C|^2 \left( \frac{\pi}{2 \alpha} \right)^{\frac{3}{2}} \tag{419}
\]

Thus, we have the normalization

\[
|C| = \left( \frac{2 \alpha}{\pi} \right)^{\frac{3}{4}} \tag{420}
\]
up to an arbitrary choice of phase.

The average value of the energy is given by the expectation value of the Hamiltonian

$$\mathcal{E} = \int d^3 r \, \Psi^* (\mathbf{r}) \, \hat{H} \, \Psi (\mathbf{r})$$

$$= \int d^3 r \, \Psi^* (\mathbf{r}) \left[ \frac{\hat{\mathbf{p}}^2}{2m} + \frac{m \omega^2 r^2}{2} \right] \Psi (\mathbf{r})$$

$$= \left( \frac{2 \alpha}{\pi} \right)^{\frac{3}{2}} \int d^3 r \, \left[ \frac{\hbar^2}{2m} \left( 6 \alpha - 4 \alpha^2 ( \mathbf{r} - \mathbf{r}_0 )^2 \right) + \frac{m \omega^2 r^2}{2} \right] \times$$

$$\times \exp \left[ -2 \alpha ( \mathbf{r} - \mathbf{r}_0 )^2 \right]$$  \hspace{1cm} (421)$$

The integral is evaluated as

$$\mathcal{E} = \frac{3 \hbar^2 \alpha}{m} + \frac{m \omega^2 \mathbf{r}_0^2}{2} - \frac{3 \hbar^2 \alpha}{2m} + \frac{3 m \omega^2}{8 \alpha}$$

$$= \frac{m \omega^2 \mathbf{r}_0^2}{2} + \frac{3 \hbar^2 \alpha}{2m} + \frac{3 m \omega^2}{8 \alpha}$$ \hspace{1cm} (422)$$

where the first term is the energy of a displaced classical harmonic oscillator. On substituting \(\alpha\), one finds

$$\mathcal{E} = \frac{m \omega^2 \mathbf{r}_0^2}{2} + \frac{3}{2} \hbar \omega$$ \hspace{1cm} (423)$$

where the last term represents the zero-point energy for the three independent degrees of freedom.

The average value of the momentum is zero, due to the fact that the wave function has no spatially varying phase. Hence, the integrand of the expectation value of \(\hat{\mathbf{p}}\) is antisymmetric around \(\mathbf{r}_0\)

$$\mathcal{P} = 2i \hbar \alpha | \mathcal{C} |^2 \int d^3 r \left[ ( \mathbf{r} - \mathbf{r}_0 ) \right] \exp \left[ -2 \alpha ( \mathbf{r} - \mathbf{r}_0 )^2 \right]$$ \hspace{1cm} (424)$$

Thus, the expectation value of the momentum vanishes.

The average value of \(\mathbf{r}^2\) is given by

$$\overline{\mathbf{r}^2} = \mathbf{r}_0^2 + \frac{3}{4 \alpha}$$ \hspace{1cm} (425)$$

Hence, the mean squared deviation is given by

$$\Delta_{\mathbf{r},ms} = \frac{3}{4 \alpha} = \frac{3 \hbar}{2m \omega}$$ \hspace{1cm} (426)$$
which corresponds to the sum of the mean square displacements along the three Cartesian axes.

3.4.49 Exercise 34

Find the average value of the $z$ component of the orbital angular momentum and square of the $z$ component of the angular momentum for the following three wave functions

\[
\begin{align*}
\Psi_{1a}(r) &= C_1 r f(r) \sin \theta \cos \varphi \\
\Psi_{1b}(r) &= C_1 r f(r) \sin \theta \sin \varphi \\
\Psi_{1c}(r) &= C_1 r f(r) \cos \theta
\end{align*}
\]

Do you need to evaluate the radial part of the integrations?

3.4.50 Solution 34

The operator corresponding to the $z$ component of the angular momentum is given by

\[
\hat{L}_z = -i \hbar \frac{\partial}{\partial \varphi}
\]

Thus, the expectation value of the angular momentum in a state $\Psi(r, \theta, \varphi)$ is given by the expression

\[
\begin{align*}
\mathcal{L}_z &= \int_0^\infty dr \ r^2 \int_0^\pi d\theta \int_0^{2\pi} d\varphi \ \Psi^*(r, \theta, \varphi) \hat{L}_z \Psi(r, \theta, \varphi) \\
&= -i \hbar \int_0^\infty dr \ r^2 \int_0^\pi d\theta \int_0^{2\pi} d\varphi \ \Psi^*(r, \theta, \varphi) \frac{\partial}{\partial \varphi} \Psi(r, \theta, \varphi)
\end{align*}
\]

The expectation value for the first two states involve the integration

\[
\int_0^{2\pi} d\varphi \ \sin \varphi \ \cos \varphi = 0
\]

whereas the third state is an eigenstate of the $z$ component of the angular momentum operator with eigenvalue zero. Hence, the average value of $\hat{L}_z$ is zero in all three states.
The mean squared value of the $z$ component of the angular momentum is given by

$$L_z^2 = \int_0^\infty dr \, r^2 \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \, \Psi^* \left(r, \theta, \varphi \right) \hat{L}_z \Psi \left(r, \theta, \varphi \right)$$

$$= -\hbar^2 \int_0^\infty dr \, r^2 \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \, \Psi^* \left(r, \theta, \varphi \right) \frac{\partial^2}{\partial \varphi^2} \Psi \left(r, \theta, \varphi \right)$$  \hspace{1cm} (431)

In the first two states one has the factors

$$-\hbar^2 \int_0^{2\pi} d\varphi \, \cos \varphi \frac{\partial^2}{\partial \varphi^2} \cos \varphi = \hbar^2 \int_0^{2\pi} d\varphi \, \cos^2 \varphi$$

$$= \hbar^2 \pi$$

$$-\hbar^2 \int_0^{2\pi} d\varphi \, \sin \varphi \frac{\partial^2}{\partial \varphi^2} \sin \varphi = \hbar^2 \int_0^{2\pi} d\varphi \, \sin^2 \varphi$$

$$= \hbar^2 \pi$$  \hspace{1cm} (432)

and the corresponding factor for the third state is identically zero as it is an eigenstate with zero eigenvalue. One recognizes that the expectation values are proportional to the normalization integral and, as the state are properly normalized, one has

$$L_z^2 = \hbar^2$$  \hspace{1cm} (433)

for the first two states and the expectation value is zero for the last state.

---

**3.4.51 Exercise 35**

Find the average values of the $x$, $y$, and $z$ component of the orbital angular momentum and square of the component of the angular momentum for the following three wave functions

$$\Psi_{1a}(r) = C_1 \left(x + i \, y \right) f(r)$$

$$\Psi_{1b}(r) = C_1 \left(x - i \, y \right) f(r)$$

$$\Psi_{1c}(r) = C_1 \, z \, f(r)$$  \hspace{1cm} (434)

where $f(r)$ is a function of the radial distance, defined via $r^2 = x^2 + y^2 + z^2$. What can one conclude about the magnitude of the angular momentum of these examples?
We shall first note that the components of the angular momentum operator are
\[ \hat{L}_x = -i \hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \]
\[ \hat{L}_y = -i \hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \]
\[ \hat{L}_z = -i \hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \]
and that any radially symmetric function \( f(r) \) is an eigenfunction of the components of the angular momentum operator with a zero eigenvalue. For example, on considering the action of the operator \( \hat{L}_z \) on an arbitrary radially symmetric function \( f(r) \), one has
\[ \hat{L}_z f(r) = -i \hbar \left( x \frac{\partial f}{\partial y} - y \frac{\partial f}{\partial x} \right) \left( x \pm i y \right) = 0 \]  
as long as \( r \neq 0 \). Likewise, the other components also produce zero when acting on an arbitrary radial function \( f(r) \).

The three functions given by \( \Psi_1(r) \) are seen to be eigenfunctions of \( \hat{L}_z \) with eigenvalues \( \pm \hbar \) and 0, since
\[ \hat{L}_z \Psi_{1a/b}(r) = -i \hbar C_1 f(r) \left( x \frac{\partial f}{\partial y} - y \frac{\partial f}{\partial x} \right) \left( x \pm i y \right) \]
\[ = -i \hbar C_1 f(r) \left( \pm x i - y 1 \right) \]
\[ = \pm \hbar C_1 f(r) \left( x \pm i y \right) \]
\[ = \pm \hbar \Psi_{1a/b} \] (437)
while
\[ \hat{L}_z \Psi_{1c}(r) = -i \hbar C_1 f(r) \left( x \frac{\partial f}{\partial y} - y \frac{\partial f}{\partial x} \right) z \]
\[ = 0 \] (438)
Thus, these states are eigenstates of \( \hat{L}_z \) and the average value of \( L_z \) is equal to either \( \pm \hbar \) or 0 respectively. Also the average values of \( L_z^2 \) are just 1 and 0.

The average value of \( \hat{L}_x \) and \( \hat{L}_y \) in states \( \Psi_{1a/b}(r) \) can be found by noting that
\[ \hat{L}_x \Psi_{1a/b}(r) = \mp \hbar \Psi_{1c}(r) \]
\[ \hat{L}_y \Psi_{1a/b}(r) = -i \hbar \Psi_{1c}(r) \] (439)
and the expectation values of $L_x$ and $L_y$ are zero in these states since the original states and the transformed states are all eigenstates of $\hat{L}_z$ corresponding to different eigenvalues, and the eigenstates of a Hermitian operator with different eigenvalues are orthogonal.

The expectation value of $\hat{L}_x$ and $\hat{L}_y$ in the state $\Psi_{1c}(\mathbf{r})$ can be found by noting that

$$\hat{L}_x \Psi_{1c}(\mathbf{r}) = -i \hbar C_1 y f(r)$$
$$= -\frac{\hbar}{2} \left( \Psi_{1a}(\mathbf{r}) - \Psi_{1b}(\mathbf{r}) \right)$$
$$\hat{L}_y \Psi_{1c}(\mathbf{r}) = +i \hbar C_1 x f(r)$$
$$= \frac{\hbar}{2} \left( \Psi_{1a}(\mathbf{r}) + \Psi_{1b}(\mathbf{r}) \right)$$

which are just linear combinations of the eigenstates of $\hat{L}_z$. The expectation value is zero as the overlap between eigenstates of $\hat{L}_z$ with different eigenvalues is zero.

We recognize that the set of functions $\Psi_{1a}(\mathbf{r})$, $\Psi_{1b}(\mathbf{r})$ and $\Psi_{1c}(\mathbf{r})$ form a closed set under the angular momentum operators, as they operators acting on any member of the set just transform them into linear combinations of the set.

By repeated use of the above relations one can show that

$$\int d^3\mathbf{r} \left| \Psi_{1a}^*(\mathbf{r}) \right| \hat{L}_x^2 \Psi_{1a}(\mathbf{r}) = -\hbar \int d^3\mathbf{r} \left| \Psi_{1a}^*(\mathbf{r}) \right| \hat{L}_x \Psi_{1c}(\mathbf{r})$$
$$= \frac{\hbar^2}{2} \int d^3\mathbf{r} \left| \Psi_{1a}^*(\mathbf{r}) \right| \left( \Psi_{1a}(\mathbf{r}) - \Psi_{1c}(\mathbf{r}) \right)$$
$$= \frac{\hbar^2}{2}$$

and also that

$$\int d^3\mathbf{r} \left| \Psi_{1b}^*(\mathbf{r}) \right| \hat{L}_x^2 \Psi_{1b}(\mathbf{r}) = +\hbar \int d^3\mathbf{r} \left| \Psi_{1b}^*(\mathbf{r}) \right| \hat{L}_x \Psi_{1c}(\mathbf{r})$$
$$= -\frac{\hbar^2}{2} \int d^3\mathbf{r} \left| \Psi_{1b}^*(\mathbf{r}) \right| \left( \Psi_{1a}(\mathbf{r}) - \Psi_{1c}(\mathbf{r}) \right)$$
$$= \frac{\hbar^2}{2}$$

Likewise, for the expectation values of $\hat{L}_y^2$ one finds that

$$\int d^3\mathbf{r} \left| \Psi_{1a}^*(\mathbf{r}) \right| \hat{L}_y^2 \Psi_{1a}(\mathbf{r}) = -i \hbar \int d^3\mathbf{r} \left| \Psi_{1a}^*(\mathbf{r}) \right| \hat{L}_y \Psi_{1c}(\mathbf{r})$$
\[ \frac{\hbar^2}{2} \int d^3 \mathbf{r} \Psi_{1a}(\mathbf{r}) \left( \Psi_{1a}(\mathbf{r}) + \Psi_{1c}(\mathbf{r}) \right) \]
\[ = \frac{\hbar^2}{2} \] (443)

and also that
\[ \int d^3 \mathbf{r} \Psi_{1b}^*(\mathbf{r}) \hat{L}_y^2 \Psi_{1b}(\mathbf{r}) = -i \hbar \int d^3 \mathbf{r} \Psi_{1b}^*(\mathbf{r}) \hat{L}_y \Psi_{1c}(\mathbf{r}) \]
\[ = -\frac{\hbar^2}{2} \int d^3 \mathbf{r} \Psi_{1b}^*(\mathbf{r}) \left( \Psi_{1a}(\mathbf{r}) + \Psi_{1c}(\mathbf{r}) \right) \]
\[ = \frac{\hbar^2}{2} \] (444)

The expectation value of \( \hat{L}_x^2 \) and \( \hat{L}_y^2 \) in the state \( \Psi_{1c}(\mathbf{r}) \) are found from
\[ \int d^3 \mathbf{r} \Psi_{1c}^*(\mathbf{r}) \hat{L}_x^2 \Psi_{1c}(\mathbf{r}) = -\frac{\hbar}{2} \int d^3 \mathbf{r} \Psi_{1c}^*(\mathbf{r}) \hat{L}_x \left( \Psi_{1a}(\mathbf{r}) - \Psi_{1b}(\mathbf{r}) \right) \]
\[ = \frac{\hbar^2}{2} \int d^3 \mathbf{r} \Psi_{1c}^*(\mathbf{r}) \Psi_{1c}(\mathbf{r}) \]
\[ = \frac{\hbar^2}{2} \] (445)

and also that
\[ \int d^3 \mathbf{r} \Psi_{1c}^*(\mathbf{r}) \hat{L}_y^2 \Psi_{1c}(\mathbf{r}) = +i \frac{\hbar}{2} \int d^3 \mathbf{r} \Psi_{1c}^*(\mathbf{r}) \hat{L}_y \left( \Psi_{1a}(\mathbf{r}) + \Psi_{1b}(\mathbf{r}) \right) \]
\[ = \frac{\hbar^2}{2} \int d^3 \mathbf{r} \Psi_{1c}^*(\mathbf{r}) \Psi_{1c}(\mathbf{r}) \]
\[ = \frac{\hbar^2}{2} \] (446)

The average value of \( \hat{L}_z^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \) is \( 2 \hbar^2 \) for all these states. In fact one can show that the states \( \Psi_{1a}(\mathbf{r}), \Psi_{1b}(\mathbf{r}), \Psi_{1c}(\mathbf{r}) \) are not only eigenstates of \( \hat{L}_z \) but are also eigenstates of the operator
\[ \hat{L}_z^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \] (447)

with eigenvalues of \( 2 \hbar^2 \). This operator corresponds to the squared length of the vector angular momentum. These states can be thought of as having angular momentum of the same magnitude, but with different orientations.
3.5 Quantization

We have emphasized that because a physical measurement results in a change of the state of the system, measurements should be represented by operators. We have also asserted that a measurement of a physical quantity $A$ yields a real value $a$ as the result of the measurement, and that immediately after the measurement has been made it is certain that the resulting state corresponds to the state in which $A$ has the definite value $a$. This means that, immediately after the measurement, the system is in an eigenstate of the operator $A$ which has an eigenvalue $a$. Furthermore, we have made a choice that the physical operators should be Hermitean so that we know that the eigenvalues are real. Thus far, we have been mainly examining the mathematics of operators and wave functions using several physical examples. It remains to discuss how these operators are chosen, and what the relationships between them are.

3.5.1 Relations between Physical Operators

A physical operator that appears in Quantum Mechanics is associated with the name of an analogous quantity or variable in Classical Mechanics. That is, we associate a classical variable with a quantum mechanical operator. In the Hamiltonian formulation of classical mechanics, the classical quantities may be expressed in terms of coordinates and momenta and perhaps time, but not in terms of derivatives. These relationships are called constitutive or definitive relationships. In quantum mechanics, the various operators representing physical quantities satisfy the same constitutive relationships as the classical variables do. That is, the classical quantities in a definitive relationship are replaced by the quantum operators. However, the order in which the quantum operators appear in the definition may have to be chosen judiciously, as they may not be commuting operators.

3.5.2 The Correspondence Principle

The relationships between the various quantum operators are chosen to correspond to the relations between variables in classical mechanics, for a specific purpose. Classical Mechanics has a well defined regime in which it provides an excellent and accurate description of nature. This is often called the regime of validity of Classical Mechanics. Quantum Mechanics, if it is to provide a better description of nature, should produce results which are identical to the results of classical mechanics (to within the experimental accuracy) within the regime of validity of classical mechanics. By assuming that the same relationships hold between classical variables and quantum operators, it is ensured that if the quantum operators can, to a good approximation, be replaced by values, i.e. real variables, then Quantum Mechanics will reduce to classical mechanics. We shall examine the conditions that are required for a quantum state to lie within the regime of validity of Classical Mechanics. One condition that is needed to be
satisfied, if quantum operators may be approximated by real variables, is that
the value associated with the commutator \([ \hat{A}, \hat{B} ]\) between two operators \(\hat{A}\) and \(\hat{B}\) should be negligibly small when compared to the products of the values associated with \(\hat{A}\) and \(\hat{B}\). The values or variables associated with the operators are
naturally identified with the expectation values for the quantum state in question. Since, in Hamiltonian mechanics, all quantities are expressed in terms of
the canonically conjugate momenta and coordinates \(q_i\) and \(p_j\), the commutators of all operators can be reduced to the non-zero combinations of the fundamental
commutator \([ \hat{q}_i, \hat{p}_j ]\). The Complementarity Principle associates the value of
the fundamental commutators with the corresponding classical Poisson Brackets, up to a constant proportional to \(\hbar\). If the commutators, hence \(\hbar\), can be
considered to be negligibly small when compared with the average values of \(p_i\) and \(q_j\) in the physical state, then Quantum Mechanics will reduce to Classical
Mechanics in this limit. The Correspondence Principle can be embodied in the
concise statement that Quantum Mechanics should reduce to Classical Mechan-
cics in the limit \(\hbar \to 0\).

3.5.3 The Complementarity Principle

The complementarity principle has the effect that the Poisson Brackets between
two classical variables are to be replaced by the commutator between two quan-
tum operators

\[
[ A, B ]_{PB} \to \frac{[ \hat{A}, \hat{B} ]}{i \hbar}
\]

where \(\hbar\) is a universal constant. The equivalence can be seen by examining
the Poisson Bracket algebra between two products of quantum operators, while
respecting the order

\[
\begin{align*}
[ \hat{A}_1 \hat{A}_2, \hat{B}_1 \hat{B}_2 ]_{PB} &= [ \hat{A}_1, \hat{B}_1 ]_{PB} \hat{B}_2 \hat{A}_2 + \hat{B}_1 [ \hat{A}_1, \hat{B}_2 ]_{PB} \hat{A}_2 \\
&\quad + \hat{A}_1 [ \hat{A}_2, \hat{B}_1 ]_{PB} \hat{B}_2 + \hat{A}_1 \hat{B}_1 [ \hat{A}_2, \hat{B}_2 ]_{PB} \\
&= [ \hat{A}_1, \hat{B}_1 ]_{PB} \hat{A}_2 \hat{B}_2 + \hat{A}_1 [ \hat{A}_2, \hat{B}_1 ]_{PB} \hat{B}_2 \\
&\quad + \hat{B}_1 [ \hat{A}_1, \hat{B}_2 ]_{PB} \hat{A}_2 + \hat{A}_1 \hat{B}_1 [ \hat{A}_2, \hat{B}_2 ]_{PB}
\end{align*}
\]

Thus, on equating these two results we find

\[
[ \hat{A}_1, \hat{B}_1 ]_{PB} [ \hat{A}_2, \hat{B}_2 ] = [ \hat{A}_2, \hat{B}_3 ]_{PB} [ \hat{A}_1, \hat{B}_1 ]
\]

which, since the pair of operators \(\hat{A}_1\) and \(\hat{B}_1\) are independent of the pair \(\hat{A}_2\) and \(\hat{B}_2\), leads to the discovery that the quantum Poisson bracket is proportional to
the commutator, with a universal constant of proportionality

\[
[ \hat{A}_1, \hat{B}_1 ] = i \hbar [ \hat{A}_1, \hat{B}_1 ]_{PB}
\]

On retaining the classical value of the Poisson bracket between canonically con-
jugate coordinates \(q_i\) and momentum \(p_j\), one finds that the quantum operators
must satisfy the commutation relations

\[
\begin{align*}
[\hat{p}_j, \hat{q}_i] &= -i\hbar \delta_{j,i} \\
[\hat{p}_j, \hat{p}_i] &= [\hat{q}_j, \hat{q}_i] = 0
\end{align*}
\] (452)

Having found the commutation relationships between the momenta and coordinate operators, the basis for quantization is complete as any operator can be expressed in terms of the canonical conjugate momenta and coordinates. However, it is usual to find explicit representations for the operators.

The procedure of quantization is simplest and free from ambiguities, if one quantizes in a Cartesian coordinate system and then transforms to other coordinate systems.

The classical limit is obtained when the operators can be replaced by their eigenvalues and this implies that the commutators are negligible. As the commutation relation between two operators ultimately involves a commutation relation between position and momentum, the commutation relation is proportional to $\hbar$. The classical limit is approached when $\hbar$ is negligible compared with the products of appropriate expectation values in a state.

### 3.5.4 Coordinate Representation

The coordinate representation is that usually used in Schrödinger’s wave mechanics. In this case, the position operator $\hat{r}$ is diagonal in that it is represented by the vector variable $r$. The momentum operator $\hat{p}$ is represented by a Hermitian first order differential operator. The wave function is a function of the position $\Psi(r)$, as $r$ is diagonal. The momentum operator is represented as the sum of a gradient term and a real function

\[
\hat{p} = r = -i\hbar \nabla + \sum \Lambda(r)
\] (453)

where $\Lambda(r)$ is an arbitrary real function. The gradient of the real function, $\nabla \Lambda$, is to be regarded as a function and not as an operator. Usually the arbitrary function is removed from the momentum operator by an appropriate choice of the phase of the wave function.

\[
\begin{align*}
\hat{p} &\to \hat{p}' = -i\hbar \nabla \\
\Psi(r) &\to \Psi'(r) = \exp \left[ + i \frac{\Lambda(r)}{\hbar} \right] \Psi(r)
\end{align*}
\] (454)

This representation is the one we shall mostly use in this class.

For example, in generalized coordinate systems, the infinitesimal displacement $ds$ is given in terms of the metric $g_{i,j}$ and the infinitesimal changes in the
generalized coordinates \( dq^i \) via

\[ ds^2 = \sum_{i,j} g_{i,j} \, dq^i \, dq^j \]  

(455)

The metric is a symmetric tensor \( g_{i,j} = g_{j,i} \). Since the kinetic energy is defined in terms of the square of the infinitesimal displacement per unit time, \( (\frac{ds}{dt})^2 \), the classical Lagrangian is given by

\[ L(q, \dot{q}) = \frac{m}{2} \sum_{i,j} \dot{q}^i \, g_{i,j} \, \dot{q}^j - V(q) \]  

(456)

The canonical momenta are defined by the derivatives of the Lagrangian w.r.t. the generalized velocities

\[ p_i = \frac{\partial L}{\partial \dot{q}^i} = m \, g_{i,j} \, \dot{q}^j \]  

(457)

The associated quantum mechanical operators have to be Hermitean with the inner product

\[ \int \prod_j dq^j \, \sqrt{g} \, \Phi^*(r) \, \Psi(r) \]  

(458)

where \( g \) is given by the determinant of the covariant metric tensor

\[ g = \det \left( g_{i,j}(q) \right) \]  

(459)

The quantum mechanical operators must satisfy the canonical commutation rules

\[
\begin{align*}
[ \hat{p}_i, \hat{q}^j ] &= -i \, \hbar \, \delta^j_i \\
[ \hat{p}_i, \hat{p}^j ] &= 0 \\
[ \hat{q}_i, \hat{q}^j ] &= 0
\end{align*}
\]  

(460)

In the coordinate representation, the generalized momenta are given by

\[ \hat{p}_j = -i \, \hbar \, g^{-\frac{1}{2}} \frac{\partial}{\partial q^j} \, g^{\frac{1}{2}} \]  

(461)

or

\[ \hat{p}_j = -i \, \hbar \left( \frac{\partial}{\partial q^j} + \frac{1}{2} \, \Gamma_j \right) \]  

(462)

where

\[ \Gamma_j = g^{-\frac{1}{2}} \left( \frac{\partial}{\partial q^j} \, g^{\frac{1}{2}} \right) \]  

(463)

The position operators are given by

\[ \hat{q}^i = q^i \]  

(464)
As shown by Podolsky\(^8\), the Hamiltonian can be written in the symmetric Hermitean form

\[ \hat{H} = \frac{1}{2m} \sum_{i,j} g^{-\frac{1}{4}} \hat{p}_i g^{\frac{1}{2}} g^{ij} g^{\frac{1}{2}} \hat{p}_j g^{-\frac{1}{4}} + V(q) \]  

(465)

where the contra-variant metric tensor is given by \( g^{ij} = g^{-1}_{ij} \).

In planar polar coordinates, \((r, \phi)\), the infinitesimal length element is given by

\[ ds^2 = dr^2 + r^2 d\phi^2 \]  

(466)

Thus, the co-variant metric has the diagonal form

\[ g_{i,j} = \begin{pmatrix} 1 & 0 \\ 0 & r^2 \end{pmatrix} \]  

(467)

and the contra-variant metric is

\[ g^{i,j} = \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{r^2} \end{pmatrix} \]  

(468)

The infinitesimal volume element is given by

\[ dr \, d\phi \sqrt{g} = dr \, d\phi \, r \]  

(469)

The generalized momenta operators are given by

\[ \hat{p}_r = -i \hbar r^{-\frac{1}{2}} \frac{\partial}{\partial r} \, r^{\frac{1}{2}} \]

\[ \hat{p}_\phi = -i \hbar r^{-\frac{1}{2}} \frac{\partial}{\partial \phi} \]  

(470)

The Hamiltonian is given by

\[ \hat{H} = \frac{1}{2m} \left[ r^{-\frac{1}{2}} \hat{p}_r \, r \hat{p}_r \, r^{-\frac{1}{2}} + r^{-\frac{1}{2}} \hat{p}_\phi \frac{1}{r} \hat{p}_\phi \, r^{-\frac{1}{2}} \right] + V(r) \]

\[ = -\frac{\hbar^2}{2m} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right] + V(r) \]  

(471)

In spherical polar coordinates, \((r, \theta, \phi)\), the infinitesimal length \( ds \) is given by

\[ ds^2 = dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta \, d\phi^2 \]  

(472)

Thus, the co-variant metric has the diagonal form

\[ g_{i,j} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & r^2 & 0 \\ 0 & 0 & r^2 \sin^2 \theta \end{pmatrix} \]  

(473)

\(^8\)B. Podolsky, Phys. Rev. 32, 812 (1928).
and the contra-variant tensor is given by the inverse matrix

\[ g^{ij} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{r^2} & 0 \\ 0 & 0 & \frac{1}{r^2 \sin^2 \theta} \end{pmatrix} \] (474)

Thus, the infinitesimal volume element is given by

\[ dr \, d\theta \, d\varphi \, \sqrt{g} = dr \, d\theta \, d\varphi \, r^2 \sin \theta \] (475)

and the canonical momentum \( \hat{p}_j \) are given by

\[
\begin{align*}
\hat{p}_r &= -i \hbar \frac{1}{r \sqrt{\sin \theta}} \frac{\partial}{\partial r} r \sqrt{\sin \theta} \\
\hat{p}_\theta &= -i \hbar \frac{1}{r \sqrt{\sin \theta}} \frac{\partial}{\partial \theta} r \sqrt{\sin \theta} \\
\hat{p}_\varphi &= -i \hbar \frac{1}{r \sqrt{\sin \theta}} \frac{\partial}{\partial \varphi} r \sqrt{\sin \theta}
\end{align*}
\] (476)

Hence, the Hamiltonian has the form

\[
\hat{H} = \frac{1}{2m} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \left( \frac{\partial}{\partial \theta} \right) \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] + V(r)
\] (477)

3.5.5 Momentum Representation

The momentum representation is the representation in which the momentum operator is diagonal, and the wave function is given as a function of \( \vec{p} \), \( \Phi(\vec{p}) \). The momentum and position operators are given by

\[
\begin{align*}
\hat{\vec{p}} &= \vec{p} \\
\hat{\vec{x}} &= + i \hbar \sum_{\vec{p}} - \sum_{\vec{p}} \Lambda(\vec{p})
\end{align*}
\] (478)

where the gradients are derivatives w.r.t. \( \vec{p} \). This representation of the operators satisfies the required commutation relations between the components of \( \hat{\vec{x}} \).
and \( \hat{p} \). In complete analogy to the real-space representation, the momentum distribution function is given by

\[
P(p) \, d^3p = |\Phi(p)|^2 \, d^3p
\]  

(479)

and is normalized to unity

\[
\int P(p) \, d^3p = 1
\]  

(480)

The transform between the real space and momentum representation is given by the integral Fourier Transform,

\[
\Psi(r) = \left(\frac{1}{2 \pi \hbar}\right)^{\frac{3}{2}} \int d^3p \exp\left[ + i \frac{p \cdot r}{\hbar} \right] \Phi(p)
\]  

(481)

and its inverse

\[
\Phi(p) = \left(\frac{1}{2 \pi \hbar}\right)^{\frac{3}{2}} \int d^3r \exp\left[ - i \frac{p \cdot r}{\hbar} \right] \Psi(r)
\]  

(482)

The components of momentum \( \hat{p} \) and \( \hat{r} \) position operators in the coordinate representation are defined by their action on an arbitrary state \( \Psi(r) \), which produces transformed states \( \psi_{p_x} \) and \( \psi_x \)

\[
\psi_{p_x}(r) = -i \hbar \sum \Psi(r)
\]

\[
\psi_x(r) = r \Psi(r)
\]  

(483)

The corresponding operators in the momentum representation are found by Fourier transforming these equations. On Fourier transforming and integrating the first equation by parts, and with appropriate boundary conditions, one finds the expression for the momentum operator in the momentum representation. Likewise, on differentiating the integral Fourier transform with respect to \( p_x \), one obtains a representation of the position operator \( \hat{r}_x \) in momentum space. The resulting equations are

\[
\phi_{p_x}(p) = p_x \Phi(p)
\]

\[
\phi_x(p) = + i \hbar \sum_{p_x} \Phi(p)
\]  

(484)

This confirms the identification of the operators in the momentum representation.

Example
The momentum space representation provides a simple way for finding the bound states of a particle moving in one dimension, in the presence of a particular potential

\[ V(x) \rightarrow \infty \quad \text{for } x < 0 \]
\[ V(x) = -\frac{e^2}{2x} \quad \text{for } x > 0 \]  

(485)

![Image potential for electrons near a metal surface](image)

Figure 21: The one-dimensional image potential \( V(x) \) which confines a particle close to an in-penetrable region for \( x < 0 \). The bound state energy is marked by a horizontal line.

Solution

On multiplying by \( x \), the energy eigenvalue equation becomes

\[
\hat{x} \hat{p}^2 \frac{1}{2m} - \frac{e^2}{2} \phi_n(p) = \hat{x} E_n \phi_n(p)
\]

(486)

A simplification has occurred for our particular choice of potential \( V(x) \), since the energy eigenvalue equation has been transformed so that it is now linear in \( \hat{x} \). Therefore,

\[
i \hbar \frac{\partial}{\partial p} \left[ \frac{p^2}{2m} - E_n \right] \phi_n(p) = \frac{e^2}{2} \phi_n(p)
\]

(487)
This is a first order differential equation
\[
\left( i \frac{\hbar}{m} - \frac{\epsilon^2}{2} \right) \phi_n(p) = - i \frac{\hbar}{m} \left( \frac{p^2}{2 m} - E_n \right) \left( \frac{\partial \phi_n}{\partial p} \right)
\] (488)

The equation can be put in the form of an integral
\[
\int_0^p dp' \frac{(\partial \phi_n)}{\phi_n(p')} = - \int_0^p dp' \left( \frac{p'}{m} + i \frac{\epsilon^2}{2 \hbar} \right) \left( \frac{\partial \phi_n}{\partial p'} \right)
\] (489)

which can be evaluated as
\[
\ln \frac{\phi_n(p)}{\phi_n(0)} = - \ln \left( 1 - \frac{p^2}{2 m E_n} \right) - i \frac{\epsilon^2}{2 \hbar} \sqrt{\frac{2 m}{-E_n}} \tan^{-1} \frac{p}{\sqrt{-2 m E_n}}
\] (490)

Hence, one finds
\[
\phi_n(p) = \left( \frac{\phi_n(0)}{1 - \frac{p^2}{2 m E_n}} \right) \exp \left[ - i \frac{\epsilon^2}{2 \hbar} \sqrt{\frac{2 m}{-E_n}} \tan^{-1} \frac{p}{\sqrt{-2 m E_n}} \right]
\] (491)

Thus, \( \phi_n(p) \) vanishes as \( p \to \pm \infty \) and is normalizable. This indicates that \( \psi_n(x) \) is also normalizable for \( E_n < 0 \) and hence satisfies the boundary condition at \( x \to \infty \).

The energy eigenvalues are found by insisting that the real space wave function \( \psi_n(x) \) satisfy the boundary condition
\[
\psi_n(0) = 0
\] (492)

at \( x = 0 \), since \( V(0) \to \infty \). The wave function in real space is given in terms of the momentum space wave function through
\[
\psi_n(x) = \frac{1}{\sqrt{2 \pi \hbar}} \int_{-\infty}^{\infty} dp \phi_n(p) \exp \left[ i \frac{p x}{\hbar} \right]
\] (493)

so the boundary condition at \( x = 0 \) becomes
\[
0 = \psi_n(0) = \frac{1}{\sqrt{2 \pi \hbar}} \int_{-\infty}^{\infty} dp \phi_n(p)
\] (494)

The boundary condition has the explicit form
\[
0 = \frac{1}{\sqrt{2 \pi \hbar}} \int_{-\infty}^{\infty} dp \left( \frac{\phi_n(0)}{1 - \frac{p^2}{2 m E_n}} \right) \exp \left[ - i \frac{\epsilon^2}{2 \hbar} \sqrt{\frac{2 m}{-E_n}} \tan^{-1} \frac{p}{\sqrt{-2 m E_n}} \right]
\] (495)
The imaginary part of the integral is odd in \( p \) and, thus, vanishes identically. Therefore, the boundary condition is satisfied, if one requires that the real part vanishes

\[
0 = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp \left( \frac{\phi_n(0)}{1 - \frac{p^2}{2mE_n}} \right) \cos \left[ \frac{e^2}{2\hbar} \sqrt{\frac{2m}{E_n}} \tan^{-1} \frac{p}{\sqrt{-2mE_n}} \right] 
\]

On integrating this, one finds the condition

\[
\sin \left( \frac{\pi e^2}{4\hbar} \sqrt{\frac{2m}{-E_n}} \right) = 0 \tag{497}
\]

Hence, the energy eigenvalues are determined by the boundary condition

\[
\frac{\pi e^2}{4\hbar} \sqrt{\frac{2m}{-E_n}} = n\pi \tag{498}
\]

and are given by

\[
E_n = -\frac{2me^4}{16\hbar^2n^2} \tag{499}
\]

which has the form of a Rydberg series.

**Example: A Particle Confined in a Uniform Force Field.**

Another problem which can be solved in the momentum representation is that of a particle of mass \( m \) moving in one dimension in the presence of a potential

\[
V(x) = -Fx \quad \text{if} \quad x < 0 \\
\rightarrow \infty \quad \text{if} \quad x > 0 \tag{500}
\]

The potential is depicted in fig(22). A potential of this type confines electrons near the interface of semiconductors with different levels of doping\(^9\). The infinite potential excludes the particle from the region \( x > 0 \) and introduces the boundary condition at \( x = 0 \)

\[
\phi(0) = 0 \tag{501}
\]

The energy eigenvalue equation becomes

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} - Fx\phi(x) = E\phi(x) \tag{502}
\]

for \( x < 0 \). The classical turning point \(-a\) is given by

\[
a = \frac{E}{F} \tag{503}
\]

Figure 22: The potential of the uniform force and the infinite potential confines the particle in the region $x < 0$. The energy eigenvalues $E_n$ are depicted by the dashed lines.

On eliminating the energy in the eigenvalue equation in favor of the turning point, one finds

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} - F(x + a) \phi = 0 \quad (504)$$

A characteristic length scale $\xi$ is defined by

$$\xi = \left(\frac{\hbar^2}{2mF}\right)^{\frac{1}{3}} \quad (505)$$

Hence, after introducing the dimensionless variable $z = \frac{x + a}{\xi}$, one finds that the eigenvalue equation for $z \xi < a$ has the form

$$\frac{\partial^2 \phi}{\partial z^2} + z \phi = 0 \quad (506)$$

This equation is related to Airy’s equation and has solutions which are linear combinations $Ai(-z)$ and $Bi(-z)$. The function $Bi(z)$ diverges exponentially as $z \to \infty$. Hence, a solution containing $Bi(-z)$ is not a physically acceptable solution in the region $x < 0$. The function $Bi(-z)$ is discarded, so the solution is of the form

$$\phi(x) = C \ A_i\left(-\frac{x + a}{\xi}\right) \quad (507)$$
for $x < 0$. The solution has the integral representation

$$Ai\left(-\frac{x+a}{\xi}\right) = \frac{\xi}{\pi} \int_0^\infty dk \cos \left(\frac{1}{3} k^3 \xi^3 - k (x + a)\right)$$

(508)

The asymptotic form of the wave function can be found by the method of stationary phase and is given by

$$\phi(x) \sim C \left(\frac{x+a}{\xi}\right)^{-\frac{1}{4}} \sin \left[\frac{2}{3} \left(\frac{x+a}{\xi}\right)^{\frac{3}{2}} + \frac{\pi}{4}\right]$$

(509)

within the classically accessible region ($0 > x > -a$), and decays like

$$\phi(x) \sim \frac{C}{2 \sqrt{\pi}} \left(-\frac{x+a}{\xi}\right)^{-\frac{1}{4}} \exp \left[-\frac{2}{3} \left(-\frac{x+a}{\xi}\right)^{\frac{3}{2}}\right]$$

(510)

in the classically forbidden region ($x < -a$). However, to be an eigenfunction, the wave function must also satisfy the boundary condition of eqn(501) at $x = 0$. Hence, one requires

$$Ai\left(-\frac{a_n}{\xi}\right) = 0$$

(511)

The boundary condition determines the allowed values of the turning point $a$ which are labeled by $a_n$, or equivalently, by using eqn(503), the boundary condition determines the energy eigenvalue $E_n$. The asymptotic large $n$ values of the ratio is given by the formula

$$a_n \frac{\xi}{\xi} = \left(\frac{3 \pi}{8} (4n - 1)\right)^{\frac{2}{3}}$$

(512)

This approximate formula is quite accurate even for $n = 1$, as can be seen from Table(1). For large $n$, the zeros vary sub-linearly as $a_n \sim n^{\frac{2}{3}}$. Hence, the asymptotic form of the energy eigenvalues is given by

$$E_n = \left(\frac{\hbar^2 F^2}{2 m}\right)^{\frac{1}{4}} \left(\frac{3 \pi}{8} (4n - 1)\right)^{\frac{2}{3}}$$

(513)

so the level spacing decreases with increasing $n$. The first few wave functions are shown in fig(23).

**3.5.6 Exercise 36**

Find the momentum representation of the kinetic energy operator $\hat{T} = \frac{\hat{p}^2}{2m}$ starting from the known expression in the real space or position representation

$$\hat{T} = -\frac{\hbar^2}{2m} \nabla^2$$

(514)
Table 1: The first few zeros of the Airy function.

<table>
<thead>
<tr>
<th>n</th>
<th>$a_n / \xi$ (exact value)</th>
<th>$a_n / \xi$ (asymptotic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.338</td>
<td>2.320</td>
</tr>
<tr>
<td>2</td>
<td>4.088</td>
<td>4.082</td>
</tr>
<tr>
<td>3</td>
<td>5.521</td>
<td>5.517</td>
</tr>
<tr>
<td>4</td>
<td>6.787</td>
<td>6.784</td>
</tr>
<tr>
<td>5</td>
<td>7.944</td>
<td>7.942</td>
</tr>
<tr>
<td>6</td>
<td>9.023</td>
<td>9.021</td>
</tr>
<tr>
<td>7</td>
<td>10.040</td>
<td>10.039</td>
</tr>
<tr>
<td>8</td>
<td>11.009</td>
<td>11.008</td>
</tr>
<tr>
<td>9</td>
<td>11.936</td>
<td>11.935</td>
</tr>
</tbody>
</table>

The lowest energy eigenfunctions

Figure 23: The $x$ dependence of the first few eigenfunctions. The wave functions are non-zero in the region $x < 0$. The wave functions decay beyond the classical turning points and are zero for $x > 0$. 
3.5.7 Exercise 37

Starting from the real space representation of the pseudo-vector angular momentum operator $\hat{L} = \hat{r} \wedge \hat{p}$, acting on a wave function, find the momentum representation of the operator through integration by parts.

3.5.8 Exercise 38

Find a momentum space representation for the Hamiltonian of a particle moving in three dimensions, in the presence of an electrostatic potential $\phi(\hat{r})$. Also write the explicit expression that occurs when the potential produces a uniform electric field $E(\hat{r}, t) = E_0$. Find the momentum space eigenfunctions for this particular Hamiltonian.

Potential due to a Uniform Force Field

![Potential due to a Uniform Force Field](image)

Figure 24: The potential $V(x) = -Fx$, which gives rise to a uniform force field $F$. The energy $E$ is denoted by a horizontal line.
Figure 25: The real space wave function $\Psi(x)$ of a particle of mass $m$ and energy $E$ moving in a uniform force field.

3.5.9 Solution 38

The Hamiltonian in the momentum representation has the form

$$\hat{H} = \frac{p^2}{2m} - i\hbar F \frac{\partial}{\partial p}$$

The energy eigenvalue equation is

$$\left( \frac{p^2}{2m} - i\hbar F \frac{\partial}{\partial p} \right) \Phi(p) = E \Phi(p)$$

and has the solution

$$\Phi(p) = C \exp \left[ - \frac{i}{\hbar F} \left( \frac{p^3}{6m} - pE \right) \right]$$

whence the real space wave function is found as

$$\Psi(x) = \frac{2C}{\sqrt{2\pi\hbar}} \int_{0}^{\infty} dp \cos \left( \frac{p^3}{6m\hbar F} - p \left( \frac{F x + E}{\hbar F} \right) \right)$$
3.5.10 Exercise 39

Find the two lowest energy eigenvalues and eigenfunctions for a one-dimensional harmonic oscillator, in the momentum representation.

3.5.11 Solution 39

The normalized ground state wave function for the one-dimensional Harmonic oscillator is given by

$$\psi_0(x) = \left(\frac{m \omega}{\pi \hbar}\right)^{\frac{1}{4}} \exp \left[-\frac{m \omega x^2}{2 \hbar}\right]$$

(519)

The momentum space wave function $\phi_0(p)$ is given by the Fourier transform

$$\phi_0(p) = \left(\frac{1}{\sqrt{2 \pi \hbar}}\right) \int_{-\infty}^{\infty} dx \ \exp \left[-i \frac{p x}{\hbar}\right] \psi_0(x)$$

(520)

which is evaluated by completing the square and integrating

$$\phi_0(p) = \left(\frac{1}{\pi \hbar m \omega}\right)^{\frac{1}{4}} \exp \left[-\frac{p^2}{2 \hbar m \omega}\right]$$

(521)

The momentum space wave function is properly normalized, thus $P(p) = |\phi_0(p)|^2$ is the probability density for finding the particle with momentum $p$. It is notable that the most probable value of the momentum is zero, as the classical particle would be at rest.

The normalized first excited state wave function is given by

$$\psi_1(x) = \left(\frac{2}{\sqrt{\pi}}\right)^{\frac{1}{4}} \left(\frac{m \omega}{\hbar}\right)^{\frac{3}{4}} x \exp \left[-\frac{m \omega x^2}{2 \hbar}\right]$$

(522)

The momentum space wave function is evaluated as

$$\phi_1(p) = \left(\frac{2}{\sqrt{\pi}}\right)^{\frac{1}{4}} \left(\frac{1}{\hbar m \omega}\right)^{\frac{3}{4}} p \exp \left[-\frac{p^2}{2 \hbar m \omega}\right]$$

(523)

which is also properly normalized. It should be noted that the most probable values of $p$ is non-zero, as in the excited state the classical particle has finite values of the momentum.
3.5.12 Exercise 40

Prove that the overlap matrix between two different states $\Psi(r)$ and $\psi(r)$ in position representation are related via

$$\int d^3r \, \Psi^*(r) \, \psi(r) = \int d^3p \, \Phi^*(p) \, \phi(p)$$  \hspace{1cm} (524)

to the corresponding wave functions, $\Phi(p)$ and $\psi(p)$, in the momentum space representation.

All observable physical quantities can be expressed in terms of matrix elements of operators.

3.5.13 Solution 40

On evaluating the integral

$$\int d^3p \, \Phi^*(p) \, \phi(p)$$  \hspace{1cm} (525)

by using the transform

$$\phi(p) = \left(\frac{1}{2 \pi \hbar}\right)^\frac{3}{2} \int d^3r \, \exp \left[ -i \frac{p \cdot r}{\hbar} \right] \psi(r)$$  \hspace{1cm} (526)

and the complex conjugate

$$\Phi^*(p) = \left(\frac{1}{2 \pi \hbar}\right)^\frac{3}{2} \int d^3r' \, \exp \left[ +i \frac{p \cdot r'}{\hbar} \right] \Psi^*(r')$$  \hspace{1cm} (527)

one has

$$\left(\frac{1}{2 \pi \hbar}\right)^3 \int d^3r \int d^3r' \int d^3p \, \exp \left[ i \frac{(r' - r) \cdot p}{\hbar} \right] \Psi^*(r') \, \psi(r)$$  \hspace{1cm} (528)

Since the integral over all space leads to the three-dimensional Dirac delta function

$$\left(\frac{1}{2 \pi \hbar}\right)^3 \int d^3p \, \exp \left[ i \frac{(r' - r) \cdot p}{\hbar} \right] = \delta^3(r' - r)$$  \hspace{1cm} (529)

the overlap between the states is given by

$$\int d^3p \, \Phi^*(p) \, \phi(p) = \int d^3r \int d^3r' \, \Psi^*(r') \, \delta(r' - r) \, \psi(r)$$

$$= \int d^3r \, \Psi^*(r) \, \psi(r)$$  \hspace{1cm} (530)
as was to be shown.

### 3.5.14 Exercise 41

Consider the following matrix elements in the position representation

\[
\int d^3r \, \Psi^*(r) \left( -i \frac{\hbar}{\hbar} \right) \nabla \psi(r)
\]  

(531)

and

\[
\int d^3r \, \Psi^*(r) \, r \, \psi(r)
\]  

(532)

Find the equivalent expressions in the momentum space representation.

### 3.5.15 Solution 41

Starting with the expression

\[
\int d^3r \, \Psi^*(r) \left( -i \frac{\hbar}{\hbar} \right) \nabla \psi(r)
\]  

(533)

and substituting the expressions for the Fourier Transformed wave functions

\[
- \frac{\hbar}{\hbar} \int d^3r \, \exp \left[ -i \frac{p'}{\hbar} \cdot \vec{r} \right] \Phi^*(p') \nabla \int d^3p \, \exp \left[ +i \frac{p}{\hbar} \cdot \vec{r} \right] \phi(p)
\]

\[
= \int \frac{d^3r}{(2\pi\hbar)^3} \int d^3p' \, \exp \left[ -i \frac{p'}{\hbar} \cdot \vec{r} \right] \Phi^*(p') \int d^3p \, p \, \exp \left[ +i \frac{p}{\hbar} \cdot \vec{r} \right] \phi(p)
\]

(534)

Then on interchanging the orders of integration and on recognizing the expression for the Dirac delta function

\[
\delta^3 \left( p - p' \right) = \int \frac{d^3r}{(2\pi\hbar)^3} \exp \left[ i \frac{(p - p') \cdot \vec{r}}{\hbar} \right]
\]

(535)

one has

\[
\int d^3r \, \Psi^*(r) \left( -i \frac{\hbar}{\hbar} \right) \nabla \psi(r) = \int d^3p \, \Phi^*(p) \, p \, \phi(p)
\]

(536)

129
The procedure for evaluating the matrix elements of the position operator is quite analogous. Starting with the expression
\[ \int d^3r \, \Psi^*(r) \, r \, \nabla \psi(r) \]  
(537)

and substituting the expressions for the Fourier Transformed wave functions
\[ \int \frac{d^3r}{(2\pi\hbar)^3} \int d^3p' \, \exp[-i \frac{p'.r}{\hbar}] \Phi^*(p') \, r \, \int d^3p \, \exp[i \frac{p.r}{\hbar}] \phi(p) \]
\[ = -i \hbar \int \frac{d^3r}{(2\pi\hbar)^3} \int d^3p' \, \exp[-i \frac{p'.r}{\hbar}] \Phi^*(p') \, \int d^3p \, \phi(p) \nabla_p \exp[i \frac{p.r}{\hbar}] \]  
(538)

Integrating by parts with respect to \( p \), and as the boundary term is zero, we find
\[ = + i \hbar \int \frac{d^3r}{(2\pi\hbar)^3} \int d^3p' \, \exp[-i \frac{p'.r}{\hbar}] \Phi^*(p') \, \int d^3p \, \phi(p) \nabla_p \phi(p) \]  
(539)

Then on interchanging the orders of integration and on recognizing the expression for the Dirac delta function
\[ \delta^3(p - p') = \int \frac{d^3r}{(2\pi\hbar)^3} \exp \left[ i \frac{(p - p') \cdot r}{\hbar} \right] \]  
(540)

one has
\[ \int d^3r \, \Psi^*(r) \, r \, \psi(r) = + i \hbar \int d^3p \, \Phi^*(p) \nabla_p \phi(p) \]  
(541)

which completes the solution. We see that the matrix elements between the wave functions and operators in the real space representation have identical values to the equivalent expressions in the momentum representation.

### 3.5.16 Commuting Operators and Compatibility

If two operators \( \hat{A} \) and \( \hat{B} \) commute, \([ \hat{A} , \hat{B} ] = 0\), these operators are compatible in the sense that it is possible to find functions that are simultaneously eigenfunctions of \( \hat{A} \) and \( \hat{B} \).

The proof is simple if the eigenfunctions of the operator \( \hat{A} \) are non-degenerate. In this case, the eigenfunctions of \( \hat{A} \) satisfy
\[ \hat{A} \phi_a(r) = a \phi_a(r) \]  
(542)
Taking the matrix elements of the commutator of $\hat{A}$ and $\hat{B}$, one has
\[
\int d^3r \phi_{a'}^*(r) [\hat{A}, \hat{B}] \phi_a(r) = 0
\] (543)
which is evaluated as
\[
( a' - a ) \int d^3r \phi_{a'}^*(r) \hat{B} \phi_a(r) = 0
\] (544)
Thus, the operator $\hat{B}$ only has non-zero matrix elements between states of the same eigenvalue $a = a'$. Since by assumption the eigenfunctions of $\hat{A}$ are non-degenerate and form a complete set, the eigenfunctions of $\hat{A}$ are simultaneously eigenfunctions of $\hat{B}$.

The converse is that, if there are simultaneous eigenfunctions of the two operators $\hat{A}$ and $\hat{B}$, then the operators commute. By definition one has,
\[
\hat{A} \phi_n(r) = a_n \phi_n(r)
\]
\[
\hat{B} \phi_n(r) = b_n \phi_n(r)
\] (545)
Then, the action of the commutator on the wave function is zero as
\[
\hat{A} \hat{B} \phi_n(r) = \hat{A} b_n \phi_n(r) = a_n b_n \phi_n(r) = \hat{B} a_n \phi_n(r) = \hat{B} \hat{A} \phi_n(r)
\] (546)
and since an arbitrary wave function $\Psi(r)$ can be expanded in terms of $\phi_n(r)$ the commutator is identically zero.

Clearly an example of two commuting operators is given by any operator $\hat{A}$ and any function $f(\hat{A})$ with a Taylor expansion,
\[
[\hat{A}, f(\hat{A})] = 0
\] (547)
The operators $\hat{A}$ and $f(\hat{A})$ do not form an independent set, as one can be expressed in terms of the other members of the set. Alternatively if $\hat{A}$ and $\hat{B}$ commute then
\[
[g(\hat{A}), f(\hat{B})] = 0
\] (548)
An example of an independent set of commuting operators is given by any of the Hermitean operators $\hat{p}_x$, $\hat{p}_y$ or $\hat{p}_z$, or alternatively $\hat{r}_x$, $\hat{r}_y$ or $\hat{r}_z$. The degeneracy of simultaneous eigenvalues of a set of operators is equal to the number of eigenfunctions corresponding to the set of eigenvalues.

A complete set of commuting operators is defined to be a maximal set of independent commuting Hermitean operators. Any state can be uniquely expanded in terms of the eigenfunctions of a complete set of commuting Hermitean
operators. What exactly constitutes a complete set of operators depends upon the physical space, i.e. whether it is one-dimensional, two-dimensional or three-dimensional, and whether there is an intrinsic space associated with the particle such as spin. If the set is not complete then one can add another independent operator to the set until the set becomes complete. A state which corresponds to an eigenfunction of a complete set of commuting operators is uniquely determined and is completely defined without any remaining arbitrariness. By successively adding operators to a set of independent commuting operators, one has reduced the degeneracy until the simultaneous eigenvalues are non-degenerate and the set of operators is complete.

3.5.17 Non-Commuting Operators

It is impossible to find a set of simultaneous eigenfunctions of non-commuting operators. Thus, if

\[ [\hat{A}, \hat{B}] = \hat{C} \tag{549} \]

and if \(\phi(\mathbf{r})\) is a simultaneous eigenfunction then

\[ [\hat{A}, \hat{B}] \phi(\mathbf{r}) = \hat{C} \phi(\mathbf{r}) = 0 \tag{550} \]

This would require that \(\phi(\mathbf{r})\) is also an simultaneous eigenfunction of \(\hat{C}\) with eigenvalue zero, which is very restrictive and very unlikely. Thus, it is impossible to know the values of \(A\) and \(B\) at the same time if they are non-commuting. An example of this is given by the momentum and position operators corresponding to the same coordinate, \(\hat{p}_x\) and \(\hat{x}_x\).

3.5.18 Exercise 42

Show that if \(\hat{A}\) and \(\hat{B}\) are Hermitian operators and

\[ [\hat{A}, \hat{B}] = i \hat{C} \tag{551} \]

then \(\hat{C}\) is Hermitian.

3.5.19 Solution 42

Consider the matrix elements of the commutator

\[ \int d^3\mathbf{r} \Phi^*(\mathbf{r}) [\hat{A}, \hat{B}] \Psi(\mathbf{r}) = \int d^3\mathbf{r} \Phi^*(\mathbf{r}) \hat{A} \hat{B} \Psi(\mathbf{r}) - \int d^3\mathbf{r} \Phi^*(\mathbf{r}) \hat{B} \hat{A} \Psi(\mathbf{r}) \tag{552} \]
On using the definition of the Hermitean conjugate of the products, we find

\[ = \left( \int d^3 \Psi^*(\mathbf{r}) \hat{B}^\dagger \hat{A}^\dagger \Phi(\mathbf{r}) \right)^* - \left( \int d^3 \Phi^*(\mathbf{r}) \hat{A}^\dagger \hat{B}^\dagger \Psi(\mathbf{r}) \right)^* \]  

(553)

and as \( \hat{A} \) and \( \hat{B} \) are Hermitean, one has

\[ = - \left( \int d^3 \Psi^*(\mathbf{r}) [ \hat{A} , \hat{B} ] \Phi(\mathbf{r}) \right)^* \]  

(554)

Hence, the Hermitean conjugate of the commutator is

\[ [ \hat{A} , \hat{B} ]^\dagger = - [ \hat{A} , \hat{B} ] \]  

(555)

so

\[ \left( i \hat{C} \right)^\dagger = - \left( i \hat{C} \right) \]  

(556)

and as the Hermitean conjugate of \( i \) is \( - i \), we have

\[ - i \hat{C}^\dagger = - i \hat{C} \]  

(557)

Thus, we recognize \( \hat{C} \) as being Hermitean.

---

### 3.5.20 The Uncertainty Principle

The Heisenberg uncertainty relation provides a quantification of the degree to which one can determine the values of two non-commuting Hermitean operators, \( \hat{A} \) and \( \hat{B} \) in a specific state \( \Psi(\mathbf{r}) \).

Consider the deviations \( \Delta \hat{A} \) and \( \Delta \hat{B} \) and form the positive definite quantity

\[ \sum_n \left| \int d^3 \Psi^*(\mathbf{r}) \left( \Delta \hat{A} + i \mu \Delta \hat{B} \right) \phi_n(\mathbf{r}) \right|^2 \geq 0 \]  

(558)

where \( \mu \) is a real variable, and \( \phi_n(\mathbf{r}) \) form a complete set of eigenfunctions. On using the completeness relation, one finds

\[ = \int d^3 \Psi^*(\mathbf{r}) \left( \Delta \hat{A}^2 + i \mu [ \Delta \hat{B} , \Delta \hat{A} ] + \mu^2 \Delta \hat{B}^2 \right) \Psi(\mathbf{r}) \]  

(559)

and since this has no zeros as a function of \( \mu \), the discriminant of this quadratic equation in \( \mu \) must be greater than zero. Hence,

\[ 4 \int d^3 \Psi^*(\mathbf{r}) \Delta \hat{A}^2 \Psi(\mathbf{r}) \int d^3 \Psi^*(\mathbf{r}') \Delta \hat{B}^2 \Psi(\mathbf{r}') \geq \left( \int d^3 \Psi^*(\mathbf{r}) i [ \Delta \hat{A} , \Delta \hat{B} ] \Psi(\mathbf{r}) \right)^2 \]  

(560)
Thus, we have the Heisenberg uncertainty relation

\[ 2 \Delta A_{\text{rms}} \Delta B_{\text{rms}} \geq \left| \int d^3\mathbf{r} \Psi^*(\mathbf{r}) i \left[ \hat{A}, \hat{B} \right] \Psi(\mathbf{r}) \right| \quad (561) \]

The equality only holds if the effects of the operators on the state \( \Psi(\mathbf{r}) \) are proportional to each other. This can be seen by examining eqn(558) with the equality sign holding. This implies that, if the equality holds, the sums of the squares of the matrix elements

\[ \int d^3\mathbf{r} \phi^*_n(\mathbf{r}) \left( \Delta \hat{A} - i \mu \Delta \hat{B} \right) \Psi(\mathbf{r}) \quad (562) \]

must be zero for all \( n \). If we expand the transformed state \( \left( \Delta \hat{A} - i \mu \Delta \hat{B} \right) \Psi \) in terms of \( \phi_n \)

\[ \left( \Delta \hat{A} - i \mu \Delta \hat{B} \right) \Psi(\mathbf{r}) = \sum_n C_n \phi_n(\mathbf{r}) \quad (563) \]

then we recognize that we just proved that if the equality is to hold \( C_n = 0 \) for all \( n \). The completeness condition then implies that we have the expansion of the zero state, so

\[ \left( \Delta \hat{A} - i \mu \Delta \hat{B} \right) \Psi(\mathbf{r}) = 0 \quad (564) \]

when the equality holds. The value of the constant, \( \mu \), can be obtained from the inequality by noting that if the equality holds, then as \( \Delta B_{\text{rms}}^2 > 0 \) the value of \( \mu \) must be a repeated root. On solving the quadratic equation for the repeated root, we find

\[ \mu = i \int d^3\mathbf{r} \Psi^*(\mathbf{r}) \frac{\left[ \hat{A}, \hat{B} \right] \Psi(\mathbf{r})}{2 \Delta B_{\text{rms}}^2} \quad (565) \]

Hence, on substituting the value of \( \mu \) back we have the equation

\[ \Delta \hat{A} \Psi(\mathbf{r}) = \left( \int d^3\mathbf{r} \Psi^*(\mathbf{r}) \frac{\left[ \hat{A}, \hat{B} \right] \Psi(\mathbf{r})}{2 \Delta B_{\text{rms}}^2} \right) \Delta \hat{B} \Psi(\mathbf{r}) \quad (566) \]

This equation is satisfied for the state \( \Psi(\mathbf{r}) \) which produces the minimum uncertainty in \( \Delta \hat{A} \) and \( \Delta \hat{B} \).

Applying the uncertainty relation to the canonically conjugate coordinates and momenta, we have the inequality

\[ \Delta p_i \Delta x_j \geq \frac{\hbar}{2} \delta_{i,j} \quad (567) \]
in which the right hand side is independent of the state of the system. The
minimum uncertainty equation takes the form
\[
\left( -i \hbar \frac{\partial}{\partial x} - p_x \right) \Psi(x) = \frac{i \hbar}{2 \Delta x_{rms}^2} \left( x - \bar{x} \right) \Psi(x) \tag{568}
\]
which has the solution
\[
\Psi(x) = \left( \frac{2 \pi \Delta x_{rms}^2}{\hbar} \right)^{-\frac{1}{4}} \exp \left[ -\frac{(x - \bar{x})^2}{4 \Delta x_{rms}^2} + i \frac{p_x x}{\hbar} \right] \tag{569}
\]

### 3.5.21 Exercise 43

Consider a particle moving in one dimension in the presence of a potential \( V(x) \). Show that the uncertainty in the energy and position are related via
\[
\Delta E_{rms} \Delta x_{rms} = \frac{\hbar}{2 \ m} p \tag{570}
\]

### 3.5.22 Solution 43

The Hamiltonian is given by
\[
\hat{H} = \frac{\hat{p}^2}{2 \ m} + V(\hat{x}) \tag{571}
\]
The commutator of \( \hat{H} \) and \( \hat{x} \) is found as
\[
\left[ \hat{H}, \hat{x} \right] = -i \frac{\hbar}{m} \hat{p} \tag{572}
\]
Then on using the generalized uncertainty principle, one has
\[
\Delta E_{rms} \Delta x_{rms} = \frac{\hbar}{2 \ m} p \tag{573}
\]
as was to be proved.
3.5.23 Exercise 44

Derive uncertainty relations for the various components of the orbital angular momenta. For what states is it possible to measure \( \hat{L}_x \) and \( \hat{L}_y \) simultaneously with minimum uncertainty?

3.5.24 Solution 44

From the commutation relation
\[
[\hat{L}_x, \hat{L}_y] = i \hbar \hat{L}_z
\]
(574)

one has the uncertainty relation
\[
(\Delta L_x)_{\text{rms}} (\Delta L_y)_{\text{rms}} \geq \frac{\hbar}{2} \overline{L_z}
\]
(575)

Thus, it is possible to measure \( \hat{L}_x \) and \( \hat{L}_y \) with minimum uncertainty in states \( \Psi(r) \) where the average value of \( \hat{L}_z \) is zero
\[
\overline{L_z} = \int d^3r \Psi^*(r) \hat{L}_z \Psi(r) = 0
\]
(576)

In particular, the state with total angular momentum zero is a simultaneous eigenstate of \( \hat{L}_x, \hat{L}_y \) and \( \hat{L}_z \), with all three eigenvalues being zero.

3.5.25 Exercise 45

If the Hermitean operators \( \hat{A}, \hat{B} \) and \( \hat{C} \) satisfy the commutation relations
\[
[\hat{B}, \hat{C}] = i \hat{A}
\]
\[
[\hat{A}, \hat{C}] = i \hat{B}
\]
(577)

then show that the uncertainty relation
\[
\Delta(AB)_{\text{rms}} \Delta C_{\text{rms}} \geq \frac{1}{2} \left( \overline{A^2} + \overline{B^2} \right)
\]
(578)

is satisfied.
3.5.26 Solution 45

This exercise is a simple example of the uncertainty principle. The commutator of the composite operator $\hat{A} \hat{B}$ with $\hat{C}$ is evaluated as

$$[ \hat{A} \hat{B} , \hat{C} ] = \hat{A} [ \hat{B} , \hat{C} ] + [ \hat{A} , \hat{C} ] \hat{B}$$

$$= i \left( \hat{A}^2 + \hat{B}^2 \right)$$

Hence, on substituting into the general statement of the uncertainty principle, one obtains the result

$$\Delta ( A B )_{rms} \Delta C_{rms} \geq \frac{1}{2} \left( \overline{A}^2 + \overline{B}^2 \right)$$

which was to be proved.

3.5.27 Exercise 46

Show that the $z$ component of the angular momentum $\hat{L}_z$ and the azimuthal angle $\varphi$ satisfy the commutation relations

$$[ \hat{L}_z , \cos \varphi ] = + i \hbar \sin \varphi$$

$$[ \hat{L}_z , \sin \varphi ] = - i \hbar \cos \varphi$$

Hence, derive the uncertainty relations

$$\Delta (\cos \varphi) \Delta L_z \geq \frac{\hbar}{2} \sin \varphi$$

$$\Delta (\sin \varphi) \Delta L_z \geq \frac{\hbar}{2} \cos \varphi$$

3.5.28 Solution 46

The uncertainty relations applied to the azimuthal angle are problematic, since it is not clear whether the angle $\varphi$ is really only well defined modulo $2\pi$. An angle $\varphi$ cannot be distinguished by a single physical measurement from $\varphi + m 2\pi$ where $m$ is an integer. If, on the other hand, $\varphi$ is considered to be defined only on the restricted interval $(0, 2\pi)$ then the uncertainty principle for $\varphi$ and $\hat{L}_z$ would read

$$(\Delta \varphi)_{rms} (\Delta L_z)_{rms} > \frac{\hbar}{2}$$
which would imply that either there are no eigenstates of $\hat{L}_z$, which is false, or that the uncertainty of $\varphi$ can be infinite, which is contrary to our assumption. The only way out of this quandry is to assert that an angle is not measurable, but that only the coordinates $\sin \varphi$ or $\cos \varphi$ are measurable. These functions uniquely define $\varphi$ modulo $2\pi$. We need to restrict our attention to functions and operators which are periodic in $\varphi$ since $\hat{L}_z$ is only Hermitean on the space of functions which are periodic in $\varphi$.

The commutation relations for the coordinates and angular momentum are evaluated as

\[
[\hat{L}_z, \cos \varphi] = i \hbar \sin \varphi \\
[\hat{L}_z, \sin \varphi] = -i \hbar \cos \varphi
\] (584)

Simple substitution into the uncertainty relation leads to the equations

\[
(\Delta L_z)^2 \left( \Delta \cos \varphi \right)^2 \geq \frac{\hbar^2}{4} \left( \frac{\sin \varphi}{\cos \varphi} \right)^2 \\
(\Delta L_z)^2 \left( \Delta \sin \varphi \right)^2 \geq \frac{\hbar^2}{4} \left( \frac{\sin \varphi}{\cos \varphi} \right)^2
\] (585)
The above equation does not produce any contradiction with the fact that

\[ \Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} \exp \left[ i m \varphi \right] \]  

are eigenstates of \( \hat{L}_z \) since the expectation value of the trigonometric functions \( \cos \varphi \) and \( \sin \varphi \) are both zero. In this case, one finds that the uncertainty relations reduce to the equality \( 0 = 0 \).
3.6 The Philosophy of Measurement

In Quantum Mechanics the measurement process disturbs the system and is, therefore, represented by an operator. The measurement of $A$ produces instantaneous changes from one state, say $\Psi(r)$ of the system to another. The state of the system immediately after the measurement is that which corresponds to an eigenstate of the operator $\hat{A}$ which has the eigenvalue that corresponds to the result of the measurement $a$. Prior to the measurement, and the discovery of the result $a$, it is impossible to predict which eigenstate the system will take. All that can be predicted is the probability that the measurement will result in a particular eigenvalue $a$. This probability is proportional to the squared modulus of the expansion coefficient $C_a$

$$\Psi(r) = \sum_a C_a \phi_a(r)$$  \hspace{1cm} (587)

Thus, one can view quantum mechanical measurement as a sort of filter, which instantaneously filters out the state $\phi_a(r)$ from the initial state of the system $\Psi(r)$. Since this resulting state after the measurement is represented as a pure eigenfunction of $\hat{A}$, it has only one expansion coefficient. Therefore, there is a probability of one for finding the result $a$ in a further measurement of $\hat{A}$, as long as this measurement is made very soon after the first measurement was made.

Example

The Hermitean operators $\hat{A}$ and $\hat{B}$ do not commute. The operator $\hat{A}$ has two non-degenerate eigenstates and eigenvalues given by

$$\hat{A} \Theta_i(r) = a_i \Theta_i(r)$$  \hspace{1cm} (588)

for $i = 1, 2$. The operator $\hat{B}$ also has two non-degenerate eigenstates

$$\hat{B} \Theta_i(r) = b_i \Theta_i(r)$$  \hspace{1cm} (589)

for $i = 1, 2$. The state $\Phi_1(r)$ can be expressed as a linear superposition of the eigenstates $\Theta_i(r)$, as

$$\Phi_1(r) = C_1 \Theta_1(r) + C_2 \Theta_2(r)$$  \hspace{1cm} (590)

where $C_1$ and $C_2$ are known complex constants.

(i) Find an expression for $\Phi_2(r)$ in terms of the $\Theta_i(r)$, and determine the expansion coefficients in terms of the known quantities $C_i$.

A quantum mechanical particle is in a state $\Psi(r)$ given by

$$\Psi(r) = \sqrt{\frac{1}{6}} \Phi_1(r) + \sqrt{\frac{5}{6}} \Phi_2(r)$$  \hspace{1cm} (591)
(ii) Determine the probabilities of finding the results $a_1$ and $a_2$ in a measurement of $\hat{A}$. The quantity $\hat{B}$ is then measured immediately after $\hat{A}$ has been measured. What is the probability that the measurement of $\hat{B}$ yields the result $b_1$?

(iii) If the measurement of $\hat{A}$ had not been performed, what is the probability that the measurement of $\hat{B}$ will result in the measured value $b_1$?

---

**Solution**

Since $\hat{B}$ is Hermitean the eigenstates of $\hat{A}$ can be expanded in terms of the eigenstates of $\hat{B}$. The eigenstate $\Phi_1(\vec{r})$ is expanded as

$$\Phi_1(\vec{r}) = C_1 \Theta_1(\vec{r}) + C_2 \Theta_2(\vec{r})$$  \hspace{1cm} (592)

and $\Phi_2(\vec{r})$ can be expanded in terms of the complete set of $\Theta_i(\vec{r})$ as

$$\Phi_2(\vec{r}) = D_1 \Theta_1(\vec{r}) + D_2 \Theta_2(\vec{r})$$  \hspace{1cm} (593)

where $D_1$ and $D_2$ are to be determined. As $\Phi_2(\vec{r})$ must be orthogonal to $\Phi_1(\vec{r})$, then

$$0 = \int d^3r \Phi_1^*(\vec{r}) \Phi_2(\vec{r})$$

$$= C_1^* D_1 \int d^3r \Theta_1^*(\vec{r}) \Theta_1(\vec{r}) + C_1^* D_2 \int d^3r \Theta_1^*(\vec{r}) \Theta_2(\vec{r})$$

$$+ C_2^* D_1 \int d^3r \Theta_2^*(\vec{r}) \Theta_1(\vec{r}) + C_2^* D_2 \int d^3r \Theta_2^*(\vec{r}) \Theta_2(\vec{r})$$  \hspace{1cm} (594)

Since $\Theta_1(\vec{r})$ and $\Theta_2(\vec{r})$ form an orthonormal set, one has

$$0 = C_1^* D_1 + C_2^* D_2$$  \hspace{1cm} (595)

Also, as the states are normalized to unity, one has

$$|C_1|^2 + |C_2|^2 = |D_1|^2 + |D_2|^2 = 1$$  \hspace{1cm} (596)

and so the unknown constants $D_i$ are found as

$$D_1 = -C_2^*$$

$$D_2 = C_1^*$$  \hspace{1cm} (597)

up to an arbitrary common phase. Hence, we have

$$\Phi_2(\vec{r}) = -C_2^* \Theta_1(\vec{r}) + C_1^* \Theta_2(\vec{r})$$  \hspace{1cm} (598)
A measurement of \( \hat{A} \) on the state
\[
\Psi(r) = \sqrt{\frac{1}{6}} \Phi_1(r) + \sqrt{\frac{5}{6}} \Phi_2(r)
\] (599)
yields the result \( a_1 \) with probability \( P(a_1) = \frac{1}{6} \) and the result \( a_2 \) occurs with probability \( P(a_2) = \frac{5}{6} \).

If the measurement \( \hat{A} \) has been performed and the result \( a_1 \) has been found, the system then is in the state \( \Phi_1(r) \). The conditional probability that a subsequent measurement of \( \hat{B} \) yields the result \( b_1 \) is given by
\[
P(a_1|b_1) = |C_1|^2
\] (600)
and the conditional probability that the measurement of \( \hat{B} \) yields the result \( b_2 \) is given by
\[
P(a_1|b_2) = |C_2|^2
\] (601)

However, if on the other hand the result of the first measurement is \( a_2 \), the system is in state \( \Phi_2(r) \) just after the first measurement. The conditional probability that a subsequent measurement of \( \hat{B} \) yields the result \( b_1 \) is given by
\[
P(a_2|b_1) = |C_2|^2
\] (602)
and the conditional probability that the measurement of \( \hat{B} \) yields the result \( b_2 \) is given by
\[
P(a_2|b_2) = |C_1|^2
\] (603)

The total probability that the second measurement of \( \hat{B} \) will result in the value \( b_1 \), no matter what value of \( \hat{A} \) is measured, is given by
\[
P(A|b_1) = \frac{1}{6} |C_1|^2 + \frac{5}{6} |C_2|^2
\] (604)

If the measurement of \( \hat{B} \) is performed directly on the state \( \Psi \), then as
\[
\Psi(r) = \left( \sqrt{\frac{1}{6}} C_1 - \sqrt{\frac{5}{6}} C_2^* \right) \Theta_1(r) + \left( \sqrt{\frac{5}{6}} C_2 + \sqrt{\frac{1}{6}} C_1^* \right) \Theta_2(r)
\] (605)
the result \( b_1 \) occurs with probability
\[
P(b_1) = \left| \sqrt{\frac{1}{6}} C_1 - \sqrt{\frac{5}{6}} C_2^* \right|^2
\] (606)
The probability $P(b_1)$ is not the same as $P(A|b_1)$ as the measurement of $\hat{A}$ disturbs the system.

The time evolution of a system between two successive instants of time is governed by the Schrödinger equation, as long as no measurements are made on the system in the time interval between the two times. In order to solve the Schrödinger equation, which is a first order differential equation in the time variable, it is necessary to have one initial condition for the wave function. This is usually given by the state of the system at the initial time $t_0$, $\Psi(r, t_0)$. Once the initial condition is known, the Schrödinger equation will predict how the state evolves with time until a measurement (say a measurement of $\hat{A}$) is performed on the system. Let us assume that the measurement occurs at time $t_1$. The measurement at $t_1$ disrupts the evolution process, and sends the system into an eigenstate of the measurement operator with a definite eigenvalue. The value of the eigenvalue is the result of the measurement. The probability of getting the result $a$, depends on the expansion coefficient of the state $\Psi(r, t_1)$. After the measurement, the system has a new initial state at $t_1$ which is $\phi_a(r)$. This new initial state should be used in the Schrödinger equation to predict the subsequent evolution of the system from $t_1$ to later times $t_2$, as long as no other measurements occur in this time interval. If there is a second measurement (such as a measurement represented by $\hat{B}$), the process repeats. The system evolves forward from the time of the second measurement according to the Schrödinger equation, and the result of the second measurement provides the new initial condition at the time of the latest measurement.

3.6.1 Exercise 47

A particle moving in three dimensions is in a quantum mechanical state described by a wave function

$$\Psi(r) = C \exp \left[ -\alpha r^2 \right]$$

(607)

in the presence of a spherically symmetric potential. The Hamiltonian is given by the operator

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{m \omega^2 r^2}{2}$$

(608)

The energy of the state is measured. Find the probability that the system is in the ground state $E_0 = \frac{3}{2} \hbar \omega$, where the ground state wave function $\phi_0(r)$ is given by

$$\phi_0(r) = \left( \frac{m \omega}{\hbar \pi} \right)^{\frac{3}{4}} \exp \left[ -\frac{m \omega r^2}{2 \hbar} \right]$$

(609)
Determine the probability that the system is found to be in an excited state.

What is the probability that the above system is found to be in a state \( \phi_1(\mathbf{r}) \) corresponding to \( E_1 = \frac{5}{2} \hbar \omega \), where

\[
\phi_1(\mathbf{r}) = (2 \pi)^{\frac{1}{2}} \left( \frac{m \omega}{\hbar} \right)^{\frac{1}{4}} r \cos \theta \exp \left[ - \frac{m \omega r^2}{2 \hbar} \right]
\]  
(610)

which is also an eigenstate of angular momentum \( l = 1 \).

3.6.2 Solution 47

The normalization constant for \( \Psi(\mathbf{r}) \) is found from the equation

\[
1 = \int d^3 \mathbf{r} | \Psi(\mathbf{r})|^2
= |C|^2 \int d^3 \mathbf{r} \exp \left[ -2 \alpha r^2 \right]
= |C|^2 \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^\infty dr r^2 \exp \left[ -2 \alpha r^2 \right]
= |C|^2 4 \pi \int_0^\infty dr \ r^2 \exp \left[ -2 \alpha r^2 \right]
\]  
(611)

Hence,

\[
| C | = \left( \frac{2 \alpha}{\pi} \right)^{\frac{3}{4}}
\]  
(612)

The wave function \( \Psi(\mathbf{r}) \) can be expanded in terms of the eigenfunctions of \( \hat{H} \), which are the \( \phi_n(\mathbf{r}) \). Since the wave functions are normalized, the probability that a measurement of \( \hat{H} \) will result in the value \( E_0 \) is given by the modulus square of the expansion coefficient. The expansion coefficient for the state \( \phi_0(\mathbf{r}) \) is found from the overlap

\[
\int d^3 \mathbf{r} \phi_0^*(\mathbf{r}) \Psi(\mathbf{r}) = 4 \pi |C|^2 \left( \frac{m \omega}{\hbar \pi} \right)^{\frac{3}{4}} \int_0^\infty dr \ r^2 \exp \left[ - \left( \alpha + \frac{m \omega}{2 \hbar} \right) r^2 \right]
= \left( \frac{4 \alpha \frac{m \omega}{2 \hbar}}{\alpha + \frac{m \omega}{2 \hbar}} \right)^{\frac{3}{4}}
\]  
(613)

The probability that the system is found in the ground state is given by

\[
P_0 = \left( \frac{4 \alpha \frac{m \omega}{2 \hbar}}{\alpha + \frac{m \omega}{2 \hbar}} \right)^{\frac{3}{2}}
\]  
(614)
and the probability that the system ends up in an excited state is given by

\[
P_{\text{exc}} = 1 - P_0 = 1 - \left( \frac{4 \alpha m \omega}{\left( \alpha + \frac{m \omega}{2 \hbar} \right)^2} \right)^{\frac{3}{2}} \tag{615}
\]

Note that if \( \alpha \) has the value

\[
\alpha = \frac{m \omega}{2 \hbar} \tag{616}
\]

then the probability that the system will undergo a transition to a different eigenstate when \( \hat{H} \) is measured is zero. That is, the system is already in an eigenstate of \( \hat{H} \) with eigenvalue \( E_0 \) and any subsequent measurements of \( \hat{H} \) (but only if infinitesimally small times have elapsed since \( \Psi(r) \) was created) will yield the same result \( E_0 \).

The probability that the system ends up in the excited state \( \phi_1(r) \) is zero, since on evaluating the expansion coefficient one finds

\[
\int d^3 \phi_0^*(r) \Psi(r) = \left( \frac{2 \pi}{\pi} \right)^{\frac{3}{2}} |C| \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{3}{2}} \int_0^\pi d\theta \sin \theta \cos \theta \int_0^\infty dr r^3 \exp \left[ - \left( \alpha + \frac{m \omega}{2 \hbar} \right) r^2 \right] = 0 \tag{617}
\]

since the integral over \( \theta \) vanishes identically. The vanishing of this matrix element is a natural consequence of the conservation of angular momentum for a spherically symmetric potential. The initial state is an eigenstate of the square of the angular momentum, \( \hat{L}^2 \), with eigenvalue zero, and is also an eigenstate of the \( z \) component of the angular momentum operator with eigenvalue zero. The state \( \phi_1(r) \) is an eigenstate of the square of the angular momentum \( \hat{L}^2 \) with eigenvalue \( 2 \hbar^2 \) and is an eigenstate of the \( z \) component of the angular momentum with angular momentum zero. Thus, these states correspond to eigenstates of \( \hat{L}^2 \) with different eigenvalues. The overlap is zero because states corresponding to different eigenvalues of Hermitean operators are orthogonal.

### 3.6.3 Exercise 48

The initial state of a system is represented by the wave function

\[
\Psi(r) = \left( \frac{m \omega \hbar}{\pi} \right)^{\frac{3}{2}} \exp \left[ - \frac{m \omega \left( r - \frac{a}{2} \right)^2}{2 \hbar} \right] \tag{618}
\]

where \( a = \hat{e}_z \cdot a \). What is the probability that after an energy measurement the system will be found in the energy eigenstates \( \phi_0(r) \) and \( \phi_1(r) \) given below?
The state $\phi_0(r)$ is given by
$$\phi_0(r) = \left(\frac{m \omega}{\hbar \pi}\right)^{\frac{3}{4}} \exp \left[-\frac{m \omega r^2}{2 \hbar}\right]$$
which is a simultaneous eigenstate of energy $E_0 = \frac{3}{2} \hbar \omega$ and of angular momentum with $l = 0$. The state $\phi_1(r)$ is given by
$$\phi_1(r) = (2 \pi)^{\frac{1}{2}} \left(\frac{m \omega}{\hbar \pi}\right)^{\frac{3}{4}} r \cos \theta \exp \left[-\frac{m \omega r^2}{2 \hbar}\right]$$
which is an eigenstate of energy $E_1 = \frac{5}{2} \hbar \omega$ and is an eigenstate of angular momentum with $l = 1$ and $m = 0$.

3.6.4 Solution 48

The probability that the system initially in the state $\Psi(r)$ is found in an eigenstate with energy $E_n$ is found from the eigenstate expansion
$$\Psi(r) = \sum_n C_n \phi_n(r)$$
as
$$P(E_n) = |C_n|^2$$
where
$$C_n = \int d^3r \phi^*_n(r) \Psi(r)$$
The expansion coefficient $C_0$ is found as
$$C_0 = \int d^3r \left(\frac{m \omega}{\pi \hbar}\right)^{\frac{3}{4}} \exp \left[-\frac{m \omega}{2 \hbar} (r - a)^2 \right] \exp \left[-\frac{m \omega}{2 \hbar} (r + a)^2 \right]$$
$$= \exp \left[-\frac{m \omega}{4 \hbar} a^2 \right]$$
Thus, we find that the probability of finding the result $E_0$ if the energy of state $\Psi(r)$ is measured is given by
$$P(E_0)_{l=0} = \exp \left[-\frac{m \omega}{2 \hbar} a^2 \right]$$
which decreases exponentially with increasing $a$. 

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The expansion coefficient $C_1$ is determined from

$$C_1 = \left(\frac{2\pi}{\hbar}\right)^{3/2} \int d^3 \vec{r} \left(\frac{m \omega}{\pi \hbar}\right)^2 (z + \frac{a_z}{2}) \exp\left[-\frac{m \omega}{\hbar} \left(\frac{r^2}{2} + \frac{a^2}{4}\right)\right]$$

$$= \left(\frac{m \omega a_z^2}{2 \hbar}\right)^{1/2} \exp\left[-\frac{m \omega}{4 \hbar} a^2\right] \tag{626}$$

where $a_z$ is the $z$ component of the vector displacement $\vec{a}$. Hence, one has the probability of finding a simultaneous eigenstate of energy $E_1$ and angular momentum $l = 1$ and $m = 0$ is given by

$$P(E_1)_{l=1,m=0} = \left(\frac{m \omega a_z^2}{2 \hbar}\right) \exp\left[-\frac{m \omega}{2 \hbar} a^2\right] \tag{627}$$

### 3.6.5 Exercise 49

A particle is confined to move in a one-dimensional interval between $x = 0$ and $x = L$. The initial state is given by

$$\Psi(x) = \sqrt{\frac{30}{L^5}} x (x - L) \tag{628}$$

for $L > x > 0$, and 0 otherwise. Find the probability that, after a measurement of the energy, the system will be found in the eigenstate

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n \pi x}{L} \tag{629}$$

corresponding to energy $E_n = \frac{\hbar^2 \pi^2}{2mL^2}$

If the energy is measured and found to be equal $9 \frac{\hbar^2 \pi^2}{2mL^2}$, what is the probability density that in a second measurement the particle will then be found in an interval of width $\delta x$ around $x = \frac{L}{2}$?

If the measurement of $E_n$ had not taken place, what would the probability density for finding the particle at $x = \frac{L}{2}$ have been?
First we shall evaluate the indefinite integrals
\[ \int x' x' \sin \alpha x' = - \frac{\partial}{\partial \alpha} \int x' \cos \alpha x' \]
\[ = \frac{\sin \alpha x - \alpha x \cos \alpha x}{\alpha^2} \]  
(630)
and
\[ \int x' x'^2 \sin \alpha x' = - \frac{\partial^2}{\partial \alpha^2} \int x' \sin \alpha x' \]
\[ = \frac{(2 - \alpha^2 x^2) \cos \alpha x + 2 \alpha x \sin \alpha x}{\alpha^3} \]  
(631)

Then the coefficients \( C_n \) in the expansion of \( \Psi(x) \) in terms of the eigenfunctions \( \phi_n(x) \) are given by
\[ C_n = \int_0^L dx' \phi_n^*(x) \Psi(x) \]
\[ = \frac{\sqrt{60}}{L^3} \int_0^L dx' x (x - L) \frac{n \pi x}{L} \]
\[ = \frac{\sqrt{60}}{n^3 \pi^3} \frac{2}{n} \cos n \pi - 1 \]  
(632)
Hence, only terms with odd values of \( n \) appear in the expansion. The probability of observing the eigenvalue \( E_n \) is only finite for odd \( n \) and is given by
\[ P(n) = |C_n|^2 \]
\[ = \frac{480}{n^6 \pi^6} (1 - \cos n \pi) \]  
(633)

Since the energy measurement picks out the non-degenerate eigenfunction corresponding to \( n = 3 \), the probability density for finding the particle at \( x = \frac{L}{2} \) is given by
\[ P(L/2) = \frac{2}{L} \]  
(634)
whereas if the measurement had not occurred then we would have anticipated that the probability density would be
\[ P(L/2) = \frac{15}{8L} \]  
(635)
Thus, the measurement of the energy has changed the probabilities of the measurement of the particle’s position made at an instant later.
3.7 Time Evolution

The evolution equation of a physical quantity $B(p, q, t)$ in Classical Mechanics is given in terms of the Poisson Brackets as,

\[
\frac{dB}{dt} = [B, H]_{PB} + \frac{\partial B}{\partial t}
\]  

(636)

where $H$ is the Hamiltonian, which is a function of the canonically conjugate momenta $\hat{p}$, coordinates $\hat{q}$ and possibly $t$. We regard this as an equation of motion for the expectation value. To obtain the quantum mechanical equation of motion from the classical equation, we replace the classical quantity $B(p, q, t)$ by the operator $\hat{B} = B(\hat{p}, \hat{q}, t)$, and the classical Hamiltonian $H(p, q, t)$ by the Hamiltonian operator $\hat{H} = H(\hat{p}, \hat{q}, t)$. In the non-relativistic limit, the classical Hamiltonian for a particle, of charge $q$, in an electromagnetic field is given by

\[
H = \frac{1}{2m} \left( \frac{\hat{p} - \frac{q}{c} A(\hat{r}, t)}{\hat{r}} \right)^2 + q \phi(\hat{r}, t)
\]  

(637)

which in the coordinate representation becomes

\[
\hat{H}(\hat{r}, t) = \frac{1}{2m} \left( -i \hbar \nabla - \frac{q}{c} A(\hat{r}, t) \right)^2 + q \phi(\hat{r}, t)
\]  

(638)

On substituting operators for the classical variables in the classical equation of motion, replacing the Poisson Bracket with the commutator divided by the $i\hbar$, and taking the expectation value in a state $\Psi(\hat{r}, t)$, one has

\[
i\hbar \frac{d}{dt} \int d^3\hat{r} \Psi^*(\hat{r}, t) \hat{B}(\hat{r}, t) \Psi(\hat{r}, t) = \int d^3\hat{r} \Psi^*(\hat{r}, t) [\hat{B}(\hat{r}, t), \hat{H}(\hat{r}, t)] \Psi(\hat{r}, t) + i\hbar \int d^3\hat{r} \Psi^*(\hat{r}, t) \frac{\partial}{\partial t} \hat{B}(\hat{r}, t) \Psi(\hat{r}, t)
\]  

(640)

This should be regarded as an equation which governs the time dependence of the expectation value of $\overline{B}(t)$

\[
\overline{B}(t) = \int d^3\hat{r} \Psi^*(\hat{r}, 0) \hat{B}(\hat{r}, t) \Psi(\hat{r}, t)
\]  

(641)

The time dependence of the expectation value $\overline{B}(t)$ has a formal solution given by

\[
\overline{B}(t) = \int d^3\hat{r} \Psi^*(\hat{r}, 0) \hat{U}(t, 0) \hat{B}(\hat{r}, t) \hat{U}(t, 0) \Psi(\hat{r}, 0)
\]  

(642)
where \( \hat{U}(t, t') \) is the time evolution operator which describes the implicit time dependence of the system and satisfies the first order equation

\[
i \hbar \frac{d}{dt} \hat{U}(t, t') = \hat{H}(\vec{r}, t) \hat{U}(t, t')
\]

(643)

with the boundary condition \( \hat{U}(t', t') = 1 \) and \( \hat{U}^\dagger(t, t') \) is its Hermitean conjugate.

From the solution given in eqn(642) one can derive a number of “pictures” of quantum mechanics. The two most popular are :

(i) The Schrödinger picture.

(ii) The Heisenberg picture.

### 3.7.1 The Schrödinger Picture.

In this picture, the operators are independent of time (the only exception is if there is some externally imposed time dependence, like a time-dependent electromagnetic field etc.). That is, the operators only change through their explicit time dependence. The implicit time dependence of the system is carried in the wave function. Thus, in the Schrödinger picture

\[
\Psi(\vec{r}, t) = \hat{U}(t, t') \Psi(\vec{r}, t') \\
\hat{B}(\vec{r}, t) = \hat{B}(\vec{r}, t')
\]

(644)

The time evolution is usually referenced with respect to an initial time \( t' \) which is usually chosen as \( t' = 0 \). If the time evolution operator \( \hat{U}(t, t') \) is unitary, the wave function will retain its initial normalization. From this, one finds that the implicit time dependence is contained in the wave function and, is governed by the first order differential equation

\[
i \hbar \frac{d}{dt} \Psi(\vec{r}, t) = \hat{H}(\vec{r}, t) \Psi(\vec{r}, t)
\]

(645)

with one initial condition. In the momentum space representation, the Schrödinger equation has the form

\[
i \hbar \frac{d}{dt} \Phi(\vec{p}, t) = \left( \frac{\vec{p}^2}{2m} + q \phi( i \hbar \nabla_p , t) \right) \Phi(\vec{p}, t)
\]

(646)
3.7.2 Exercise 50

Derive the momentum space form the Schrödinger equation from the real space form.

3.7.3 Solution 50

The time-dependent Schrödinger equation is

\[ i \hbar \frac{\partial \Psi(r, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + q \phi(r, t) \Psi(r, t) \quad (647) \]

in position representation, where \( \Psi(r, t) \) is the time-dependent wave function. The time-dependent momentum space wave function \( \Phi(p, t) \) is related to \( \Psi(r, t) \) via the generalized Fourier transform

\[ \Psi(r, t) = \left( \frac{1}{2\pi \hbar} \right)^{\frac{3}{2}} \int d^3p' \Phi(p', t) \exp \left[ + i \frac{p' \cdot r}{\hbar} \right] \quad (648) \]

On substituting this relation in the first term on the right hand side, one obtains the contribution

\[ -\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) = \frac{\hbar^2}{2m} \left( \frac{1}{2\pi \hbar} \right)^{\frac{3}{2}} \int d^3p' \Phi(p', t) \frac{p'^2}{\hbar^2} \exp \left[ + i \frac{p' \cdot r}{\hbar} \right] \]

\[ = \left( \frac{1}{2\pi \hbar} \right)^{\frac{3}{2}} \int d^3p' \Phi(p', t) \frac{p'^2}{2m} \exp \left[ + i \frac{p' \cdot r}{\hbar} \right] \quad (649) \]

On performing the inverse Fourier Transform

\[ \Phi(p, t) = \left( \frac{1}{2\pi \hbar} \right)^{\frac{3}{2}} \int d^3r \Psi(r, t) \exp \left[ - i \frac{p \cdot r}{\hbar} \right] \quad (650) \]

on the time-dependent Schrödinger equation, one has

\[ i \hbar \frac{\partial \Phi(p, t)}{\partial t} = \left( \frac{1}{2\pi \hbar} \right)^{\frac{3}{2}} \int d^3r \int d^3p' \exp \left[ i \frac{(p' - p) \cdot r}{\hbar} \right] \frac{p'^2}{2m} \Phi(p', t) \]

\[ + q \left( \frac{1}{2\pi \hbar} \right)^{\frac{3}{2}} \int d^3r \Psi(r, t) \phi(r, t) \exp \left[ - i \frac{p \cdot r}{\hbar} \right] \quad (651) \]

where we have switched the order of the wave function and the scalar potential in the last term. On recognizing the integral over \( r \) as being proportional to the
integral representation of the delta function $\delta^3(p - p')$, and then performing the integration over $p$, one obtains

$$
\begin{align*}
\frac{i}{\hbar} \frac{\partial \Phi(p, t)}{\partial t} &= \frac{p^2}{2m} \Phi(p, t) + q \left( \frac{1}{2\pi\hbar} \right)^{\frac{3}{2}} \int d^3r \Psi(r, t) \phi(r, t) \exp \left[-i \frac{p \cdot r}{\hbar} \right] \\
&= \frac{p^2}{2m} \Phi(p, t) + q \phi(i \hbar \nabla_r, t) \left( \frac{1}{2\pi\hbar} \right)^{\frac{3}{2}} \int d^3r \Psi(r, t) \exp \left[-i \frac{p \cdot r}{\hbar} \right] \\
&= \frac{p^2}{2m} \Phi(p, t) + q \phi(i \hbar \nabla_r, t) \Phi(p, t) 
\end{align*}
$$

(652)

The last term can be manipulated as

$$
\begin{align*}
\frac{i}{\hbar} \frac{\partial \Phi(p, t)}{\partial t} &= \frac{p^2}{2m} \Phi(p, t) + q \phi(i \hbar \nabla_r, t) \left( \frac{1}{2\pi\hbar} \right)^{\frac{3}{2}} \int d^3r \Psi(r, t) \exp \left[-i \frac{p \cdot r}{\hbar} \right] \\
&= \frac{p^2}{2m} \Phi(p, t) + q \phi(i \hbar \nabla_r, t) \Phi(p, t) 
\end{align*}
$$

(653)

In the last line we have used the definition of the inverse Fourier transform. Thus, we have derived the equation that governs the time dependence of the momentum space wave function

$$
\frac{i}{\hbar} \frac{\partial \Phi(p, t)}{\partial t} = \left[ \frac{p^2}{2m} + q \phi(i \hbar \nabla_r, t) \right] \Phi(p, t) 
$$

(654)

analogous to the Schrödinger equation in the position representation.

3.7.4 The Heisenberg Picture.

In the Heisenberg picture, the wave function is chosen to be independent of time and the operators carry the implicit time dependence which represents the dynamics of the system. Thus, in this picture we have

$$
\begin{align*}
\Psi(r, t) &= \Psi(r, t') = \Psi(r, 0) \\
\hat{B}(r(t), t) &= \hat{U}(t, t') \hat{B}(r(t'), t) \hat{U}(t, t') 
\end{align*}
$$

(655)

Hence, the equation of motion for the implicit time dependence comes from the equation of motions for the operators and is given by

$$
\frac{i}{\hbar} \frac{d}{dt} \hat{B}(r(t), t) = \left[ \hat{B}(r(t), t) , \hat{H}(r(t), t) \right] + \frac{i}{\hbar} \frac{\partial}{\partial t} \hat{B}(r(t), t) 
$$

(656)
3.7.5 Exercise 51
Find the equation of motion for the position operator $\hat{r}(t)$ in the Heisenberg picture for a system with the Hamiltonian given by

$$\hat{H}(t) = \frac{\hat{p}(t)^2}{2m} + V(\hat{r}(t)) \quad (657)$$

3.7.6 Solution 51
We shall examine the Heisenberg equation of motion

$$i\hbar \frac{d\hat{r}}{dt} = [\hat{r}(t), \hat{H}(t)] + i\hbar \frac{\partial\hat{r}}{\partial t} \quad (658)$$

at the instant of time, say $t = 0$. Then in the position representation with $\hat{r}(0) = r$ and $\hat{p}(0) = -i\hbar \nabla$ one has no explicit time dependence for $\hat{r}$ and the implicit dependence is governed by

$$i\hbar \frac{dr}{dt} = [r, \hat{H}]$$

$$= [r, \frac{\hat{p}^2}{2m}] + [r, V(r)]$$

$$= 2i\hbar \frac{\hat{p}}{2m}$$

Thus, we find the operator equation

$$\frac{d\hat{r}}{dt} = \frac{\hat{p}}{m} \quad (659)$$

This operator equation has the same form as the momentum velocity relation in classical mechanics.
3.7.7 Exercise 52

Find the Heisenberg picture equation of motion for the momentum operator $\hat{p}(t)$ for a system with the Hamiltonian given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r}) \quad (660)$$

3.7.8 Solution 52

We shall examine the Heisenberg equation of motion

$$i \hbar \frac{d\hat{p}}{dt} = [ \hat{p}(t) , \hat{H}(t) ] + i \hbar \frac{\partial \hat{p}}{\partial t} \quad (661)$$

at the instant of time, say $t = 0$. Then in the position representation with $\hat{r}(0) = r$ and $\hat{p}(0) = -i\hbar \nabla$, one has no explicit time dependence for $\hat{p}$ and the implicit dependance is governed by

$$i \hbar \frac{d\hat{p}}{dt} = [ \hat{p} , \hat{H} ] = [ \hat{p} , \frac{\hat{p}^2}{2m} ] + [ \hat{p} , V(r) ] = -i\hbar \nabla V(r) \quad (662)$$

Thus, we find the operator equation

$$\frac{d\hat{p}}{dt} = -\nabla V(r) \quad (663)$$

This equation has the same form as Newton’s laws, except the classical quantities are replaced by operators.

The rate of change with respect to time of the operators found in Exercises 51 and 52 should look exactly like Hamilton’s equations of motion in classical mechanics.
3.7.9 Exercise 53

Prove that in the Heisenberg picture the rate of change of the angular momentum operator satisfies the equation

\[
\frac{d}{dt} \hat{L}(t) = -q \hat{r}(t) \wedge \nabla \phi(\hat{r}(t), t)
\]  

(664)

which is similar to the corresponding equation involving the torque classical mechanics.

If an operator \( \hat{B} \) does not explicitly depend on time \( t \), then the Heisenberg equation of motion reduces to

\[
i \hbar \frac{d}{dt} \hat{B}(\hat{r}(t)) = [ \hat{B}(\hat{r}(t)), \hat{H}(\hat{r}(t), t) ]
\]  

(665)

and so we find that the operator does not change with time if \( \hat{B} \) commutes with the Hamiltonian \( \hat{H} \). As the wave function is time independent in the Heisenberg picture, the expectation values of the operator will also be time independent. Thus, \( B \) will be a constant of motion, or a conserved quantity, if

\[
[ \hat{B}, \hat{H} ] = 0
\]  

(666)

Since any operator commutes with itself, when one substitutes \( \hat{H} \) for \( \hat{B} \), one finds that the Hamiltonian commutes with itself. Thus, if the Hamiltonian has no explicit dependence on time then the energy is a constant of motion.

3.7.10 Exercise 54

Find the time dependence of a Hermitean operator \( \hat{B} \) which has no explicit time dependence, if the commutator with the Hamiltonian is a complex constant \( C \), i.e.

\[
[ \hat{H}, \hat{B} ] = C
\]  

(667)

3.7.11 Solution 54

The time dependence of the operator \( \hat{B} \) is governed by the Heisenberg equation of motion

\[
i \hbar \frac{d\hat{B}}{dt} = [ \hat{B}, \hat{H} ]
\]  

(668)
Hence, on using the commutation relation

\[ i \hbar \frac{d\hat{B}}{dt} = -C \quad (669) \]

which leads to

\[ \hat{B}(t) = \hat{B}(0) + i \frac{C}{\hbar} t \quad (670) \]

This has an application for the rate of change of momentum \( \hat{p} \) for a particle in a uniform applied field \( \vec{F} \),

\[ \hat{H} = \frac{\hat{p}^2}{2m} - \vec{F} \cdot \vec{r} \quad (671) \]

which leads to the commutation relation

\[ [\hat{p}, \hat{H}] = + i \hbar \vec{F} \quad (672) \]

Thus, we have the time dependence of the momentum operator

\[ \hat{p}(t) = \hat{p}(0) + \vec{F} \cdot t \quad (673) \]

which is analogous to the classical solution for the momentum of a particle in an applied uniform field.

---

3.7.12 Exercise 55

Consider a free particle moving in one dimension, calculate the r.m.s. position \( \Delta x_{rms}(t) \) as a function of time, by using the Heisenberg equations of motion repeatedly. Do not assume any particular form for the wave packet. Show that

\[ ( \Delta x_{rms}(t) )^2 = ( \Delta x_{rms}(0) )^2 + \]
\[ + \frac{2}{m} \left[ \frac{1}{2} \hat{p}^2 + \hat{p} x(0) - \overline{x}(0) \overline{\hat{p}}(0) \right] t + \]
\[ + \frac{(\Delta p_{rms}(0))^2}{m^2} t^2 \]

\[ ( \Delta p_{rms}(t) )^2 = ( \Delta p_{rms}(0) )^2 \quad (674) \]

The average value of the momentum and the r.m.s. momenta are time independent as a consequence of \( p \) being conserved.
3.7.13 Exercise 56

Consider a one-dimensional harmonic oscillator with the Hamiltonian.

\[ \hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2} x^2 \]  

(675)

Derive the equations of motion for the expectation value of \( x \). Solve this equation to show that the mean position oscillates

\[ \bar{x}(t) = \bar{x}(0) \cos \omega t + \frac{\bar{p}(0)}{m \omega} \sin \omega t \]  

(676)

and that the r.m.s. position is given by

\[ \Delta x^2(t) = \Delta x^2(0) \cos^2 \omega t + \frac{\Delta p^2(0)}{m^2 \omega^2} \sin^2 \omega t + \left[ \frac{1}{2} \frac{\bar{x}}{\bar{p}} + \frac{\bar{p}}{\bar{x}}(0) - \bar{x}(0) \bar{p}(0) \right] \frac{\sin 2\omega t}{m \omega} \]  

(677)

Show that this result reduces to that of the previous exercise when \( \omega \to 0 \).

The Schrödinger and Heisenberg pictures are equivalent since the only physically important quantities are measurable and, therefore, are in the form of an expectation value, as displayed in eqn(642). We shall mainly be concerned with the Schrödinger picture, in the position space representation.

3.7.14 The Schrödinger Equation

In the Schrödinger picture, the operators are time independent and the wave functions evolve with time according to

\[ \Psi(\mathbf{r}, t) = \hat{U}(t, t_0) \Psi(\mathbf{r}, t_0) \]  

(678)

The time-dependent wave functions satisfy the Schrödinger equation,

\[ i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H}(\mathbf{r}, t) \Psi(\mathbf{r}, t) \]

(679)

This linear partial differential equation is first order in time and, therefore, requires one initial condition. At the initial time \( t_0 = 0 \) the initial condition is given by knowledge of \( \Psi(\mathbf{r}, 0) \). For the case where the Hamiltonian contains a
time-independent scalar electrostatic potential $\phi(\mathbf{r})$, the Schrödinger equation has the form

$$i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + q \phi(\mathbf{r}) \right] \Psi(\mathbf{r}, t) \quad (680)$$

In this case, where the Hamiltonian $\hat{H}$ is time independent, one has a formal solution

$$\Psi(\mathbf{r}, t) = \hat{U}(t, 0) \Psi(\mathbf{r}, 0)$$

$$= \exp \left[ -i \frac{\hat{H} t}{\hbar} \right] \Psi(\mathbf{r}, 0) \quad (681)$$

which contains the wave function at the initial time. It should be noted that, since the time evolution operator $\hat{U}(t, 0)$ satisfies the equation

$$\hat{U}^\dagger(t, 0) \hat{U}(t, 0) = \hat{I} \quad (682)$$

it is a unitary operator. The unitarity condition ensures that the normalization of the wave function $\Psi(\mathbf{r}, t) = \hat{U}(t, 0) \Psi(\mathbf{r}, 0)$ is independent of time.

Let us now consider a Hamiltonian which contains a time-dependent external field, due to some classical source. For example,

$$\hat{H}(t) = \frac{\hat{p}^2}{2m} + V(\mathbf{r}) - \left( F \cdot \mathbf{\hat{r}} \right) \sin \omega t \quad (683)$$

We should be aware that the Hamiltonian at different times does not commute

$$[ \hat{H}(t_1), \hat{H}(t_2) ] = -i \hbar \left( \hat{F} \cdot \mathbf{\hat{p}} \right) \left( \sin \omega t_1 - \sin \omega t_2 \right) \quad (684)$$

When the Hamiltonian has an explicit time dependence, $\hat{H}(t)$, due to an external field then the solution of the Schrödinger equation can be expressed as

$$\Psi(\mathbf{r}, t) = \hat{U}(t, 0) \Psi(\mathbf{r}, 0) \quad (685)$$

where the time dependence of the evolution operator is governed by the equation

$$i \hbar \frac{\partial}{\partial t} \hat{U}(t, 0) = \hat{H}(t) \hat{U}(t, 0) \quad (686)$$

On integrating the time evolution equation, one obtains

$$\hat{U}(t, 0) = 1 - i \frac{\hbar}{\hbar} \int_0^t dt_1 \hat{H}(t_1) \hat{U}(t_1, 0) \quad (687)$$

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This involves the time evolution operator $\hat{U}$ on both sides of the equation. We shall iterate this equation, that is, substitute the expression for $\hat{U}(t,0)$ with the two terms on the right hand side as an expression for $\hat{U}(t_1,0)$ in the right hand side. After the substitution, the equation now possesses two completely known terms, one of order zero in $\hat{H}$ and the second linear in $\hat{H}$ and the unknown term involving $\hat{U}$ appears in a third term and has a coefficient which is proportional to $\hat{H}^2$. On further iterating this equation an infinite number of times, one obtains an infinite series in the operator $\hat{H}$,

$$\hat{U}(t,0) = 1 - \frac{i}{\hbar} \int_0^t dt_1 \hat{H}(t_1) - \frac{1}{\hbar^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \hat{H}(t_1) \hat{H}(t_2) + \ldots$$

(688)

where one recognizes that the Hamiltonian at earlier times always appears to the right of Hamiltonian at later times. The general higher order term in this infinite series is given by

$$+ \left( -\frac{i}{\hbar} \right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n \hat{H}(t_1) \hat{H}(t_2) \ldots \hat{H}(t_n)$$

(689)

which we again note has a time ordered structure, in that the time $t_{m+1}$ is always earlier than the time $t_m$, and $\hat{H}(t_{m+1})$ is on the right of $\hat{H}(t_m)$. In the general term in this expansion, the intermediate times in the integration are always ordered and the Hamiltonian operators are also time ordered.

We could permute the dummy variables $t_1$ to $t_n$ in many ways, in fact there are $n!$ such permutations. Each permutation would result in a different time ordering of the labels, and each permutation gives the same result as long as the Hamiltonians are ordered such that the Hamiltonians at consecutive times are adjacent to each other with the earlier time to the right. This procedure is called time ordering and was first introduced by the Gian-Carlo Wick. We shall define an operator $\hat{W}$ which time orders a string of Hamiltonians according to the time label. We note that each of the $n!$ permutations involve integrations over different sectors of the “space” defined by the set of times $(t_1, t_2, \ldots, t_n)$ where $t > t_m > 0$, and that the $n!$ sectors completely run over the entire “volume”, $t^n$, of this space. Hence, we can re-write the general term as an integration over the entire volume, as long as we keep the Hamiltonian in the correct time ordered places, and this is done by following the instruction $\hat{W}$,

$$+ \frac{1}{n!} \left( -\frac{i}{\hbar} \right)^n \int_0^t dt_1 \int_0^t dt_2 \ldots \int_0^t dt_n \hat{W} \hat{H}(t_1) \hat{H}(t_2) \ldots \hat{H}(t_n)$$

(690)

On summing the series, we find

$$\hat{U}(t,0) = \hat{W} \exp \left[ -\frac{i}{\hbar} \int_0^t dt' \hat{H}(t') \right]$$

(691)

This is the best we can do for an arbitrary time-dependent Hamiltonian. However, if $\hat{H}$ has no explicit time dependence, then the effect of $\hat{W}$ can be neglected
since all the $\hat{H}(t_m)$ are the same. In this case we recover our previous result, namely

$$\hat{U}(t,0) = \exp\left[-\frac{i}{\hbar} \int_0^t dt' \hat{H}\right]$$

$$= \exp\left[-i \frac{\hat{H} t}{\hbar}\right] \quad (692)$$

### 3.7.15 Exercise 57
Find the time dependence of a state representing a particle in a field free environment, with the initial condition that at $t = 0$ the particle is in momentum eigenstate given by

$$\Psi(r,0) = \left(\frac{1}{2\pi\hbar}\right)^{\frac{3}{2}} \exp\left[+i \frac{p_0 \cdot r}{\hbar}\right] \quad (693)$$

### 3.7.16 Solution 57
The time dependence of the wave function is given by the Schrödinger equation

$$i \hbar \frac{d}{dt} \Psi(r,t) = \hat{H} \Psi(r,t) \quad (694)$$

The solution can found first by integrating

$$\Psi(r,t) = \Psi(r,0) - \frac{i}{\hbar} \int_0^t dt' \hat{H} \Psi(r,t') \quad (695)$$

and then by iterating

$$\Psi(r,t) = \Psi(r,0) - \frac{i}{\hbar} \int_0^t dt' \hat{H} \Psi(r,0) - \frac{1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' \hat{H}^2 \Psi(r,t'') \quad (696)$$

The equation simplifies, since the initial wave function $\Psi(r,0)$ is also an eigenstate of the free-particle Hamiltonian $\hat{H}$

$$\hat{H} = \frac{\hat{p}^2}{2m} \quad (697)$$

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so that

$$\hat{H} \Psi(r, 0) = E(p_0) \Psi(r, 0)$$

(698)

where

$$E(p_0) = \frac{p_0^2}{2m}$$

(699)

is the energy eigenvalue. On substituting the eigenvalue for $\hat{H}$ in eqn(696) and iterating an infinite number of times, one finds that

$$\Psi(r, t) = \exp \left[ -i \frac{E(p_0)}{\hbar} t \right] \Psi(r, 0)$$

$$= \left( \frac{1}{2\pi\hbar} \right)^{\frac{3}{2}} \exp \left[ +i \left( \frac{p_0 \cdot r - E(p_0)}{\hbar} t \right) \right]$$

(700)

### 3.7.17 Time Development of a Wave Packet

A wave packet $\Psi(r, t)$ representing a free particle evolves according to

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t)$$

(701)

since the potential is a constant $q \phi(r, t) = V_0$ which can be absorbed into the reference energy, and can be set to zero.

The evolution equation can be solved by Fourier decomposition, since for free particles the momentum eigenfunctions are also eigenfunctions of the Hamiltonian. By Fourier decomposition of the initial wave function $\Psi(r, 0)$, one finds $\Phi(p, 0)$ as the coefficient of the momentum eigenfunction, $\phi_p(r)$. Then

$$\phi_p(r) \propto \exp \left[ i \frac{p \cdot r}{\hbar} \right]$$

(702)

the wave function in momentum representation evolves with time according to

$$\Phi(p, t) = \exp \left[ -i \frac{E t}{\hbar} \right] \Phi(p, 0)$$

(703)

where $E = \frac{p^2}{2m}$. Thus, as the initial value of the wave function in momentum representation is given by

$$\Phi(p, 0) = \left( \frac{1}{2\pi\hbar} \right)^{\frac{3}{2}} \int d^3r' \Psi(r', 0) \exp \left[ -i \frac{p \cdot r'}{\hbar} \right]$$

(704)
we find that the time development of the wave function in momentum representation is governed by

$$
\Phi(p, t) = \left( \frac{1}{2 \pi \hbar} \right)^{\frac{3}{2}} \int d^3 \mathbf{r}' \Psi(\mathbf{r}', 0) \exp \left[ -i \left( \frac{p \cdot \mathbf{r}' + E t}{\hbar} \right) \right] \tag{705}
$$

On performing the inverse Fourier transform of $\Phi(p, t)$, we obtain the wave function in the position representation at time $t$ as, $\Psi(\mathbf{r}, t)$ where

$$
\Psi(\mathbf{r}, t) = \left( \frac{1}{2 \pi \hbar} \right)^{\frac{3}{2}} \int d^3 p \Phi(p, 0) \exp \left[ +i \left( \frac{p \cdot \mathbf{r} - p^2 t}{2m \hbar} \right) \right] \tag{706}
$$

Thus, all one needs to do is to evaluate the Fourier transform $\Phi(p, 0)$ of the initial condition, eqn(704), and the inverse transform, given in eqn(706), to obtain the time dependence of the free particle wave function.

### 3.7.18 Exercise 58

Given the initial wave function

$$
\Psi(\mathbf{r}, 0) = \left( \frac{1}{2 \pi \delta x^2} \right)^{\frac{3}{4}} \exp \left[ -\frac{(\mathbf{r} - \mathbf{r}_0)^2}{4 \delta x^2} \right] \exp \left[ +i \frac{p_0 \cdot \mathbf{r}}{\hbar} \right] \tag{707}
$$

find the time evolution of the wave function for a free particle, the time dependence of the average position, $\langle \mathbf{r}(t) \rangle$, and the mean squared deviation of the particle’s position, $\Delta(\mathbf{r}(t))^2$.

### 3.7.19 Solution 58

The momentum space wave function, at time $t = 0$ is found from the initial wave function in real space via the Fourier transform

$$
\Phi(\mathbf{r}, 0) = \left( \frac{1}{2 \pi \hbar} \right)^{\frac{3}{2}} \int d^3 \mathbf{r} \Psi(\mathbf{r}, 0) \exp \left[ -i \frac{p \cdot \mathbf{r}}{\hbar} \right] \\
= \left( \frac{2 \delta x^2}{\pi \hbar} \right)^{\frac{3}{4}} \exp \left[ -\frac{(p - p_0)^2 \delta x^2}{h^2} \right] \exp \left[ -i \frac{\mathbf{r}_0 \cdot (\mathbf{r} - \mathbf{r}_0)}{\hbar} \right] \tag{708}
$$
Figure 27: The time dependence of the probability density for an initial Gaussian wavepacket, $\Psi(x,t)$. The wavepacket moves with velocity $\frac{p}{m}$ and disperses with increasing $t$.

Then, the momentum space wave function at time $t$ is given by

$$\Phi(p,t) = \left(\frac{2}{\pi \hbar^2}\right)^{\frac{3}{2}} \exp\left[ -\left(\frac{p - p_0}{\hbar}\right)^2 \frac{\delta x^2}{\hbar^2} \right] \times \exp\left[ -i \frac{p_0 \cdot (p - p_0)}{\hbar} \right] \exp\left[ -i \frac{p^2 t}{2 m \hbar} \right]$$

(709)

The time dependence only enters via the phase. Since the momentum probability distribution involves the modulus squared wave function $|\Phi(p,t)|^2$, we find that the momentum distribution is time independent. Furthermore the average momentum is $p_0$ and the distribution has a r.m.s. width, in each of the three orthogonal directions, which is equal to $\frac{\hbar}{2 \delta x}$, independent of time. The wave packet does not spread in momentum space.

The real space wave function at time $t$ is given by the inverse Fourier transform of $\Phi(p,t)$

$$\Psi(r,t) = \left(\frac{1}{2 \pi \hbar}\right)^{\frac{3}{2}} \int d^3p \, \Phi(p,t) \exp\left[ + i \frac{p \cdot r}{\hbar} \right]$$

(710)
This has the explicit form

$$
\Psi(r, t) = \left( \frac{1}{2 \pi \hbar} \right)^{\frac{3}{2}} \int d^3p \left( \frac{2 \delta x^2}{\pi \hbar^2} \right)^{\frac{3}{4}} \exp \left[ - \left( \frac{p - p_0}{\hbar} \right)^2 \right] \\
\times \exp \left[ - i \cdot \frac{p_0 \cdot (p - p_0)}{\hbar} \right] \exp \left[ - i \frac{p^2 t}{2 m \hbar} \right] \exp \left[ + i \frac{p \cdot r}{\hbar} \right]
$$

(711)

Combining the exponential factors and completing the square by changing variable from $p$ to $z$ where

$$
z = p - p_0 - \frac{i}{2} \left( \frac{r - r_0}{\delta x^2} + i t \frac{\hbar}{2 m} \right)
$$

(712)

one finds that

$$
\Psi(r, t) = \left( \frac{1}{2 \pi (\delta x^2 + i t \frac{\hbar}{2 m})} \right)^{\frac{3}{4}} \exp \left[ - \left( \frac{r - r_0}{\delta x^2} - \frac{1}{4} \frac{p_0^2 t}{2 m \hbar} \right)^2 \right] \\
\times \exp \left[ + i \frac{p_0 \cdot r - \frac{p^2 t}{2 m \hbar}}{\hbar} \right]
$$

(713)

From this we see that the wave packet corresponds to a real space probability distribution function in which the maximum moves along the classical trajectory,

$$
r = r_0 + \frac{p_0 t}{m}
$$

(714)

The width of the distribution function, however, increases with increasing $t$, corresponding to a spreading of the wave packet. The root mean squared width is given by

$$
\Delta x^2(t)_{rms} = \sqrt{\delta x^4 + t^2 \frac{\hbar^2}{4 m^2}}
$$

(715)

which increases linearly with $t$ for sufficiently large $t$. This corresponds to the spread in the positions of a set of classical particles which have a momentum distribution of width $\frac{\hbar}{2 \delta x^2}$.

---

### 3.7.20 Time Evolution and Energy Eigenfunctions

The analysis of the time development of a wave packet for a free particle can be extended to motion in an arbitrary potential, with the knowledge of the energy eigenfunctions of the time-independent Hamiltonian operator.

$$
\hat{H} \phi_n(r) = E_n \phi_n(r)
$$

(716)
The energy eigenstates evolve according to the Schrödinger equation

\begin{equation}
    i \hbar \frac{\partial}{\partial t} \phi_n(r, t) = \hat{H} \phi_n(r, t) = E_n \phi_n(r, t)
\end{equation}

(717)
since they are eigenstates. The solution of the Schrödinger equation yields the time dependence of the energy eigenstates as

\begin{equation}
    \phi_n(r, t) = \exp \left[ -i \frac{E_n}{\hbar} t \right] \phi_n(r)
\end{equation}

(718)
The energy eigenstates are often called stationary states, as the only time dependence occurs through a phase factor, which is generally unobservable.

Given that the eigenstates of the Hamiltonian form a complete set, we can expand the initial wave function in terms of the energy eigenstates

\begin{equation}
    \Psi(r, 0) = \sum_n C_n \phi_n(r)
\end{equation}

(719)
where the expansion coefficients are given by

\begin{equation}
    C_n = \int d^3r' \phi_n^*(r') \Psi(r', 0)
\end{equation}

(720)
Hence, we have the formal solution

\begin{equation}
    \Psi(r, t) = \sum_n C_n \phi_n(r) \exp \left[ -i \frac{E_n}{\hbar} t \right]
\end{equation}

\begin{equation}
    \Psi(r, t) = \sum_n \int d^3r' \phi_n(r, 0) \phi_n^*(r') \exp \left[ -i \frac{E_n}{\hbar} t \right] \Psi(r', 0)
\end{equation}

(721)
This expression for the time-dependent wave function involves an infinite sum of energy eigenfunctions, and satisfies the time-dependent Schrödinger equation as can be seen by direct substitution. We are implicitly assuming that the summation converges for all times, including \( t = 0 \) where the sum reduces to the Dirac delta function

\begin{equation}
    \delta(r' - r)
\end{equation}

due to the completeness relation. Thus, at \( t = 0 \), the integration over \( r' \) yields the initial wave function \( \Psi(r, 0) \).
3.7.21 Exercise 59

A two-level system has energy eigenfunctions $\phi_1$ and $\phi_2$ with energy eigenvalues $E_1$ and $E_2$ respectively. The operator $\hat{A}$ does not commute with the Hamiltonian and has eigenfunctions $\theta_1$ and $\theta_2$ corresponding to the eigenvalues $a_1$ and $a_2$. If the system is in the eigenstate $\theta_1$ at time $t = 0$ (i.e. $\Psi(\vec{r},0) = \theta_1(\vec{r})$), show that it is possible for the expectation value of $\hat{A}$ to obey the equation

$$\bar{a}(t) = \left(\frac{a_1 + a_2}{2}\right) + \left(\frac{a_1 - a_2}{2}\right) \cos\left(\frac{E_1 - E_2}{\hbar} t\right)$$

(723)

where the expectation value is defined by

$$\bar{a}(t) = \int d^3\vec{r} \, \Psi^*(\vec{r},t) \, \hat{A} \, \Psi(\vec{r},t)$$

(724)

Also find the probabilities that a measurement of $\hat{A}$ at time $t$ will give the result $a_1$ or $a_2$, respectively.

3.7.22 Solution 59

The principle of linear superposition, together with the Schrödinger equation for the time-independent Hamiltonian yields, the wave function of the system as

$$\Psi(\vec{r},t) = C_1 \, \phi_1(\vec{r}) \, \exp\left[ -i \frac{E_1}{\hbar} t \right] + C_2 \, \phi_2(\vec{r}) \, \exp\left[ -i \frac{E_2}{\hbar} t \right]$$

(725)

At $t = 0$ the system is in an eigenstate of $\hat{A}$ with eigenvalue $a_1$. Thus,

$$\theta_1(\vec{r}) = C_1 \, \phi_1(\vec{r}) + C_2 \, \phi_2(\vec{r})$$

(726)

By orthogonality of the eigenstates of $\hat{A}$ we have

$$\theta_2(\vec{r}) = C_2^* \, \phi_1(\vec{r}) - C_1^* \, \phi_2(\vec{r})$$

(727)

Hence, on solving for the energy eigenstates in terms of the eigenstates of $\hat{A}$, we find that the state of the system is given by

$$\Psi(\vec{r},t) = \left( |C_1|^2 \, \exp\left[ -i \frac{E_1}{\hbar} t \right] + |C_2|^2 \, \exp\left[ -i \frac{E_2}{\hbar} t \right] \right) \theta_1(\vec{r}) + C_1 \, C_2 \left( \exp\left[ -i \frac{E_1}{\hbar} t \right] - \exp\left[ -i \frac{E_2}{\hbar} t \right] \right) \theta_2(\vec{r})$$

(728)
The expectation value of $\hat{A}$ in this state is given by

$$\pi(t) = \int d^3\mathbf{r} \Psi^*(\mathbf{r}, t) \hat{A} \Psi(\mathbf{r}, t)$$

$$= a_1 \left( |C_1|^4 + |C_2|^4 + 2 |C_1|^2 |C_2|^2 \cos \left( \frac{E_1 - E_2}{\hbar} t \right) \right) + a_2 \left( |C_1|^2 |C_2|^2 \left( 1 - \cos \left( \frac{E_1 - E_2}{\hbar} t \right) \right) \right)$$

(729)

This yields the required result if

$$|C_1|^4 + |C_2|^4 = \frac{1}{2}$$

(730)

and

$$2 |C_1|^2 |C_2|^2 = \frac{1}{2}$$

(731)

On using the normalization condition in the last equation, one finds a quadratic equation. The solution of the quadratic equation leads to

$$|C_1|^2 = |C_2|^2 = \frac{1}{2}$$

(732)

The probability of finding the result $a_1$ is given by

$$P(a_1) = \left( |C_1|^4 + |C_2|^4 + 2 |C_1|^2 |C_2|^2 \cos \left( \frac{E_1 - E_2}{\hbar} t \right) \right)$$

(733)

and the probability of finding the result $a_2$ is

$$P(a_2) = 2 |C_1|^2 |C_2|^2 \left( 1 - \cos \left( \frac{E_1 - E_2}{\hbar} t \right) \right)$$

(734)

Note that, due to the normalization, the sum of the probabilities is unity

$$P(a_1) + P(a_2) = \left( |C_1|^2 + |C_2|^2 \right)^2 = 1$$

(735)

and independent of $t$. 

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3.7.23 The Correspondence Principle

The correspondence principle, as previously stated, implies that quantum mechanics should reduce to classical mechanics in the limit $\hbar \rightarrow 0$. We shall show how quantum mechanics reproduces the Hamilton-Jacobi equations of classical mechanics, in this limit.

Starting from the Schrödinger equation in the case where the vector potential is absent

$$i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left( - \frac{\hbar^2}{2m} \nabla^2 + q \phi(\mathbf{r}, t) \right) \Psi(\mathbf{r}, t) \tag{736}$$

one can write the complex wave function in terms of two real functions $A(\mathbf{r}, t)$ and $S(\mathbf{r}, t)$ representing the amplitude and phase

$$\Psi(\mathbf{r}, t) = A(\mathbf{r}, t) \exp \left[ + \frac{i S(\mathbf{r}, t)}{\hbar} \right] \tag{737}$$

Then, on substituting this form in the Schrödinger equation and taking the real parts and the imaginary parts, one has two equations. The first represents the real part of the Schrödinger equation

$$- \left( \frac{\partial S}{\partial t} \right) = \frac{1}{2m} \left( \nabla S(\mathbf{r}, t) \right)^2 + q \phi(\mathbf{r}, t) - \frac{\hbar^2}{2m} \frac{\nabla^2 A}{A} \tag{738}$$

and the second represents the imaginary part

$$i \hbar \frac{\partial A}{\partial t} = -i \frac{\hbar}{2m} A \nabla^2 S - \frac{\hbar}{m} \left( \nabla A \right) \cdot \left( \nabla S \right) \tag{739}$$

On taking the limit $\hbar \rightarrow 0$, one finds that the equation for the phase $S$ satisfies the Hamilton-Jacobi equation of classical mechanics,

$$- \left( \frac{\partial S}{\partial t} \right) = \frac{1}{2m} \left( \nabla S(\mathbf{r}, t) \right)^2 + q \phi(\mathbf{r}, t) \tag{740}$$

In the Hamilton-Jacobi formulation of classical mechanics one identifies the classical momentum with the gradient of $S$

$$p = \nabla S \tag{741}$$

The equation for the amplitude $A$ can be reduced to

$$\left( \frac{\partial A^2}{\partial t} \right) = - \nabla \cdot \left( \frac{A^2 \nabla S}{m} \right) \tag{742}$$

by multiplying by an integrating factor of $A(\mathbf{r}, t)$. This last equation is identified as a continuity equation which relates the probability density $\rho(\mathbf{r}, t) =$
\[ |\Psi(\mathbf{r}, t)|^2 = A(\mathbf{r}, t)^2, \] to the probability current density \( j(\mathbf{r}, t) \) defined by
\[ j(\mathbf{r}, t) = \nabla S \rho. \] The continuity equation is
\[ \frac{\partial}{\partial t} \rho(\mathbf{r}, t) + \nabla \cdot j(\mathbf{r}, t) = 0 \quad (743) \]
Thus, to lowest order in \( \hbar \), the phase of the wave function satisfies the Hamilton-Jacobi equation and the amplitude satisfies a continuity equation.

Applying this analysis to a wave packet, one finds that the wave packet follows a trajectory which is governed by the classical action \( S \) that appears in the exponent. The phase factor has the slowest variation along the classical trajectory. The continuity condition shows that the probability density \( \rho \) will vanish outside the region that moves along the classical trajectory. Furthermore, the value of any physical quantity can be approximated by the classical value if the wave function is dominated by the exponential factor. In this case one can consider the unitary transformation, which when applied to the momentum operator results in
\[ \exp \left[ -\frac{i S}{\hbar} \right] \hat{p} \exp \left[ +\frac{i S}{\hbar} \right] = \hat{p} + \nabla S \quad (744) \]
This leads to the operator being represented by the classical value of the momentum and a quantum correction. Thus, for an arbitrary operator \( \hat{B} = B(\mathbf{r}, \hat{p}) \) one has
\[ \exp \left[ -\frac{i S}{\hbar} \right] B(\mathbf{r}, \hat{p}) \exp \left[ +\frac{i S}{\hbar} \right] = B(\mathbf{r}, \hat{p} + \nabla S) \quad (745) \]
If the amplitude \( A(\mathbf{r}, t) \) has a sufficiently slow variation, then the expectation value of \( \hat{B} \) can be replaced by its classical value, since
\[ \int d^3 \mathbf{r} \Psi^*(\mathbf{r}) \hat{B} \Psi(\mathbf{r}) = \int d^3 \mathbf{r} A \exp \left[ -\frac{i S}{\hbar} \right] B(\mathbf{r}, \hat{p}) \exp \left[ +\frac{i S}{\hbar} \right] A \]
\[ = \int d^3 \mathbf{r} A B(\mathbf{r}, \hat{p} + \nabla S) A \approx B(\mathbf{r}, \nabla S) \quad (746) \]
where the real function \( B \) is evaluated on the classical trajectory on which \( A \) is non-vanishing.

Let us examine the conservation of probability density that is inherent in the exact quantum mechanical Schrödinger equation.

### 3.7.24 The Continuity Equation and Particle Conservation

An exact continuity equation can be derived from the Schrödinger equation, which ensures that the number of particles (i.e. the probability of finding the
particle anywhere), is conserved. The form of the equation is

$$\frac{\partial}{\partial t} \rho(r, t) + \nabla \cdot j(r, t) = 0 \quad (747)$$

where $\rho(r, t) = \Psi^*(r, t) \Psi(r, t)$ is the probability density and (in the absence of a vector potential) the probability current density $j(r, t)$ is given by

$$j(r, t) = \frac{\hbar}{2m} i \left[ \Psi^*(r, t) \nabla \Psi(r, t) - \Psi(r, t) \nabla \Psi^*(r, t) \right] \quad (748)$$

The expression for the probability current density, $j(r, t)$, corresponds to the real function given by the velocity operator sandwiched between the wave functions

$$j(r, t) = \text{Real} \left[ \Psi^*(r) \frac{\hat{\mathbf{p}}}{m} \Psi(r) \right] \quad (749)$$

The current density is real, and the real part is found by adding the expression and its complex conjugate, and then dividing by two.

The proof that $j(r, t)$ and $\rho(r, t)$ satisfy the continuity equation starts from the Schrödinger equation

$$i \hbar \frac{\partial}{\partial t} \Psi(r, t) = \left( -\frac{\hbar^2}{2m} \nabla^2 + q \phi(r, t) \right) \Psi(r, t) \quad (750)$$

and its complex conjugate

$$-i \hbar \frac{\partial}{\partial t} \Psi^*(r, t) = \left( -\frac{\hbar^2}{2m} \nabla^2 + q \phi(r, t) \right) \Psi^*(r, t) \quad (751)$$

Multiplying the first equation by $\Psi^*(r, t)$ and the complex conjugate equation by $\Psi(r, t)$ and then subtracting it, one obtains

$$i \hbar \frac{\partial}{\partial t} \Psi(r, t) \Psi^*(r, t) = -\frac{\hbar^2}{2m} \left( \Psi^*(r, t) \nabla^2 \Psi(r, t) - \Psi(r, t) \nabla^2 \Psi^*(r, t) \right)$$

$$= -\frac{\hbar^2}{2m} \nabla \cdot \left( \Psi^*(r, t) \nabla \Psi(r, t) - \Psi(r, t) \nabla \Psi^*(r, t) \right) \quad (752)$$

which was to be proved.

Thus, the total probability of finding the particle is unity, and remains unity for all times. This can be seen by integrating the continuity equation over a large fixed volume of space

$$\int d^3r \frac{\partial}{\partial t} \rho(r, t) + \int d^3r \left( \nabla \cdot j(r, t) \right) = 0 \quad (753)$$
On using Green’s theorem to express the integral over the divergence of the current as an integral over the surface of the volume $\Sigma$, one has
\[
\int d^3\ell \frac{\partial}{\partial t} \rho(\xi, t) + \int d^2\Sigma \cdot \mathbf{j}(\mathbf{r}, t) = 0 \tag{754}
\]
If the current falls to zero at the boundary of the surface, one is left with
\[
\int d^3\ell \frac{\partial}{\partial t} \rho(\xi, t) = 0 \tag{755}
\]
which, as the volume of integration is fixed, becomes
\[
\frac{d}{dt} \int d^3\ell \rho(\xi, t) = 0 \tag{756}
\]
Thus, one finds that the wave function that satisfies the Schrödinger equation remains normalized
\[
\int d^3\mathbf{r} \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) = 1 \tag{757}
\]
for all times.

---

**Example: The Probability Current Density of a Spherical Wave.**

Spherical Waves have wave functions of the form
\[
\Psi(\mathbf{r}) = \frac{\exp \left[ \pm i k r \right]}{r} \tag{758}
\]
where $k$ is a constant. This wave function is not normalizable and is independent of time. It should be interpreted as representing a steady state of a large number of beams of particles which are either diverging from or converging on the origin.

The probability current density $\mathbf{j}(\mathbf{r})$ is calculated from
\[
\mathbf{j}(\mathbf{r}) = \frac{\hbar}{2m i} \left[ \Psi^*(\mathbf{r}) \nabla \Psi(\mathbf{r}) - \Psi(\mathbf{r}) \nabla \Psi^*(\mathbf{r}) \right] \tag{759}
\]
which involves the gradient of the spherical wave. The gradient is evaluated as
\[
\nabla \Psi(\mathbf{r}) = \hat{e}_r \left( \pm i k - \frac{1}{r} \right) \exp \left[ \pm i k r \right] \tag{760}
\]
which is purely radial. Hence, the current density is purely radial
\[
\mathbf{j} = \pm \frac{\hbar k}{m} \frac{1}{r^2} \hat{e}_r \tag{761}
\]
and falls off as \( r^{-2} \), with increasing \( r \). The exponential phase factor in the wave functions cancel in the expression for the probability current density. The \( r^{-2} \) dependence of the probability current density is a consequence of continuity in the steady state, since it shows that the same number of particles, per unit time, pass through any spherical shell surrounding the origin, irrespective of the radius \( r \) of the shell. This is seen as follows: The number of particles passing through an infinitesimal area \( d^2S \) per unit time is given by the product

\[
\hat{J} \cdot d^2S = \pm \frac{\hbar k}{m} \frac{\hat{e}_r}{R^2} \cdot d^2S
\]

where \( R \) is the radial distance of the surface element from the origin. On integrating this over the surface of a sphere of radius \( R \), for which \( d^2S \) is also radially directed, one finds

\[
-\frac{dN}{dt} = \int d^2S \cdot \hat{J} = \pm 4 \pi \frac{\hbar k}{m}
\]

since, the surface area of the sphere is given by \( 4 \pi R^2 \). Therefore, the number of particles passing through the spherical surface is independent of \( R \).

---

Figure 28: Outgoing Spherical Waves.

The continuity condition is not satisfied at the origin and, depending on the sign of the probability current, the origin either acts as a source or sink where
particles are created or annihilated.
4 Applications of Quantum Mechanics

4.1 Exact Solutions in One Dimension

One-dimensional problems are instructive, as they are often exactly soluble, and are relatively easy to solve. They also provide good illustrations of the principles of quantum mechanics. However, some phenomena found in one dimension may lead to conclusions that do not hold in higher dimensions. For example, an attractive potential in one dimension always leads to the formation of a bound state, but this does not remain true in higher dimensions. Nevertheless, we shall now examine some exactly soluble one-dimensional eigenstate problems.

4.1.1 Particle Confined in a Deep Potential Well

Let us consider the problem of a quantum mechanical particle, moving in one dimension. The particle is confined by a potential to move in a region of space where 0 < x < L, because the potential satisfies

\[ V(x) = \begin{cases} 0 & \text{if } L > x > 0 \\ \infty & \text{otherwise} \end{cases} \]  

(764)

A classical particle with energy \( E < \infty \) is forbidden to exist in the region of space outside the interval of length \( L \). The particle’s motion consists of an orbit which moves back and forth with momentum \( p = \pm \sqrt{2 m E} \). The average position of the particle is given by \( x = \frac{L}{2} \) and the root mean squared deviation of the particle’s position is given by \( \frac{L}{\sqrt{12}} \). The average value of the momentum is zero because it spends half the time moving forward with momentum \(+ p\) and half the time moving backward with momentum \(- p\). However, the root mean squared value of the particle’s momentum is exactly equal to \( p \).

Inside the interval \( L > x > 0 \), the energy eigenvalue equation takes the form

\[ -\frac{\hbar^2}{2 m} \frac{\partial^2}{\partial x^2} \Psi_E(x) = E \Psi_E(x) \]  

(765)

which corresponds to the motion of a free particle. This equation is satisfied by the form

\[ \Psi_E(x) = A \exp \left[ + i k x \right] + B \exp \left[ - i k x \right] \]  

(766)

with arbitrary \( A \) and \( B \), and \( p = \hbar k = \sqrt{2 m E} \). Within the region defined by \( L > x > 0 \), the form of the solution appears to correspond to a linear superposition of momentum eigenstates, with momentum \( \pm p \).
Infinite Potential Well

Figure 29: The potential of a deep potential well of depth $V_0$, where $V_0 \to \infty$. The zero of energy is chosen to be the bottom of the potential well.

Outside the interval, the energy eigenvalue equation has the form

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_0\right] \Psi_E(x) = E \Psi_E(x) \quad (767)$$

where the limit $V_0 \to \infty$ should be taken. In this range only the form $\Psi_E(x) = 0$ satisfies this equation. This corresponds to the classical expectation that the particle should only be found within the interval of length $L$.

The solution must be continuous for all values of $x$, even at the boundaries $x = 0$ and $x = L$. Thus, we require $\Psi_E(x)$ to satisfy the boundary conditions

$$\Psi_E(0) = \Psi_E(L) = 0 \quad (768)$$

That is, the wave function inside the interval should match smoothly onto the solution outside the interval. This yields the two conditions

$$A + B = 0 \quad (769)$$

at $x = 0$ and

$$A \exp \left[ + i \frac{k}{L} \right] + B \exp \left[ - i \frac{k}{L} \right] = 0 \quad (770)$$
at $x = L$. The first condition yields $A = -B$ and so inside the potential well the wave function is just

$$\Psi_E(x) = A \left( \exp \left[ i k x \right] - \exp \left[ -i k x \right] \right)$$

$$= 2 i A \sin k x$$

(771)

for $L > x > 0$. The continuity condition at $x = L$ then becomes

$$\Psi_E(L) = 2 i A \sin k L = 0$$

(772)

Since we require $A \neq 0$, this places a condition on the allowed values of $k$ which must satisfy $k L = n \pi$ for integer values of $n$. The negative integer values of $n$ give the same solution as the positive integers, and thus are not needed. The value $n = 0$ gives a trivial solution which doesn’t describe a particle at all. The solution $n = 0$ is not normalizable, and there is no probability for finding a particle in an interval $\Delta x$ even if $L > x > 0$. Thus, the allowed values of $k$ are given by $k_n = n \frac{\pi}{L}$ where $n$ is a positive integer greater than zero. Therefore, the allowed values of the energy eigenvalue are also given by the discrete values

$$E_n = \frac{\hbar^2 k_n^2}{2 m}$$

$$= \frac{\hbar^2 n^2 \pi^2}{2 m L^2}$$

(773)

The energy eigenvalues are discrete as the particle is trapped in a region of finite spatial extent. The corresponding energy eigenfunctions are given by

$$\Psi_n(x) = C \sin n \frac{\pi x}{L}$$

(774)

where $C$ is an arbitrary complex number. The normalization condition

$$\int_{-\infty}^{+\infty} dx \ |\Psi_n(x)|^2 = 1$$

(775)

reduces to

$$\int_{0}^{L} dx \ |\Psi_n(x)|^2 = 1$$

(776)

since $\Psi_n(x)$ vanishes outside the region of integration. Using the form of $\Psi_n(x)$ one finds that $|C|$ is given by

$$1 = |C|^2 \int_{0}^{L} dx \sin^2 n \frac{\pi x}{L}$$

$$= |C|^2 \int_{0}^{L} dx \frac{1}{2} \left( 1 - \cos \frac{2 n \pi x}{L} \right)$$

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Thus, the properly normalized wave functions are,

\[ \Psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n \pi x}{L} \left[ \Theta(x) - \Theta(x - L) \right] \]  

(778)

where \( \Theta(x) \) is the Heaviside step function defined by

\[ \Theta(x) = \begin{cases} 1 & \text{if } x > 0 \\ 0 & \text{if } x < 0 \end{cases} \]  

(779)

Eigenfunctions of the infinite potential well

Figure 30: The energy eigenfunctions \( \Psi_n(x) \) of a particle in a deep potential well.

These wave functions are the eigenfunctions of a Hermitean operator \( \hat{H} \). We see that the eigenvalues are real

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{2 m L^2} \]  

(780)
and are non-degenerate. The eigenfunctions are orthogonal, as can be seen by directly evaluating the integral

\[
\int_{-\infty}^{+ \infty} dx \, \Psi_m^{*}(x) \, \Psi_n(x) = \frac{2}{L} \int_{0}^{L} dx \, \sin \left( \frac{m \pi x}{L} \right) \sin \left( \frac{n \pi x}{L} \right) \\
= \frac{1}{L} \int_{0}^{L} dx \left( \cos \left( \frac{m - n \pi x}{L} \right) - \cos \left( \frac{m + n \pi x}{L} \right) \right) \\
= \frac{1}{\pi} \left( \frac{\sin \left( \frac{m - n \pi}{m - n} \right)}{m - n} - \frac{\sin \left( \frac{m + n \pi}{m + n} \right)}{m + n} \right) \\
= \delta_{m,n}
\]

(781)

The overlap integral is zero for \( m \neq n \) and for \( m = n \) the wave functions are normalized to unity, as can be seen via invoking l’Hôpital’s rule. Also one recognizes that functions in the finite interval \( L > x > 0 \) can, by the theory of finite Fourier series, be expanded in terms of the set of eigenfunctions. The choice of interval for the function which is to be expanded in a Fourier series, usually extends from \( -L \) to \(+L\), and the series contains terms of \( \cos \frac{n \pi x}{L} \) in addition to the terms \( \sin \frac{n \pi x}{L} \). However, if we insist that our wave functions \( \Psi(x) \) over the enlarged interval are odd, i.e. \( \Psi(-x) = -\Psi(x) \) then only the \( \sin \) terms remain in the Fourier series expansion. That is, the eigenfunctions form a complete set, only in the interval \( L > x > 0 \).

The average values of the position of the particle in these energy eigenstates is given by

\[
\bar{x} = \int_{0}^{L} dx \, \Psi_{n}^{*}(x) \, x \, \Psi_{n}(x) \\
= \frac{2}{L} \int_{0}^{L} dx \, x \sin^{2} \left( \frac{n \pi x}{L} \right) \\
= \frac{1}{L} \int_{0}^{L} dx \, x \left( 1 - \cos \frac{2 \pi x}{L} \right)
\]

(782)

However, the integral can be evaluated via

\[
\int dx \, x \cos \alpha x = \frac{\partial}{\partial \alpha} \int dx \, \sin \alpha x \\
= -\frac{\partial}{\partial \alpha} \left( \frac{\cos \alpha x}{\alpha} \right) \\
= \left( \frac{\cos \alpha x + x \alpha \sin \alpha x}{\alpha^{2}} \right)
\]

(783)

Thus, we find that the average position is given by

\[
\bar{x} = \frac{L}{2}
\]

(784)

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Figure 31: The quantum mechanical probability density \( P(x) = |\Psi_n(x)|^2 \) for a particle in an energy eigenstate with energy eigenvalue \( E \) is compared with the classically calculated probability density for a particle with energy \( E \). The classical probability density is calculated by averaging over the initial conditions for classical trajectories with energy \( E \). In accordance with the correspondence principle, the probability densities should agree in the limit \( \hbar \to 0 \), which is exactly the same as the classical average.

The mean squared deviation in the particle’s position is given by

\[
\Delta x^2 = \int_0^L dx \, \Psi_n^*(x) \left( x - \frac{L}{2} \right)^2 \Psi_n(x)
\]

\[
= \frac{2}{L} \int_0^L dx \left( x^2 - \frac{L^2}{4} \right) \sin^2 \frac{n \pi x}{L}
\]

\[
= \frac{1}{L} \int_0^L dx \left( x^2 - \frac{L^2}{4} \right) \left( 1 - \cos \frac{2 n \pi x}{L} \right)
\]

\[
= \frac{1}{L} \int_0^L dx \left( x^2 - \frac{L^2}{4} \right) \left( 1 - \cos \frac{2 n \pi x}{L} \right)
\] (785)

This integral is evaluated with the aid of the equality

\[
\int dx \, x^2 \cos \alpha x = - \frac{\partial^2}{\partial \alpha^2} \int dx \, \cos \alpha x
\]
\[
\begin{align*}
\frac{\partial^2}{\partial \alpha^2} \left( \frac{\sin \alpha x}{\alpha} \right) & = \left( -2 \frac{\sin \alpha x}{\alpha} + 2 \frac{\alpha x}{\alpha} \cos \alpha x + \alpha^2 \frac{x^2}{\alpha^3} \sin \alpha x \right) \\
\end{align*}
\]

(786)

Thus, the mean squared deviation becomes

\[
\Delta x^2 = \frac{L^2}{12} - \frac{L^2}{2 n^2 \pi^2}
\]

(787)

which for large enough \(n\) becomes identical to the classical value. This is another manifestation of the correspondence principle at work. These results correspond to a particle which has an average position half way along the allowed interval, and fluctuates back and forth with excursions proportional to the root mean squared deviation.

The average value of the momentum is given by

\[
\begin{align*}
\overline{p} & = -i \hbar \int_{-\infty}^{\infty} dx \, \Psi_n^*(x) \frac{d}{dx} \Psi_n(x) \\
& = -i \frac{2 \hbar}{L} \int_0^L dx \sin \frac{n \pi x}{L} \frac{d}{dx} \sin \frac{n \pi x}{L} \\
& \quad -i \frac{2 \hbar}{L} \int_0^L dx \sin^2 \frac{n \pi x}{L} \frac{d}{dx} \left[ \Theta(x) - \Theta(x - L) \right] \\
& = -i \frac{2 \pi n \hbar}{L^2} \int_0^L dx \sin \frac{n \pi x}{L} \cos \frac{n \pi x}{L} \\
& \quad -i \frac{2 \hbar}{L} \int_0^L dx \sin^2 \frac{n \pi x}{L} \left[ \delta(x) - \delta(x - L) \right] \\
& = -i \frac{\pi n \hbar}{L^2} \int_0^L dx \sin \frac{2 n \pi x}{L} \\
& = i \frac{\pi n \hbar}{L} \left( \cos \frac{2 n \pi}{L} - 1 \right) \\
& = 0
\end{align*}
\]

(788)

The average value of the momentum of the quantum mechanical particle is zero, like the classical average of \(p\). The root mean squared momentum is just given by

\[
\begin{align*}
\overline{p^2} & = -\hbar^2 \int_{-\infty}^{\infty} dx \, \Psi_n^*(x) \frac{d^2}{dx^2} \Psi_n(x) \\
& = -\frac{2 \hbar^2}{L} \int_0^L dx \sin \frac{n \pi x}{L} \frac{d^2}{dx^2} \sin \frac{n \pi x}{L}
\end{align*}
\]

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\[-2 \frac{\hbar^2}{L} \int_0^L dx \sin \frac{n \pi x}{L} \left( \frac{d}{dx} \sin \frac{n \pi x}{L} \right) \left( \Theta(x) - \Theta(x-L) \right)\]

\[-2 \frac{\hbar^2}{L} \int_0^L dx \sin^2 \frac{n \pi x}{L} \frac{d^2}{dx^2} \left( \Theta(x) - \Theta(x-L) \right)\]

\[= - \frac{2 \hbar^2}{L} \int_0^L dx \sin \frac{n \pi x}{L} \frac{d^2}{dx^2} \sin \frac{n \pi x}{L} \]

\[-2 \frac{\hbar^2}{L} \int_0^L dx \sin \frac{n \pi x}{L} \left( \frac{d}{dx} \sin \frac{n \pi x}{L} \right) \left( \delta(x) - \delta(x-L) \right)\]

\[-2 \frac{\hbar^2}{L} \int_0^L dx \sin^2 \frac{n \pi x}{L} \frac{d}{dx} \left( \delta(x) - \delta(x-L) \right)\]

\[= + \frac{2 \pi^2 n^2 \hbar^2}{L^3} \int_0^L dx \sin \frac{n \pi x}{L} \sin \frac{n \pi x}{L}\]

\[= \frac{\pi^2 n^2 \hbar^2}{L^2} \]  

(789)

In these calculations, the contributions from the discontinuities in the first and second derivatives of the Heaviside step functions vanish identically. Thus, the average momentum is zero just like for the classical particle, and the root mean squared deviation of the momentum is equal to \( p = \frac{\hbar n \pi}{L} \). This is similar to the classical particle, except that the r.m.s. momentum is quantized, that is, it only has discrete values.

The momentum space wave function \( \Phi_n(p) \) is given by

\[ \Phi_n(p) = \frac{1}{\sqrt{2 \pi \hbar}} \int_0^L dx \sqrt{\frac{2}{L}} \sin \frac{n \pi x}{L} \exp \left[ -i \frac{p x}{\hbar} \right] \]  

(790)

which yields

\[ \Phi_n(p) = 2 i \frac{L}{\sqrt{\pi \hbar L}} \frac{n \pi \sin \left( \frac{p L}{2 \hbar} + \frac{n \pi}{2} \right)}{\left( n \pi \right)^2 - \left( \frac{p L}{\hbar} \right)^2} \exp \left[ -i \frac{p L}{\hbar} + \frac{n \pi}{2} \right] \]  

(791)

Hence, the momentum distribution function \( P(p) \) is given by

\[ P(p) = | \Phi_n(p) |^2 \]

\[= \frac{4 L}{\pi \hbar} \left( \frac{n \pi}{2} \right)^2 \sin^2 \left( \frac{p L}{2 \pi} + \frac{n \pi}{2} \right) \]

\[= \frac{4 L}{\pi \hbar} \left[ \left( \frac{n \pi}{2} \right)^2 - \left( \frac{p L}{\pi} \right)^2 \right] \]  

(792)

which is peaked at \( p = \pm \frac{n \pi L}{\hbar} \).
Figure 32: The momentum distribution function $P_n(p) = |\Phi_n(p)|^2$ of a particle in a deep potential well, with $n = 4$.

The uncertainty in the momentum is given by $\Delta p_{rms} = \frac{\hbar n \pi}{L}$ and the uncertainty in the position is

$$\Delta x_{rms} = L \sqrt{\left(\frac{1}{12} - \frac{1}{2} n^2 \frac{\pi^2}{\pi^2}\right)}$$  \hspace{1cm} (793)

The uncertainties satisfy the uncertainty principle,

$$\Delta x_{rms} \Delta p_{rms} \geq \frac{\hbar}{2}$$  \hspace{1cm} (794)

### 4.1.2 Time Dependence of a Particle in a Deep Potential Well

Consider a particle in an initial state given by an arbitrary wave function $\Psi(x; 0)$, which satisfies the boundary conditions $\Psi(0) = \Psi(L) = 0$. Then on decomposing this into energy eigenstates via the expansion

$$\Psi(x; 0) = \sum_n C_n \sqrt{\frac{2}{L}} \sin \frac{n \pi x}{L}$$  \hspace{1cm} (795)
one finds that the expansion coefficients are given by

\[ C_n = \sqrt{\frac{2}{L}} \int_0^L dx \, \sin \frac{n \pi x}{L} \, \Psi(x;0) \]  

(796)

Then, the solution of the Schrödinger equation at time \( t \) is given by the expression

\[ \Psi(x; t) = \sum_n C_n \exp \left[ -i \frac{\hbar}{2m} \frac{n^2}{L^2} t \right] \sqrt{\frac{2}{L}} \sin \frac{n \pi x}{L} \]  

(797)

in which each term has a different time dependence.

### 4.1.3 Exercise 60

Find the time development of the initial wave function \( \Psi(x; 0) = \delta(x - x_0) \), of a particle in a box. Plot the time dependence of the probability density \( P(x; t) \) for finding the particle at position \( x \) at various times. Find the time dependence of the average value of the particle’s position \( \langle x \rangle(t) \).

### 4.1.4 Particle Bound in a Shallow Potential Well

Let us consider the problem of a quantum mechanical particle moving in one dimension, in the presence of a potential given by

\[ V(x) = \begin{cases} -V_0 & \text{if } L > x > 0 \\ 0 & \text{otherwise} \end{cases} \]  

(798)

The energy of our particle is \( E < 0 \).

Classically, the particle would confined by the potential to move in a region of space where \( 0 < x < L \) and the energy of the particle would be restricted by \( 0 > E > -V_0 \). Hence, the classical particle would be confined to the region near the origin.

Inside the interval \( L > x > 0 \), the energy eigenvalue equation takes the form

\[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi_E(x) = \left( E + V_0 \right) \Psi_E(x) \]  

(799)

which corresponds to the motion of a free particle. This equation is satisfied by the form

\[ \Psi_E(x) = A \exp \left[ + i k x \right] + B \exp \left[ - i k x \right] \]  

(800)
with arbitrary $A$ and $B$, and $p = \hbar k = \sqrt{2 m ( E + V_0 )}$. Within this region, the form of the solution appears to correspond to a linear superposition of momentum eigenstates, with momentum $\pm p$.

Outside the interval $L > x > 0$, the particle should satisfy the equation,

$$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi_E(x) = E \Psi_E(x)$$

which corresponds to the motion of a free particle but with negative energy. The kinetic energy instead of being positive must be negative, so this implies that we should consider imaginary values for the momentum. That is, we should try looking for solutions in which the momentum is given by $p = i \hbar \kappa$. In fact the energy eigenvalue equation is satisfied by the general form

$$\Psi_E(x) = C_\alpha \exp \left[ + \kappa x \right] + D_\alpha \exp \left[ - \kappa x \right]$$

where $\hbar \kappa = \sqrt{2 m |E|}$. The coefficients $C_\alpha$ and $D_\alpha$ are arbitrary and have to be separately determined in each region. The form of the solution corresponds to a linear superposition of momentum eigenstates, with imaginary value of the momentum $\pm i \hbar \kappa$. 

Figure 33: A potential well $V(x)$ of width $L$ and depth $-V_0$. The bound state energy $E$ is indicated by a horizontal line.
In the region where \( x > L \) the solution must be of the form of a decreasing exponential

\[
\Psi_E(x) = D_> \exp \left[ -\kappa x \right] \quad \text{for } x > L \tag{803}
\]

The term proportional to the coefficient \( C_> \) has been discarded as the wave function must be square integrable, and since the term proportional to \( C_> \) would diverge when \( x \to \infty \). The above wave function falls to zero at the boundary, \( x \to \infty \).

In the region where \( x < 0 \), the solution must be of the form

\[
\Psi_E(x) = C_< \exp \left[ +\kappa x \right] \quad \text{for } x < 0 \tag{804}
\]

as this tends to zero as \( x \to -\infty \). The term proportional to the coefficient \( D_< \) has been discarded as the wave function must be square integrable.

The above forms of the solution involve four (as yet) unknown constants \( A \), \( B \), \( C \) and \( D \). These constant must be determined by the boundary conditions at \( x = 0 \) and \( x = L \), and the normalization condition. As we shall presently see, the wave function and its derivative must be continuous at each of these points. Thus, there appears to be five conditions and only four unknowns. However, if we also regarded the energy \( E \) as a variable, then the above conditions may restrict the energy to discrete allowed values\(^\text{10}\).

The wave function should be continuous and also the first derivative should be continuous at both the points \( x = 0 \) and \( x = L \). The need for the derivative of the wave function be continuous at these points can be seen by writing the potential as

\[
V(x) = + V_0 \left( \Theta(x - L) - \Theta(x) \right) \tag{805}
\]

and integrating the energy eigenvalue equation over a small interval of width 2\( \epsilon \) around either \( x = L \) or \( x = 0 \). Then

\[
- \frac{\hbar^2}{2m} \frac{\partial}{\partial x} \Psi_E(x) \bigg|_{L-\epsilon}^{L+\epsilon} + \int_{L-\epsilon}^{L+\epsilon} dx \ V(x') \Psi_E(x') = E \int_{L-\epsilon}^{L+\epsilon} dx \ \Psi_E(x') \tag{806}
\]

Since the wave function is continuous, the term proportional to the energy has a magnitude of \( 2E \Psi_E(L) \epsilon \). Also, as we are considering potentials \( V(x) \) which only have finite discontinuities and the wave function is continuous, the term

\[^{10}\text{More precisely, the boundary conditions at } |x| \to \infty \text{ are responsible for quantizing the energy. This can be shown by solving the eigenvalue equation for } \Psi_E(x) \text{ (up to the normalization) for an arbitrary energy. If one enforces one boundary condition (say at } x \to -\infty \text{) and integrates the equation, then the solution will diverge at the other boundary } (x \to +\infty) \text{ unless } E \text{ is restricted to have certain discrete values.}\]
Energy-dependence of trial energy-eigenfunctions
of the attractive square well potential

\[ -0.5 \quad 0 \quad 0.5 \quad 1 \quad 1.5 \quad 2 \]
\[ x/L \]
\[ \Psi_{E}(x) \]
\[ E > E_0 \]
\[ E < E_0 \]
\[ E = E_0 \]

Figure 34: The energy-dependence of trial energy eigenfunctions \( \Psi_E(x) \) for a shallow potential well. The solution is chosen to satisfy the boundary condition at \( x \to -\infty \) and is normalized to unity at \( x = 0 \). It is seen that the solution does not satisfy the boundary condition at \( x \to \infty \) unless \( E = E_0 \). This suggests that the discreteness of the bound state energy is caused by the boundary conditions at infinity.

Involving the integral of the potential has a magnitude of \(-V_0 \epsilon \Psi_E(L)\). In the limit \( \epsilon \to 0 \), one finds

\[
\frac{\partial}{\partial x} \Psi_E(x) \bigg|_{x = L + \epsilon} = \frac{\partial}{\partial x} \Psi_E(x) \bigg|_{x = L - \epsilon}
\] (807)

Thus, the first derivative of the wave function must be continuous at the boundary.

The continuity of the wave function at \( x = L \) yields the condition

\[
\Psi_E(L) = A \exp \left[ + i k L \right] + B \exp \left[ - i k L \right] = D \exp \left[ - \kappa L \right]
\] (808)

and the continuity of the first derivative yields

\[
\frac{\partial}{\partial x} \Psi_E(L) = i k \left( A \exp \left[ + i k L \right] - B \exp \left[ - i k L \right] \right)
\]
The continuity of the wave function at \( x = 0 \) results in the equation

\[
\Psi_E(0) = A + B = C
\]

(810)

and the continuity of the first derivative yields

\[
\frac{\partial}{\partial x} \Psi_E(0) = i k \left( A - B \right) = + \kappa C
\]

(811)

Solving for \( A \) and \( B \) in terms of \( C \), we find

\[
A = \frac{i k + \kappa}{2 i k} C \\
B = \frac{i k - \kappa}{2 i k} C
\]

(812)

The two continuity conditions at \( x = L \) can be used to eliminate \( D \) and yields another equation, involving \( A \) and \( B \)

\[
- \kappa \left( A \exp[i k L] + B \exp[-i k L] \right) = i k \left( A \exp[i k L] - B \exp[-i k L] \right)
\]

(813)

However, since \( A \) and \( B \) have already been determined in terms of \( C \), and since \( C \) can be factored out (the magnitude of \( C \) is determined by the normalization condition), the above condition restricts the possible values of the energy \( E \). Hence, we obtain the secular equation which determines the eigenvalues

\[
\exp[i k L] = \left( \frac{(i k - \kappa)^2}{(i k + \kappa)^2} \right)
\]

(814)

On taking the square root, we can rewrite this as

\[
\exp[i k L] = \pm \left( \frac{(i k - \kappa)^2}{(k^2 + \kappa^2)} \right)
\]

(815)

which can be rewritten as an equation for the ratio of the imaginary and real parts, in which case the \( \pm \) sign drops out

\[
\tan k L = \frac{2 k \kappa}{k^2 - \kappa^2}
\]

(816)
which we shall refer to later on. What we really need to do is to take the fourth root of the equation (814), which yields the two equations

\[
\exp \left[ \frac{i k L}{2} \right] = \pm i \frac{(i k - \kappa)}{\sqrt{(k^2 + \kappa^2)}}
\]

and

\[
\exp \left[ i k L / 2 \right] = \pm \frac{(i k - \kappa)}{\sqrt{(k^2 + \kappa^2)}}
\]

which correspond to the four fourth roots of unity. On taking the ratio of the imaginary to the real parts, these two equations can be re-written as two conditions

\[
k \tan \frac{k L}{2} = + \kappa
\]

\[
k \cot \frac{k L}{2} = - \kappa
\]

The above two conditions determine the bound state energies \(E\) as the wave vector \(k\) and the value \(\kappa\) are related to the energy through

\[
\kappa^2 = - \frac{2m E}{\hbar^2}
\]

\[
k^2 = \frac{2m (E + V_0)}{\hbar^2}
\]

The conditions on \(k\) can be solved graphically for the bound states, by squaring the equation.

For the first condition, as both \(k\) and \(\kappa\) are positive, squaring introduces spurious solutions, corresponding to regions where \(k \tan \frac{k L}{2}\) is negative. We then plot

\[
\kappa^2 = \frac{2m V_0}{\hbar^2} - k^2
\]

as a function of \(k\), on the same graph as the function

\[
k^2 \tan^2 \frac{k L}{2}
\]

For positive \(V_0\) we have a parabola that intersects the \(k\) axis at \(k = \sqrt{\frac{2m V_0}{\hbar^2}}\).

The function \(k^2 \tan^2 \frac{k L}{2}\) is never negative, but falls to zero at \(k = \frac{2n \pi}{L}\) for integer \(n\) and diverges to infinity at \(k = \frac{(2n + 1) \pi}{L}\). Thus, for \(k\) in the range \(0 < k < \sqrt{\frac{2m V_0}{\hbar^2}}\), one has roots near \(k = \frac{(2n + 1) \pi}{L}\). Since \(\tan \frac{k L}{2}\) is negative in each alternate segment \(\frac{2n \pi}{L} < k < \frac{(2n + 1) \pi}{L}\) where the slope of our function is negative, the solution in these regions are spurious. The solutions of our condition corresponds to the intersections of our function with
Figure 35: Graphical solution of the equations determining the bound state energies of the shallow potential well. The \( k \) values where the inverted parabola intersects the curves \( k^2 \tan^2 \frac{kL}{2} \) or \( k^2 \cot^2 \frac{kL}{2} \) represents possible allowed wave vectors \( k \). As explained in the text, there is a maximum of one allowed solution for \( k \) in each interval of \( \frac{\pi}{L} \), as the second solution is spurious.

Let us note that for large enough \( V_0 \) the bound states correspond to the set of \( k \) values given by

\[
k \approx \frac{n \pi}{L}
\]

if the values of \( k \) are sufficiently small and are limited by

\[
\frac{\hbar^2 k^2}{2m} \ll V_0
\]
In this case, the eigenvalues are related to the eigenvalues of the infinite potential well.

Since the values of \( k \) are found to be discrete, the energy eigenvalues are also discrete. The allowed values of \( E \) are found to be in the range \( 0 \geq E \geq -V_0 \). The only remaining undetermined constant is the value of \( C \) which can be found by normalizing the wave function.

![Bound state wave functions for a shallow potential well](image)

Figure 36: Bound state wave functions \( \Psi_n(x) \) for a shallow potential well.

4.1.5 Exercise 61

A particle of mass \( m \) is confined to move in a one-dimensional potential \( V(x) \) where

\[
V(x) \rightarrow \infty \quad x < 0 \\
V(x) = -V_0 \quad 0 < x < a \\
V(x) = 0 \quad a < x
\]

Derive the equation for the bound state energy. Find the minimum value of \( V_0 \) which will produce a bound state.
Figure 37: A one-dimensional potential $V(x)$, which excludes the particle from the region $x < 0$. The minimum value of the potential is $-V_0$. The potential $V_0$ has to exceed a minimum value if the particle is to be bound.

4.1.6 Solution 61

The bound state wave function is given by

$$\Psi(x) = 0 \quad \text{for } x < 0$$

where $V(x) \to \infty$. In the region of positive $x$, the energy eigenvalue equation is given by

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V_0 \Psi(x) = E \Psi(x) \quad (826)$$

inside the potential well where $a > x > 0$, and

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = E \Psi(x) \quad (827)$$

outside the potential well where $x > a$. This has the solution

$$\Psi(x) = A \exp \left[ + i k x \right] + B \exp \left[ - i k x \right] \quad (828)$$
Figure 38: The form of the bound state wave function, for a value of the potential $V_0$ which is just sufficiently strong enough to create one bound state.

where the energy eigenvalue is given by

$$E = - V_0 + \frac{\hbar^2}{2m} k^2$$  \hspace{1cm} (829)

Since the wave function has to be continuous at $x = 0$, one has

$$A + B = 0$$  \hspace{1cm} (830)

Thus, the solution inside the well is of the form

$$\Psi(x) = 2i A \sin k x$$  \hspace{1cm} (831)

Outside the potential well, the eigenvalue equation has the solution of the form

$$\Psi(x) = C \exp\left[-\kappa x\right] + D \exp\left[+\kappa x\right]$$  \hspace{1cm} (832)

However, as the wave function must vanish as $x \to \infty$ then one has $D = 0$. Thus, the wave function for $x > a$ is simply given by

$$\Psi(x) = C \exp\left[-\kappa x\right]$$  \hspace{1cm} (833)
and the energy eigenvalue is given by

\[ E = -\frac{\hbar^2}{2m} \kappa^2 \]  

(834)

Continuity at \( x = a \) yields

\[ 2i A \sin ka = C \exp \left[ -\kappa a \right] \]  

(835)

and continuity of the derivative yields

\[ 2i k A \cos ka = -\kappa C \exp \left[ -\kappa a \right] \]  

(836)

Hence on dividing the above equations, one has

\[ k \cot ka = -\kappa \]  

(837)

On squaring this equation, one has

\[ k^2 \cot^2 ka = \frac{2mV_0}{\hbar^2} - k^2 \]  

(838)

or

\[ k^2 = \frac{2mV_0}{\hbar^2} \sin^2 ka \]  

(839)

Thus,

\[ \frac{2m(V_0 + E)}{\hbar^2} = \frac{2mV_0}{\hbar^2} \sin^2 ka \]  

(840)

If a bound state is just formed, it has the maximum bound state energy which is zero, \( E = 0 \). Hence, in this case, the above equation simplifies to

\[ 1 = \sin^2 ka \]  

(841)

Thus, the minimum value of \( k \) is found as

\[ k = \frac{\pi}{2a} \]  

(842)

and since \( E = 0 \), one has

\[ 0 = -V_0 + \frac{\hbar^2}{2m} \frac{\pi^2}{4a^2} \]  

(843)

Hence, the minimum value of \( V_0 \) needed to produce a bound state is given by

\[ V_0 = \frac{\hbar^2 \pi^2}{8ma^2} \]  

(844)

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Alternatively, the result can be derived from the condition that the kinetic energy inside the well and outside the well must be minimized. The wave function inside the well is oscillatory, but must have the minimum number of oscillations. The wave function outside the well must decay slowly, therefore, the decay constant for the wave function for \( x > a \) is given by \( \kappa = 0 \). Thus, the matching condition for the derivative of the wave function shows that the slope must be zero at the edge of the potential well \( x = a \) and, since \( E = 0 \). Since the wave function has a maximum at \( x = a \), one has

\[
k \cos k a = 0
\]

from which one has \( k = \frac{\pi}{2a} \). Hence, as

\[
E = -\frac{\hbar^2}{2m} \kappa^2 \\
= -V_0 + \frac{\hbar^2}{2m} k^2
\]

the minimum value of the potential needed to produce a bound state is given by

\[
V_0 = \frac{\hbar^2 \pi^2}{8m a^2}
\]

4.1.7 Scattering from a Shallow Potential Well

The shallow potential well is described by

\[
V(x) = -V_0 \quad \text{for} \quad 0 < x < L \\
V(x) = 0 \quad \text{otherwise}
\]

Classically, the energy \( E = 0 \) separates the bound states, which have \( E < 0 \), and the scattering states, which have \( E > 0 \). We shall now consider states where the energy \( E \) is greater than zero so that the particle may travel to infinity.

The allowable forms for the wave function in the three regions are

\[
\Psi(x) = A \exp\left[ + i k x \right] + B \exp\left[ - i k x \right] \quad 0 > x \\
\Psi(x) = C \exp\left[ + i k' x \right] + D \exp\left[ - i k' x \right] \quad L > x > 0 \\
\Psi(x) = F \exp\left[ + i k x \right] + G \exp\left[ - i k x \right] \quad x > L
\]

(849)
Figure 39: Scattering from a shallow potential well \( V(x) \) of depth \(-V_0\). The energy of the scattering states \( E \) is \( > 0 \), so classically the particle is free to move to infinity.

where the energy eigenvalue is given by \( E = \frac{\hbar^2 k^2}{2m} \) and \( E + V_0 = \frac{\hbar^2 k'^2}{2m} \). However, as we only have four matching conditions, the six coefficients are not determined, and \( k \) is a continuous real variable. We can choose one coefficient to set the normalization of the wave function. The other coefficient can be chosen as desired. We shall choose the coefficient \( G \) to be zero. This represents a beam of particles being produced at \( x \rightarrow -\infty \) with momentum \( p \) falling incident on the potential at \( x = 0 \). Some fraction of the beam is reflected back towards \( x \rightarrow -\infty \), with momentum \(-p\) and a certain fraction being transmitted to \( x \rightarrow +\infty \) with momentum \( p \). The vanishing of \( G \) corresponds to the absence of a source of particles, with momentum \(-p\), at \( x \rightarrow \infty \).

The matching conditions at \( x = 0 \) yield

\[
A + B = C + D \\
k ( A - B ) = k' ( C - D )
\]

(850)

The matching conditions at \( x = L \) are given by

\[
C \exp \left[ + i k' L \right] + D \exp \left[ - i k' L \right] = F \exp \left[ + i k L \right]
\]
\[ k' \left( C \exp \left[ + i k' L \right] - D \exp \left[ - i k' L \right] \right) = k F \exp \left[ + i k L \right] \] (851)

This pair of equations can be solved for \( C \) and \( D \) in terms of the amplitude of the transmitted beam \( F \),

\[
\begin{align*}
C \exp \left[ + i k' L \right] &= \left( \frac{k' + k}{2 k'} \right) F \exp \left[ i k L \right] \\
D \exp \left[ - i k' L \right] &= \left( \frac{k' - k}{2 k'} \right) F \exp \left[ i k L \right] 
\end{align*}
\] (852)

whereas the amplitudes of the incident beam \( A \) and reflected beam \( B \) are given by

\[
\begin{align*}
A &= \left( \frac{k + k'}{2 k} \right) C + \left( \frac{k - k'}{2 k} \right) D \\
B &= \left( \frac{k - k'}{2 k} \right) C + \left( \frac{k + k'}{2 k} \right) D 
\end{align*}
\] (853)

Thus, we find

\[
\begin{align*}
A \exp \left[ - i k L \right] &= \left( \frac{2 k' k \cos k' L - i \left( k^2 + k'^2 \right) \sin k' L}{2 k k'} \right) F \\
B \exp \left[ - i k L \right] &= \left( \frac{\left( k'^2 - k^2 \right) i \sin k' L}{2 k k'} \right) F
\end{align*}
\] (854)

The amplitude of the incident beam is assumed to be known, as it can be controlled by the particle accelerator. Thus, we shall express the amplitudes of the transmitted and reflected beams as ratios with respect to the incident beam. The ratio of the transmitted beam to the incident beam is given by

\[
\frac{F}{A} = \left( \frac{2 k' k \exp \left[ - i k L \right]}{2 k k' \cos k' L - i \left( k^2 + k'^2 \right) \sin k' L} \right) 
\] (855)

The ratio of the amplitudes of the reflected beam to the incident beam is given by

\[
\frac{B}{A} = \left( \frac{\left( k'^2 - k^2 \right) i \sin k' L}{2 k k' \cos k' L - i \left( k^2 + k'^2 \right) \sin k' L} \right) 
\] (856)

The amplitude of the reflected beam is proportional to \( k'^2 - k^2 \) and thus, is proportional to \( V_0 \), and the denominator varies as \( E \) for large \( E \). The denominator is non-zero when both \( k \) and \( k' \) are real. This is because the magnitude

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of the denominator is given by the sum of two squares
\[ 4 k^2 k'^2 \cos^2 k'L + (k^2 + k'^2)^2 \sin^2 k'L \] (857)
and when the sine factor is zero, the cosine factor is positive. Thus, there are
no simultaneous zeros.

In the above expressions \( k \) and \( k' \) are continuous variables and so the energy
eigenvalues have a continuous spectrum in the range \( E \geq 0 \).

The intensities of the reflected and transmitted beams add to equal the
intensity of the incident beam,
\[ |A|^2 = |B|^2 + |F|^2 \] (858)
This is a necessary condition for the probability to be conserved. As the proba-
bility does not build up with time at any point in space, but is in a steady state,
the probability currents entering any region of space must be equal to those
leaving. As the magnitude of the velocities outside the potential well are simply
given by \( \frac{\hbar}{m} k \), the equality of incoming flux with the outgoing flux reduces to
the above statement about the intensities of the beams.

The reflection coefficient is defined as the ratio
\[ R = \frac{|B|^2}{|A|^2} \] (859)
which takes into account that the magnitude of the velocity of the incident
beam is always the same as that of the reflected beam, as they are moving in
the same region of space, and thus experience the same potential. The reflection
coefficient is given by
\[ R(k) = \left( \frac{(k'^2 - k^2)^2 \sin^2 k'L}{4 k^2 k'^2 \cos^2 k'L + (k^2 + k'^2)^2 \sin^2 k'L} \right) \] (860)
We see that the reflection coefficient has a numerator proportional to \( V_0^2 \), and
the denominator grows like \( E^2 \) for sufficiently large \( E \). It should be noted that,
in this case, quantum mechanics produces results which are completely different
from classical mechanics as, in one dimension, a classical particle is not reflected
by an attractive potential well.

The transmission coefficient is defined as the ratio
\[ T = \frac{k_t |F|^2}{k_i |A|^2} \] (861)
in which \( k_t \) is the magnitude of the wave vector of the transmitted beam
\( F \exp[ i k_t x] \) and \( k_i \) is the magnitude of the wave vector for the incident
Reflection Coefficient for a beam of particles incident on a shallow potential well

Figure 40: The reflection coefficient $R(k)$ for a beam of particles of momentum $\hbar k$ incident on a shallow potential well of depth $-V_0$ and width $L$. Note that, due to the Ramsauer effect, the reflection coefficient falls to zero periodically.

In our examples $k_i$ and $k_t$ have the same value and, therefore, cancel. In the more general case, the velocities have to be included, and then the reflection and transmission coefficients will satisfy the equation,

$$ R + T = 1 \quad \text{(862)} $$

In the above example, the transmission coefficient is evaluated as

$$ T(k) = \left( \frac{4}{4 k^2 k'^2 \cos^2 k' L + (k^2 + k'^2)^2 \sin^2 k' L} \right) \quad \text{(863)} $$

It is seen that the beam is totally transmitted whenever $\sin k' L = 0$. The transmission coefficient shows oscillations with increasing $k'$. The minimum in the reflection coefficient and the corresponding maximum in the transmission coefficient is known as the Ramsauer effect\(^{11}\). It is seen in the scattering of low-energy electrons from inert gas atoms.

\(^{11}\) C. Ramsauer, Ann. Phys. (Leipzig) 64, 546 (1921).
4.1.8 Exercise 62

Consider a particle of mass $m$ moving in one dimension in a potential given by

\[
V(x) = \begin{cases} 
0 & \text{if } x < 0 \\
-V_0 & \text{if } x > 0 
\end{cases} 
\]  

(864)

Consider the energy eigenstate which corresponds to a beam of particles of momentum $-p$ incident on the potential step from $x \to \infty$, find the amplitude of the reflected and transmitted waves, for $E > 0$. Also find the reflection and transmission coefficients and show that they add up to unity.

4.1.9 Solution 62

The incident beam is in the region $x > 0$ and is represented by the wave travelling along the negative $x$ direction

\[
A \exp \left[ -i k' x \right] 
\]  

(865)

In addition, for positive $x$, one expects a reflected wave of amplitude $B$ that travels along the positive $x$ direction. The form of the solution for $x > 0$ is given by

\[
\Psi(x) = A \exp \left[ -i k' x \right] + B \exp \left[ +i k' x \right] 
\]  

(866)

On substituting the trial form of the solution in the energy eigenvalue equation for $x > 0$

\[
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) - V_0 \Psi(x) = E \Psi(x) 
\]  

(867)

where we have used $V(x) = -V_0$ for $x > 0$, one obtains a relation between the energy eigenvalue and $k'$,

\[
\frac{\hbar^2}{2m} k'^2 - V_0 = E 
\]  

(868)

The solution for $x < 0$ corresponds to the transmitted beam

\[
\Psi(x) = C \exp \left[ -i k x \right] 
\]  

(869)
which on substituting into the energy eigenvalue equation
\[- \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) = E \Psi(x) \]  
leads to
\[\frac{\hbar^2}{2m} k^2 = E \]  

The matching conditions at \(x = 0\) yield
\[C = A + B \]  
\[kC = k' (A - B) \]  
These can be solved to yield the amplitude of the reflected and transmitted waves
\[\frac{B}{A} = \left( \frac{k' - k}{k' + k} \right) \]  
\[\frac{C}{A} = \left( \frac{2k'}{k' + k} \right) \]  
as ratios to the amplitude of the incident wave. The transmission coefficient, \(T\), is given by
\[T = \left( \frac{k}{k'} \right) \left| \frac{C}{A} \right|^2 \]  
where the factor \(k / k'\) represents the change in the flux of particles due to the difference in the velocities of the transmitted incident beam. The reflection coefficient \(R\) is given by
\[R = \left( \frac{B}{A} \right)^2 \]  
\[= \left( \frac{k' - k}{k + k'} \right)^2 \]  

Hence, we find that reflection and transmission coefficients add
\[R + T = \left( \frac{k' - k}{k + k'} \right)^2 + \left( \frac{4k k'}{(k + k')^2} \right) \]  
\[= \left( \frac{k + k'}{(k + k')} \right)^2 \]  
\[= 1 \]
to yield unity.

4.1.10 Exercise 63

By considering the solution of the Schrödinger equation with the initial state described by the energy eigenstate found in the previous example, show that the system is in a steady state. Find the probability current density in the two regions, and show that it satisfies the continuity condition, when $E > 0$. Also, show that the continuity condition is satisfied in the two regions when $E < 0$.

4.1.11 Solution 63

The probability density $\rho(x, t)$ for finding a particle in the region $x > 0$ is given by

$$
\rho(x, t) = | \Psi(x, t) |^2 = \left| A \exp \left[ -i k' x \right] + B \exp \left[ +i k' x \right] \right|^2 \exp \left[ -i \frac{\hbar}{\hbar} E t \right] \\
= | A |^2 + | B |^2 + A B^* \exp \left[ -2 i k' x \right] + A^* B \exp \left[ +2 i k' x \right] \\
= | A |^2 \left[ 2 \left( \frac{k^2 + k'^2}{(k + k')^2} \right) + 2 \left( \frac{k' - k}{k' + k} \right) \cos 2 k' x \right] \quad (877)
$$

which is time independent, but exhibits oscillations due to the interference between the incident and reflected wave. The probability density $\rho(x, t)$ for finding a particle in the region $x < 0$ is given by

$$
\rho(x, t) = | \Psi(x, t) |^2 = \left| C \exp \left[ -i k' x \right] \exp \left[ -i \frac{\hbar}{\hbar} E t \right] \right|^2 \\
= | C |^2 \\
= | A |^2 \frac{4 k'^2}{(k + k')^2} \quad (878)
$$

which is spatially uniform and time independent.
The probability current density $j_x(x, t)$ is given by

$$j_x(x, t) = \text{Real} \left[ \Psi^*(x, t) \left( - \frac{i \hbar}{m} \frac{\partial}{\partial x} \right) \Psi(x, t) \right] \quad (879)$$

For $x > 0$, one finds the

$$j_x(x, t) = \text{Real} \left[ - \frac{\hbar}{m} k' \left( |A|^2 - |B|^2 \right) \right]$$

$$+ \text{Real} \left[ - \frac{\hbar}{m} \left( A B^* \exp \left[ - 2 i k' x \right] - B A^* \exp \left[ + 2 i k' x \right] \right) \right]$$

$$= \text{Real} \left[ - \frac{\hbar}{m} k' \left( |A|^2 - |B|^2 \right) \right] \quad (880)$$

as the last term is purely imaginary. This represents the net flux along the positive direction, which is the difference between the transmitted flux and the incident flux. Note that the ratio of these two fluxes is (apart from a sign) just the reflection coefficient $R$. The total probability current density for $x > 0$ is evaluated as

$$j_x(x, t) = - \frac{\hbar}{m} k' \left( \frac{4 k k'}{(k + k')^2} \right) |A|^2 \quad (881)$$

For $x < 0$, one finds

$$j_x(x, t) = - \frac{\hbar}{m} k \left( \frac{4 k'^2}{(k + k')^2} \right) |A|^2 \quad (882)$$

On evaluating the probability current density for $x < 0$, one finds that the current density is time independent and spatially uniform. The current density has a value of

$$j_x(x, t) = - \frac{\hbar}{m} k \left( \frac{4 k'^2}{(k + k')^2} \right) |A|^2 \quad (883)$$

Note that this just represents the flux corresponding to the transmitted beam. The ratio of the transmitted flux to the incident flux is just the transmission coefficient $T$.

Since, the probability current density has the same value for $x > 0$ and $x < 0$ it is independent of $x$. The probability density is also independent of $t$. Thus, the continuity condition

$$\frac{\partial \rho(x, t)}{\partial t} + \frac{\partial j_x(x, t)}{\partial x} = 0 \quad (884)$$
is trivially satisfied.

4.1.12 The Threshold Energy for a Bound State

We have examined the shallow potential well and found energy eigenstates in the energy regions, $E > 0$, which corresponded to scattering states with continuous energy, and the energy region $0 > E > -V_0$ which had bound states with discrete energy eigenvalues. This raises the question as to whether there are any states with energy $E$ less than $-V_0$. Classically, it is impossible to have states with an energy lower than the minimum of the potential energy as the only other contribution to the total energy, apart from the potential, is the kinetic energy which is positive definite. We shall now prove that it is impossible to have quantum states with energy eigenvalues that are lower than the minimum value of the potential.

If a bound state exists, then $|\Psi(x)|^2$ must decay exponentially as $|x| \to \infty$ in order that the wave function be normalized. This means that $|\Psi(x)|^2$ must have at least one maximum. This means that

$$\frac{\partial}{\partial x} |\Psi(x)|^2 = 0 \quad (885)$$

and

$$\frac{\partial^2}{\partial x^2} |\Psi(x)|^2 < 0 \quad (886)$$

at the value of $x = x_0$ where the maximum is located.

We shall start with the energy eigenvalue equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + \left(V(x) - E\right) \Psi = 0 \quad (887)$$

and pre-multiply by the complex conjugate wave function $\Psi^*$ and add this to the complex conjugate of the energy eigenvalue equation post-multiplied by $\Psi$. The result is

$$-\frac{\hbar^2}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} + \Psi \frac{\partial^2 \Psi^*}{\partial x^2}\right) + 2 \left(V(x) - E\right) |\Psi|^2 = 0 \quad (888)$$

We can re-write the above equation as

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} |\Psi|^2\right) + 2 \left(V(x) - E\right) |\Psi|^2 = -\frac{\hbar^2}{m} \left|\frac{\partial \Psi}{\partial x}\right|^2 \quad (889)$$

This must hold at all values of $x$, including $x_0$. But at the maximum we have

$$\frac{\partial}{\partial x} |\Psi(x_0)| = 0 \quad (890)$$
and
\[ \frac{\partial^2}{\partial x^2} |\Psi(x_0)|^2 < 0 \] (891)

Hence, we find that the equality
\[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} |\Psi(x_0)|^2 \right) = 2 \left( E - V(x_0) \right) |\Psi(x_0)|^2 \] (892)
holds at \( x_0 \). Since the first term is positive, the second term must also be positive. Furthermore, as \( |\Psi(x_0)|^2 \geq 0 \), we must have
\[ E \geq V(x_0) \] (893)

By definition, \( V(x_0) \) is greater than or equal to the minimum value of \( V(x) \). Therefore, the bound state energy \( E \) must be greater than or equal to the minimum value of the potential.

4.1.13 Transmission through a Potential Barrier

Let us now consider a particle with energy \( E > 0 \) moving in a potential which now has the form
\[ V(x) = +V_0 \quad \text{if} \quad L > x > 0 \]
\[ V(x) = 0 \quad \text{otherwise} \] (894)

We shall consider states in the energy range where \( V_0 > E > 0 \). In this energy range, a classical particle would be forbidden to exist in the region \( L > x > 0 \) but could be found in the other regions of space.

A specific form of the solution of the Schrödinger equation can be written as
\[ \Psi(x) = A \exp \left[ +i k x \right] + B \exp \left[ -i k x \right] \quad x < 0 \]
\[ \Psi(x) = C \exp \left[ +\kappa x \right] + D \exp \left[ -\kappa x \right] \quad L > x > 0 \]
\[ \Psi(x) = F \exp \left[ +i k x \right] \quad x > L \] (895)

where \( k \) is related to the energy eigenvalue \( E \) via
\[ k^2 = +\frac{2mE}{\hbar^2} \]
\[ \kappa^2 = \frac{2m(V_0 - E)}{\hbar^2} \] (896)

This form is appropriate to the case where a beam of particles of momentum \( p = \hbar k \) is incident from \( x \to -\infty \) onto the potential barrier. A portion of
Figure 41: A potential \( V(x) \) with a barrier of height \( V_0 \) and width \( L \).

The beam will be reflected back to \( x \to -\infty \) and a portion will be transmitted to \( x \to \infty \). The continuity condition at \( x = 0 \) can be solved to yield

\[
A = \left( \frac{\kappa + i \frac{k}{2}}{\frac{2 i \kappa}{k}} \right) C + \left( -\frac{\kappa + i \frac{k}{2}}{\frac{2 i \kappa}{k}} \right) D \\
B = \left( \frac{-\kappa + i \frac{k}{2}}{\frac{2 i \kappa}{k}} \right) C + \left( +\frac{\kappa + i \frac{k}{2}}{\frac{2 i \kappa}{k}} \right) D
\] (897)

The continuity condition at \( x = L \) yields \( C \) and \( D \) in terms of \( F \). This leads to

\[
C = \left( \frac{\kappa + i \frac{k}{2}}{\frac{2 i \kappa}{k}} \right) F \exp \left[ i \frac{k}{k} L \right] \exp \left[ -\kappa L \right] \\
D = \left( \frac{\kappa - i \frac{k}{2}}{\frac{2 i \kappa}{k}} \right) F \exp \left[ i \frac{k}{k} L \right] \exp \left[ +\kappa L \right]
\] (898)

On substituting the expressions for \( C \) and \( D \) into the previous expressions for \( A \) and \( B \), one obtains

\[
A = \frac{\exp \left[ i k L \right]}{4 i \kappa \frac{k}{k}} \left( 4 i \frac{k}{k} \kappa \cosh \kappa L + 2 \left( k^2 - \kappa^2 \right) \sinh \kappa L \right) F
\]
The ratio of the amplitude of the transmitted wave to the incident wave is \( F / A \) which is found as

\[
\frac{F}{A} = \frac{4 i k \kappa \exp \left[-i kL\right]}{4 i k \kappa \cosh \kappa L + 2 (k^2 - \kappa^2) \sinh \kappa L}
\]

(899)

whereas the ratio of the amplitude of the reflected wave to the incident wave is \( B / A \) where

\[
\frac{B}{A} = \frac{2 (k^2 + \kappa^2) \sinh \kappa L}{4 i k \kappa \cosh \kappa L + 2 (k^2 - \kappa^2) \sinh \kappa L}
\]

(900)

These expressions are obviously related to the amplitudes for reflection from and transmission through a shallow potential well, via the analytic continuation

\[ k' \to i \kappa \]

(902)

The transmission coefficient \( T(k) \) is evaluated as

\[
T(k) = \left| \frac{F}{A} \right|^2 = \frac{4 k^2 \kappa^2}{4 k^2 \kappa^2 \cosh^2 \kappa L + (k^2 - \kappa^2)^2 \sinh^2 \kappa L}
\]

(903)

For large \( \kappa L \), we have \( \cosh \kappa L \simeq \frac{1}{2} \exp \left[\kappa L\right] \) and \( \sinh \kappa L \simeq \frac{1}{2} \exp \left[\kappa L\right] \). Thus, we find that transmission coefficient decreases exponentially with increasing \( L \). The amplitude of the transmitted wave is exponentially suppressed, and the leading exponential term is

\[
\frac{F}{A} \approx \frac{4 i k \kappa}{(k + i \kappa)^2} \exp \left[-\kappa L\right] \exp \left[-i k L\right]
\]

(904)

The phenomenon in which particles are transmitted through a potential barrier (known as quantum tunnelling) is due to the exponentially small probability of finding the particles in the region of space where they are classically forbidden to exist due to energetic reasons. In the classically forbidden regions, the classical
Transmission through a potential barrier

Figure 42: Transmission Through a Potential Barrier. The real part of the wave function $\Phi_k(x)$ is plotted as a function of $x$. A beam of particles is emitted from a source located at $x \rightarrow -\infty$ and falls incident on the potential barrier. The barrier extends from $x = 0$ up to $x = a$, and its extremities are marked by the red vertical lines. The height of the barrier $V_0$ is greater than the kinetic energy $E$ of the incident particles, and hence is impenetrable to a beam of classical particles of energy $E$. Most of the incident beam is reflected from the potential barrier. The remaining part of the beam tunnels through the potential barrier and is transmitted to infinity. Therefore, some of the particles quantum mechanically tunnel through the classically forbidden region.

The kinetic energy would have to be negative. In the limit of large $\kappa L$, within the approximation of leading exponential terms, the reflected wave has a relative amplitude of unity

$$\frac{B}{A} \approx \frac{(k^2 + \kappa^2)}{(k + i\kappa)^2}$$

as is needed if the probability current is to satisfy the continuity equation.

4.1.14 Exercise 64

Construct the probability current density in the three regions and show that the continuity equations is satisfied in each region, including the region where
Figure 43: The transmission coefficient $T(k)$ of a beam of particles, of wave vector $k$, incident on a potential barrier of height $V_0$. For energies in the range $V_0 > E > 0$, where a beam of classical particles would be totally reflected, the quantum mechanical particles have an exponentially small probability of being transmitted.

tunnelling occurs.

4.1.15 Solution 64

Since the states are energy eigenstates, the probability density is time independent. For $x < 0$, the probability density

$$
\rho(x,t) = |A|^2 + |B|^2 + \left( A B^* \exp \left[ i \frac{2}{k} x \right] + B A^* \exp \left[ - i \frac{2}{k} x \right] \right)
$$

(906)

is oscillatory. For $L > x > 0$, the probability density is also non-uniform

$$
\rho(x,t) = |C|^2 \exp \left[ + 2 \kappa x \right] + |D|^2 \exp \left[ - 2 \kappa x \right] + \left( C D^* + D C^* \right)
$$

(907)
For $x > L$, the probability density is spatially uniform
\[ \rho(x, t) = |F|^2 \] (908)

The probability current density $j_x(x, t)$ in the region $x < 0$ is given by
\[ j_x(x, t) = \frac{\hbar k}{m} \left( |A|^2 - |B|^2 \right) \] (909)

In the barrier region, the probability current density is given by
\[ j_x(x, t) = -i \frac{\hbar k}{m} \left( C D^* - C^* D \right) \] (910)

for $L > x > 0$. This quantity is only finite if the coefficients $C$ and $D$ are complex. Since the coefficients are determined via the matching conditions, the probability current density is only finite if the wave function shows periodic oscillations in some regions of space. In the last region, the probability current density is also spatially uniform
\[ j_x(x, t) = \frac{\hbar k}{m} |F|^2 \] (911)

for $x > L$.

On evaluating the probability current density, it is found to be given by
\[ j_x(x, t) = \frac{\hbar k}{m} \frac{4 k^2 \kappa^2}{4 k^2 \kappa^2 \cosh^2 \kappa L + (k^2 - \kappa^2)^2 \sinh^2 \kappa L} |A|^2 \] (912)

and is uniform throughout space. Since the probability current density is constant and the probability density is time independent, the continuity equation
\[ \frac{\partial \rho}{\partial t} + \frac{\partial j_x}{\partial x} = 0 \] (913)

is trivially satisfied.

### 4.1.16 The Double Well Potential

Consider a particle of mass $m$ moving in one dimension in the presence of a double well potential
\[
\begin{align*}
V(x) &= \infty \quad \text{for } |x| > (a + b) \\
V(x) &= 0 \quad \text{for } (a + b) > |x| > (b - a) \\
V(x) &= V_0 \quad \text{otherwise}
\end{align*}
\] (914)
The potential $V(x)$ is a symmetric function of $x$. The parity operator $\hat{P}$ is defined as the operator which, when acting on an arbitrary function $\psi(x)$, has the effect

$$\hat{P} \psi(x) = \psi(-x) \quad (915)$$

On applying the parity operator twice, it is seen that it satisfies the relation

$$\hat{P}^2 = \hat{I} \quad (916)$$

The eigenfunctions $\phi_p(x)$ of the parity operator satisfy the equations

$$\hat{P} \phi_p(x) = p \phi_p(x) \quad (917)$$

where $p$ is the parity eigenvalue. Because of the relation expressed by eqn(916), the eigenvalues of the parity operator are restricted to have values $\pm 1$. Since the potential is an even function of $x$, the Hamiltonian commutes with the parity operator

$$[\hat{P}, \hat{H}] = 0 \quad (918)$$

so that the parity is a conserved quantity. In other words, parity is a constant of motion. Since the Hamiltonian commutes with the parity operator, one can find simultaneous eigenstates of $\hat{H}$ and $\hat{P}$. We shall seek such solutions for which $E < V_0$. In this case, classical particles are excluded from traversing the region containing the potential barrier.
The even parity eigenfunctions can be expressed in the form
\[
\phi(x) = \begin{cases} 
A \sin k (x - a - b) & \text{for} \ (a + b) > x > (b - a) \\
B \cosh \kappa x & \text{for} \ (b - a) > |x|
\end{cases}
\] (919)
where the energy eigenvalue is related to \(k\) and \(\kappa\) via
\[
E = \frac{\hbar^2 k^2}{2m} = V_0 - \frac{\hbar^2 \kappa^2}{2m}
\] (920)
Since \(\phi(x)\) is an even parity eigenfunction \(\phi(-x) = \phi(x)\), the form of the solution for \(-(b - a) > x > -(b + a)\) is given by
\[
\phi(x) = -A \sin k (x + a + b) \quad \text{for} \ -(b - a) > x > -(b + a)
\] (921)

The above form of the solution \(\phi(x)\) identically satisfies the boundary conditions at the hard walls \(x = \pm (b + a)\). The remaining matching conditions at \(x = \pm (b - a)\) lead to the self-consistency equation
\[
k \cot 2ka = -\kappa \tanh \kappa (b - a)
\] (922)
This equation together with the relation
\[
k^2 + \kappa^2 = \frac{2mV_0}{\hbar^2}
\] (923)
can be solved graphically. The solutions determine the quantized values of \(k\).

The odd parity eigenfunctions can be expressed as
\[
\phi(x) = \begin{cases} 
A \sin k (x - a - b) & \text{for} \ (a + b) > x > (b - a) \\
B \sinh \kappa x & \text{for} \ (b - a) > |x|
\end{cases}
\] (924)
The form of the solution for negative values of \(x\) can be obtained from those of positive values of \(x\) by noting that they have odd parity \(\phi(-x) = -\phi(x)\). If the above forms of \(\phi(x)\) are to satisfy the differential equation, the energy eigenvalue must be related to \(k\) and \(\kappa\) via eqn(920). The above form of the solution \(\phi(x)\) automatically satisfies the boundary conditions at the hard walls \(x = \pm (b + a)\). The matching conditions for the odd parity eigenfunctions at \(x = \pm (b - a)\) lead to the equation
\[
k \cot 2ka = -\kappa \coth \kappa (b - a)
\] (925)
The quantized values of \(k\) are given by the solutions of the above self-consistency equation.
Consistency conditions

![Graphical solution of the self consistency conditions for the double potential well. The right hand side for odd parity solutions is shown by the dashed line, the right hand side for even parity solutions is shown by the solid line.](image)

Figure 45: The graphical solution of the self consistency conditions for the double potential well. The right hand side for odd parity solutions is shown by the dashed line, the right hand side for even parity solutions is shown by the solid line.

Graphical solution of the even and odd parity self consistency equations shows that, for large barrier heights or large barrier widths such that

\[
tanh \kappa (b - a) \sim 1
\]

(926)

the eigenvalues occur in pairs which are almost degenerate. The pairs of energies have magnitudes which are close to the bound state energies of the isolated wells, so

\[
k \cot 2ka \sim -\kappa
\]

(927)

The splitting \( \Delta E \) between the lowest pairs of eigenvalues is exponentially small, and is approximated by

\[
\Delta E \sim \frac{\hbar^2 \pi^2}{2m a^2} \frac{2}{\kappa a} \exp \left[ -2\kappa (b - a) \right]
\]

(928)

The tunnel splitting between the pairs of energy levels increases for the higher energy levels.
4.1.17 The delta function Potential

Let us consider a beam of particles of mass \( m \) and momentum \( \hbar k \) scattering from an attractive potential \( V(x) \) localized at the origin

\[
V(x) = -V_0 a \delta(x)
\]  

(929)

where \( V_0 a \) is a measure of the strength of the potential. In the strength, \( V_0 \) has units of potential and \( a \) has units of length.

The energy eigenvalue equation becomes

\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - V_0 a \delta(x) \right] \phi_k(x) = E \phi_k(x)
\]  

(930)

We shall look for a solution which is of the form

\[
\phi_k(x) = A \exp \left[ +i k x \right] + B \exp \left[ -i k x \right]
\]  

(931)

in the region \( 0 > x \) and has the form

\[
\phi_k(x) = F \exp \left[ +i k x \right]
\]  

(932)
Delta function potential

\[ V(x) = -V_0 a \delta(x) \]

Figure 47: The attractive delta function potential. The bound state energy is shown by a horizontal dashed line.

for \( x > 0 \). These forms satisfy the energy eigenvalue equation in these two regions if

\[ E = \frac{\hbar^2 k^2}{2m} \]

since, the potential vanishes identically in these two separate regions. Again, the form is appropriate for discussion of the scattering of a beam of particles with energy \( E > 0 \) and momentum \( \hbar k \) incident on the potential from \( x \to -\infty \).

The matching conditions at \( x = 0 \) are affected by the presence of the non-zero potential. The continuity of the wave function yields

\[ A + B = F \]

The discontinuity in the first derivative is produced by the infinite potential at the origin. Let us integrate the energy eigenvalue equation from \( x = -\epsilon \) to \( x = +\epsilon \) and let \( \epsilon \to 0 \). Then, as \( E \) and \( \phi_k(0) \) are finite, in the limit \( \epsilon \to 0 \) one has

\[
\int_{-\epsilon}^{+\epsilon} dx \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - V_0 a \delta(x) \right] \phi_k(x) = E \int_{-\epsilon}^{+\epsilon} dx \phi_k(x) \\
- \frac{\hbar^2}{2m} \frac{\partial}{\partial x} \phi_k(0) \bigg|_{-\epsilon}^{+\epsilon} - V_0 a \phi_k(0) = E 2 \epsilon \phi_k(0)
\]
which reduces to
\[- \frac{\hbar^2}{2m} \frac{\partial}{\partial x} \phi_k(x) \bigg|^{+}_- = V_0 a \phi_k(0) \] (936)

This yields the second condition
\[- \frac{\hbar^2}{2m} \left( i k F \right) + \frac{\hbar^2}{2m} \left( i k A - i k B \right) = V_0 a F \] (937)

These two equations can be solved to yield $B$ and $F$ in terms of $A$,
\[
\frac{B}{A} = \frac{-1}{1 + \frac{i k \hbar^2}{m a V_0}}, \quad \frac{F}{A} = \frac{i k \hbar^2}{1 + \frac{i k \hbar^2}{m a V_0}} \] (938)

Thus, we again have
\[
\frac{|B|^2}{|A|^2} + \frac{|F|^2}{|A|^2} = 1 \quad T + R = 1 \] (939)

and $E$ is a continuous variable, in the range $E > 0$. We note that for large $E$, $R \to 0$ and $T \to 1$, as the potential becomes ineffective in scattering particles with sufficiently high energies.

4.1.18 Bound States of a delta function Potential

We shall now consider the bound states of a delta function potential which must have $E < 0$ and as a result
\[ E = -\frac{\hbar^2 \kappa^2}{2m} \] (940)

where $\kappa$ is a positive real number. Accordingly, the wave function in the two regions must have the forms given by
\[ \phi_\kappa(x) = A \exp \left( -\kappa x \right) + B \exp \left( +\kappa x \right) \] (941)
when $0 > x$ and
\[ \phi_\kappa(x) = F \exp \left( -\kappa x \right) \] (942)
when $x > 0$, corresponding to the analytic continuation $k \to i \kappa$. In order for the wave function to be normalizable at $x \to -\infty$, one must have $A = 0$. The matching conditions then yield
\[ B = F \] (943)
and

\[-\frac{\hbar^2}{2m} \left( -\kappa F \right) + \frac{\hbar^2}{2m} \left( +\kappa B \right) = V_0 a F \] (944)

which yields the energy eigenvalue condition

\[\frac{\hbar^2}{m} \kappa = V_0 a \] (945)

Thus, the energy eigenvalue is given by

\[E = -\frac{(V_0)^2}{\left(\frac{2\hbar^2}{m a^2}\right)} \] (946)

which has the dimensions of energy.

This result could have been obtained directly by noting that the reflection and transmission coefficients have poles at

\[\frac{\hbar^2}{m} i k = - V_0 a \] (947)

which is satisfied for imaginary values of \(k\). Furthermore, since \(A\) can be neglected in comparison with \(B\) and \(F\) for this imaginary value of \(k\), and since \(k = i \kappa\), the wave function decays away from the origin

\[\phi_\kappa(x) = B \exp\left[ + \kappa x \right] \] (948)

in the region \(0 > x\) and

\[\phi_\kappa(x) = B \exp\left[ - \kappa x \right] \] (949)

for \(x > 0\). The amplitudes of the decaying wave functions are equal (\(B = F\)), as can be seen from eqn(938) by noting that at the pole \(i k \frac{\hbar^2}{m a V_0} = -1\). Thus, we have recovered the bound state energy and the form of the wave function by analytic continuation to negative energies.

The normalization of the wave function yields the amplitude, up to an arbitrary phase, as

\[B = \sqrt{\kappa} \] (950)

**Solution in the Momentum Representation**
Figure 48: The bound state wave function of an attractive delta function potential. Note that the wave function has a discontinuous first derivative at $x = 0$.

The bound states of the attractive one-dimensional delta function potential can be found by transforming to the momentum representation. The energy eigenvalue equation is

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - V_0 a \delta(x) \right] \psi_0(x) = E_0 \psi_0(x) \quad (951)$$

which after performing the Fourier Transform

$$\phi_0(k) = \left( \frac{1}{2\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dx \, \psi_0(x) \exp \left[ -i k x \right] \quad (952)$$

becomes

$$\frac{\hbar^2}{2m} k^2 \phi_0(k) - \frac{V_0 a}{\sqrt{2}\pi} \psi_0(0) = E_0 \phi_0(k) \quad (953)$$

On expressing the energy eigenvalue $E_0$ in terms of $\kappa$

$$E_0 = -\frac{\hbar^2 \kappa^2}{2m} \quad (954)$$

the equation is solved for $\phi_0(k)$ as

$$\phi_0(k) = \frac{1}{\sqrt{2\pi}} \left( \frac{2m V_0 a}{\hbar^2} \right) \frac{\psi_0(0)}{k^2 + \kappa^2} \quad (955)$$
The real space wave function \( \psi_0(x) \) is given by the inverse Fourier Transform of \( \phi_0(k) \)

\[
\psi_0(x) = \left( \frac{1}{2\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dk \, \phi_0(k) \exp \left[ +i \, k \, x \right] \quad (956)
\]

On performing the integral via Cauchy’s method, in which the contour is completed with a semi-circle in either the upper or lower half of the complex plane depending on the sign of \( x \), one finds that the real space wave function is given by

\[
\psi_0(x) = \left( \frac{m \, V_0 \, a}{\hbar^2 \, \kappa} \right) \psi_0(0) \exp \left[ -\kappa \, |x| \right] \quad (957)
\]

If the form of the solution for \( \psi_0(x) \) is consistent with the value of \( \psi_0(0) \) at \( x = 0 \), the value of \( \kappa \) must satisfy the equation

\[
\kappa = \frac{m \, V_0 \, a}{\hbar^2} \quad (958)
\]

This condition determines the allowed value of the bound state energy.

---

**Example: The Bound States of a Triple delta function Potential.**

We shall examine the bound states of a particle of mass \( m \) moving in one dimension, in the presence of a potential \( V(x) \) given by

\[
V(x) = -V_0 \, a \left[ \delta(x - a) + \delta(x) + \delta(x + a) \right] \quad (959)
\]

where \( V_0 \) is a positive constant with units of potential and \( a \) is a length scale. The potential is an even function of \( x \). The parity operator \( \hat{P} \) is defined as the operator which, when acting on an arbitrary function \( \psi(x) \), has the effect

\[
\hat{P} \, \psi(x) = \psi(-x) \quad (960)
\]

Since the potential is an even function of \( x \), the Hamiltonian commutes with the parity operator

\[
[ \hat{P}, \hat{H} ] = 0 \quad (961)
\]

so that the parity is a conserved quantity. In other words, parity is a constant of motion.

We shall search for bound states that are simultaneous eigenstates of the parity operator and the Hamiltonian. We shall look for eigenfunctions which are of the form

\[
\phi_n(x) = A \exp \left[ -\kappa \, x \right] \quad (962)
\]
Figure 49: The potential $V(x)$ for three equally spaced attractive delta functions.

in the region $x > a$ and which are of the form

$$\phi_n(x) = B \exp\left[ -\kappa x \right] + C \exp\left[ +\kappa x \right] \tag{963}$$

in the region $a > x > 0$. The forms of the solution for $x < 0$ are found from the above forms by requiring that the eigenfunctions either have even or odd parities. The above forms satisfy the energy eigenvalue equation in the regions where the potential is zero, as long as the energy eigenvalue of the bound state $E_n$ is expressed in terms of $\kappa$ via

$$E_n = -\frac{\hbar^2 \kappa^2}{2m} \tag{964}$$

The above form of the eigenfunction is a solution of the differential equation as long as it satisfies the differential equation at the boundary points $x = 0$ and $x = \pm a$. The boundary conditions at $x = a$ are the condition of continuity of the wave function and the condition that the discontinuity of its first derivative is related to the integral of the potential. These boundary conditions can be expressed as

$$A = B + C \exp\left[ 2\kappa a \right] \tag{965}$$
and
\[ A \left( 1 - \frac{2 m V_0 a}{\hbar^2 \kappa} \right) = B - C \exp\left[ 2 \kappa a \right] \]  
\hspace{1cm} (966)

The above two equations can be combined to yield
\[ A \left( 1 - \frac{m V_0 a}{\hbar^2 \kappa} \right) = B \]  
\hspace{1cm} (967)

and
\[ \frac{m V_0 a}{\hbar^2 \kappa} A = C \exp\left[ 2 \kappa a \right] \]  
\hspace{1cm} (968)

The eigenfunctions also have to satisfy boundary conditions at \( x = 0 \). The explicit forms of the boundary conditions at \( x = 0 \) depend on the parity of the eigenfunctions, therefore, we shall discuss the two cases separately.

**Odd Parity**

For odd parity solutions, \( \phi_n(-x) = -\phi_n(x) \), so the boundary condition at \( x = 0 \) reduces to
\[ \phi_n(0) = 0 \]  
\hspace{1cm} (969)

or
\[ B = -C \]  
\hspace{1cm} (970)

Hence, one finds that \( B \) and \( C \) are completely determined by \( A \), and \( A \) is determined, up to the phase, by the normalization condition. The above conditions imply that for odd parity solutions, \( \kappa \) must satisfy the equation
\[ \left( \frac{m V_0 a^2}{\hbar^2} - \kappa a \right) = \frac{m V_0 a^2}{\hbar^2} \exp\left[ -2 \kappa a \right] \]  
\hspace{1cm} (971)

This equation can be solved graphically by plotting the left hand side and the right hand side as a function of \( \kappa a \) on the same graph, as seen in fig(50). The solutions for \( \kappa \) correspond to the points where the two curves cross. Both curves start at the same value
\[ \frac{m V_0 a^2}{\hbar^2} \]  
\hspace{1cm} (972)

when \( \kappa a = 0 \), and are both decreasing functions of \( \kappa a \). The left hand side decreases linearly with increasing \( \kappa \) and becomes negative at
\[ \kappa a = \frac{m V_0 a^2}{\hbar^2} \]  
\hspace{1cm} (973)

and the right hand side approaches the value of 0 exponentially as \( \kappa a \to \infty \). By considering the initial slopes of both curves, one finds that if
\[ 2 \frac{m V_0 a^2}{\hbar^2} > 1 \]  
\hspace{1cm} (974)
Odd Parity Consistency Equation

Figure 50: The graphical solution for the odd parity bound states, shown for two different strengths of the potential \( V_0 \). The left hand side of eqn(971) is shown by a red line, and the right hand side by a blue line. For large values of the potential or the separation, the equation (represented by the pair of solid lines) has one solution at a non-zero value of \( \kappa \). For small values of \( V_0 \), the left hand and right hand sides of the equation are depicted by the dashed lines. The dashed curves only intersect at \( \kappa = 0 \).

then the two curves also cross at a finite value of \( \kappa a \). The value of \( \kappa a \) at the crossing yields a bound state solution with odd parity. The solution at \( \kappa a = 0 \) represents an odd parity zero energy resonance.

**Even Parity**

For even parity solutions, \( \phi_n(-x) = \phi_n(x) \). Therefore, the matching condition at the \( x = 0 \) boundary leads to

\[
\left( B - C \right) = \frac{m V_0 a}{\hbar^2 \kappa} \left( B + C \right)
\]

or

\[
B \left( 1 - \frac{m V_0 a}{\hbar^2 \kappa} \right) = C \left( 1 + \frac{m V_0 a}{\hbar^2 \kappa} \right)
\]

On combining these conditions with the boundary conditions at \( x = a \), one finds that \( \kappa a \) must satisfy the equation

\[
\left( \kappa a - \frac{m V_0 a^2}{\hbar^2} \right)^2 = \frac{m V_0 a^2}{\hbar^2} \left( \kappa a + \frac{m V_0 a^2}{\hbar^2} \right) \exp \left[ -2 \kappa a \right]
\]

221
This equation determines the energy eigenvalues and energy eigenfunctions with even parity. The above transcendental equation can be solved graphically, as seen in fig(51). The left hand side and right hand side take on the same value

![Even Parity Consistency Equations](image)

Figure 51: The graphical solution of eqn(977) for the even parity bound states, shown for two different strengths of the potential. The left hand side of the equation is shown by a red line, and the right hand side by a blue line. For large values of \( \frac{V_0 \, ma^2}{\hbar^2} \), the equation (represented by the solid lines) has two solutions at non-zero values of \( \kappa \). For small values of \( V_0 \), the equation only has one solution at a non-zero value of \( \kappa \), located at the intersection of the dashed lines.

at \( \kappa a = 0 \). The left hand side is always positive but touches zero at

\[
\kappa a = \frac{m \, V_0 \, a^2}{\hbar^2}
\]  

(978)

and varies quadratically as \( \kappa a \to \infty \). The right hand side is monotonically decreasing and approaches zero as \( \kappa a \to \infty \). From consideration of the initial slope, it is found that there are three solutions of this equation if

\[
2 \frac{m \, V_0 \, a^2}{\hbar^2} > 3
\]  

(979)

and, otherwise, only has two solutions. The solution at \( \kappa a = 0 \) corresponds to a zero energy bound state or resonance. The solutions at finite values of \( \kappa a \) have finite binding energies.
Figure 52: The bound state energy eigenvalues $E_n$, for the triple delta function potential.

Figure 53: The bound state wave functions $\phi_n(x)$, for the triple delta function potential.
The three bound state energies $E_n$ are plotted as a function of $\kappa a$ in fig(52). It is seen that the number of bound states increases as the value of $V_0$ increases. As the separation between the wells is increased, all the bound state energies approach the asymptotic expression

$$E_n \rightarrow -\frac{m V_0^2 a^2}{2 \hbar^2}$$

(980)

expected for three isolated delta function potentials. The three bound state wave functions $\phi_n(x)$ are shown in fig(53). It is seen that the number of nodes increases with increasing energy.

---

**4.1.19 Exercise 65**

Find the reflection and transmission coefficients for a potential

$$V(x) = V_0 \Theta(x) - V_0 a \delta(x)$$

(981)

where $\Theta(x)$ is the Heaviside step function,

$$\Theta(x) =
\begin{cases}
  1 & \text{for } x > 0 \\
  0 & \text{for } x < 0
\end{cases}$$

(982)

The potential is shown in fig(54). Show that the reflection and transmission coefficients add up to unity.

---

**4.1.20 Solution 65**

The energy eigenfunction corresponding to a scattering experiment where the incident beam is travelling towards the right is given by

$$\phi_k(x) =
\begin{cases}
  A \exp \left[ i k x \right] + B \exp \left[ -i k x \right] & x < 0 \\
  C \exp \left[ i k' x \right] & x > 0
\end{cases}$$

(983)

where $E = \frac{\hbar^2 k^2}{2m}$ and $E = V_0 + \frac{\hbar^2 k'^2}{2m}$

The continuity condition leads to

$$C = A + B$$

(984)
$$V(x) = -V_0 \delta(x) + V_0 \Theta(x)$$

Figure 54: The potential $V(x)$ used in Exercise 65.

whereas the discontinuity in the first derivative satisfies the equation

$$\left( i k' + \frac{2 m V_0 a}{h^2} \right) C = i k \left( A - B \right)$$

Therefore

$$\frac{A}{C} = \left( \frac{k + k' - i \frac{2 m V_0 a}{h^2}}{2 k} \right)$$

and

$$\frac{B}{C} = \left( \frac{k - k' + i \frac{2 m V_0 a}{h^2}}{2 k} \right)$$

Thus, we have the transmission coefficient

$$T = \frac{k' \left| C \right|^2}{k \left| A \right|^2}$$

$$T = \frac{4 k k'}{(k + k')^2 + \left( \frac{2 m V_0 a}{h^2} \right)^2}$$

and the reflection coefficient is given by

$$R = \frac{\left| B \right|^2}{\left| A \right|^2}$$

$$R = \frac{(k - k')^2 + \left( \frac{2 m V_0 a}{h^2} \right)^2}{(k + k')^2 + \left( \frac{2 m V_0 a}{h^2} \right)^2}$$
Figure 55: The transmission coefficient $T(k)$ and the reflection coefficient $R(k)$ calculated in Exercise 65.

### 4.1.21 Exercise 66

Find the reflection and transmission coefficients for a beam of particles incident on the potential $V(x)$ given by

$$V(x) = -V_0 a \left( \delta(x - a) + \delta(x + a) \right)$$  \hspace{1cm} (990)

Also, find the bound states.

### 4.1.22 Solution 66

The energy eigenfunctions corresponding to the scattering states of energy

$$E = \frac{\hbar^2 k^2}{2m}$$  \hspace{1cm} (991)
Figure 56: The potential for two attractive delta function potentials.

can be expressed in terms of a steady state in which a particle beam of momentum $\hbar k$ is incident from $x \to -\infty$ or where a particle beam is incident from $x \to +\infty$. We shall consider the solution corresponding to a beam incident from the left travelling to the right. The energy eigenfunction can be expressed as

$$
\phi_k(x) = \begin{cases} 
A \exp \left[ i k x \right] + B \exp \left[ -i k x \right] & x < -a \\
C \exp \left[ i k x \right] + D \exp \left[ -i k x \right] & -a < x < a \\
F \exp \left[ i k x \right] & a < x
\end{cases}
$$

The continuity conditions at $x = -a$ is given by

$$
A \exp \left[ -i k a \right] + B \exp \left[ i k a \right] = C \exp \left[ -i k a \right] + D \exp \left[ i k a \right]
$$

where $A$ is the amplitude of the incident beam and $B$ and $F$ are the amplitudes of the reflected and transmitted beams, respectively.
whereas, from integrating the energy eigenvalue equation, one finds the discontinuity in the first derivative satisfies

\[
\left( A \exp\left[ -i k a \right] - B \exp\left[ +i k a \right] \right) = \left( C \exp\left[ -i k a \right] - D \exp\left[ +i k a \right] \right) + \frac{2 m V_0 a}{i k \hbar^2} \left( C \exp\left[ -i k a \right] + D \exp\left[ +i k a \right] \right)
\]  

This pair of equations can be solved for \( A \) and \( B \) in terms of \( C \) and \( D \).

\[
A = C \left( 1 + \frac{m V_0 a}{i k \hbar^2} \right) + D \exp\left[ +2 i k a \right] \left( \frac{m V_0 a}{i k \hbar^2} \right) \\
B = D \left( 1 - \frac{m V_0 a}{i k \hbar^2} \right) - C \exp\left[ -2 i k a \right] \left( \frac{m V_0 a}{i k \hbar^2} \right)
\]  

The boundary conditions at \( x = a \) are similar, the continuity equation is

\[
C \exp\left[ +i k a \right] + D \exp\left[ -i k a \right] = F \exp\left[ +i k a \right]
\]  

whereas, from integrating the energy eigenvalue equation, one finds the discontinuity in the first derivative satisfies

\[
\left( C \exp\left[ +i k a \right] - D \exp\left[ -i k a \right] \right) = F \exp\left[ +i k a \right] \left( 1 + \frac{2 m V_0 a}{i k \hbar^2} \right)
\]  

This pair of equations can be solved to yield

\[
C = F \left( 1 + \frac{m V_0 a}{i k \hbar^2} \right) \\
D = -\left( \frac{m V_0 a}{i k \hbar^2} \right) F \exp\left[ +2 i k a \right]
\]  

The expressions for \( C \) and \( D \) can be substituted in the expressions for \( A \) and \( B \), yielding the amplitudes of the reflected and transmitted beam

\[
\frac{A}{F} = \left( 1 + \frac{m V_0 a}{i k \hbar^2} \right)^2 - \left( \frac{m V_0 a}{i k \hbar^2} \right)^2 \exp\left[ +4 i k a \right]
\]
\[
\frac{B}{F} = - \left( \frac{m V_0 a}{i k \hbar^2} \right) \left( \exp \left[ + 2 i k a \right] + \exp \left[ - 2 i k a \right] \right)
\]

(999)

The transmission coefficient is given by the inverse of the squared modulus of the first equation and the reflection coefficient is found by dividing the one equation by the other and then multiplying by its complex conjugate.

Figure 57: A graphical solution for the bound state energies.

The bound states are given by the analytic continuation \( k \rightarrow i \kappa \) and the values of \( \kappa \) are determined from the poles of the transmission and reflection coefficients, i.e. \( A = 0 \). Hence, we find

\[
\left( \kappa - \frac{m V_0 a}{\hbar^2} \right)^2 = \left( \frac{m V_0 a}{\hbar^2} \right)^2 \exp \left[ - 4 \kappa a \right]
\]

(1000)

For large \( \kappa a \) the solution reduces to the solution for two independent delta function potentials, but these are subject to the exponentially small bonding and anti-bonding splitting

\[
\kappa \approx \left( \frac{m V_0 a}{\hbar^2} \right) \left( 1 \mp \exp \left[ - 2 \frac{m V_0 a^2}{\hbar^2} \right] \right)
\]

(1001)

For small \( \kappa a \) the splitting becomes larger and one obtains the values of \( \kappa \) as

\[
\kappa \approx 2 \left( \frac{m V_0 a}{\hbar^2} \right)
\]
Figure 58: The bound state wave functions for the double delta function potential.

\[ \kappa \approx 0 \]  

This potential may serve as a one-dimensional model for a molecule, in which the levels are doubly degenerate. If the atoms are far apart, the energies just correspond to the energies of the individual atoms. However, when the atoms are brought closer together, there is an energy gain for doubly occupying the lowest energy state. This gain occurs through the bonding - anti-bonding splitting and results in the molecule being stabilized.

**Alternate Derivation of the Bound State Solutions.**

We shall find the bound states of particles moving in one dimension, in the presence of the potential \( V(x) \) given by

\[ V(x) = -V_0 a \left( \delta(x - a) + \delta(x + a) \right) \]  

The energy eigenvalue equation

\[ \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - V(x) \right] \psi_\alpha(x) = E_\alpha \psi_\alpha(x) \]
will be solved in the momentum space representation. On Fourier Transforming

\[ \phi_\alpha(k) = \left( \frac{1}{2 \pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dx \, \psi_\alpha(x) \exp \left[ -i k x \right] \]  

(1005)

the energy eigenvalue equation, one obtains

\[ \frac{\hbar^2 k^2}{2 m} \phi_\alpha(k) - \frac{V_0 a}{\sqrt{2} \pi} \left( \psi_\alpha(a) \exp \left[ -i k a \right] + \psi_\alpha(-a) \exp \left[ +i k a \right] \right) = E_\alpha \phi_\alpha(k) \]  

(1006)

On expressing the energy eigenvalue \( E_\alpha \) in terms of \( \kappa \)

\[ E_\alpha = -\frac{\hbar^2 \kappa^2}{2 m} \]  

(1007)

the momentum space form of the energy eigenvalue equation is solved for \( \phi_\alpha(k) \), yielding

\[ \phi_\alpha(k) = \frac{1}{\sqrt{2} \pi} \left( \frac{2 m}{\hbar^2} \frac{V_0 a}{\kappa} \right) \left( \psi_\alpha(a) \exp \left[ -i k a \right] + \psi_\alpha(-a) \exp \left[ +i k a \right] \right) \]  

(1008)

The real space wave function \( \psi_\alpha(x) \) is given by the inverse Fourier Transform of \( \phi_\alpha(k) \)

\[ \psi_\alpha(x) = \left( \frac{1}{2 \pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dk \, \phi_\alpha(k) \exp \left[ +i k x \right] \]  

(1009)

The integrals are performed using Cauchy’s method, in which the contours are completed with semi-circles at infinity. One finds that the real space wave function is given by

\[ \psi_\alpha(x) = \left( \frac{m V_0 a}{\hbar^2 \kappa} \right) \left( \psi_\alpha(a) \exp \left[ -\kappa |x - a| \right] + \psi_\alpha(-a) \exp \left[ -\kappa |x + a| \right] \right) \]  

(1010)

This solution must be consistent at the two points \( x = \pm a \). This yields the two consistency conditions

\[ \psi_\alpha(\pm a) \left[ 1 - \frac{m V_0 a}{\hbar^2 \kappa} \right] = \psi_\alpha(\mp a) \left( \frac{m V_0 a}{\hbar^2 \kappa} \right) \exp \left[ -2 \kappa a \right] \]  

(1011)

These equations determine the allowed values of \( \kappa \). On combining these equations, one has

\[ \left[ 1 - \left( \frac{m V_0 a}{\hbar^2 \kappa} \right) \right]^2 = \left( \frac{m V_0 a}{\hbar^2 \kappa} \right)^2 \exp \left[ -4 \kappa a \right] \]  

(1012)

which has two non-trivial solutions if

\[ 2 \left( \frac{m V_0 a^2}{\hbar^2} \right) > 1 \]  

(1013)
Otherwise, the above equation only has one non-trivial solution, and the trivial solution $\kappa = 0$.

4.1.23 Exercise 67

A particle of mass $m$ moves in one dimension under the influence of an attractive delta function potential centered at the origin, and of strength $V_0 a$. The particle is in the bound state at $t = 0$ and then the strength of the attractive potential is suddenly changed to $V'_0 a$. What is the probability that the particle will remain bound to the potential?

4.1.24 Solution 67

The energy eigenstate $\Psi_0(x)$ of the initial Hamiltonian $\hat{H}$ is governed by the eigenvalue equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi_0(x) - V_0 a \delta(x) \Psi_0(x) = E_0 \Psi_0(x) \quad (1014)$$

For $x \neq 0$ the eigenvalue equation reduces to

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi_0(x) = E_0 \Psi_0(x) \quad (1015)$$

and has a solution of the form

$$\Psi_0(x) = A \exp \left[ -\kappa x \right] \quad x > 0$$

$$\Psi_0(x) = B \exp \left[ +\kappa x \right] \quad x < 0 \quad (1016)$$

where

$$E_0 = -\frac{\hbar^2}{2m} \kappa^2 \quad (1017)$$

The matching condition at $x = 0$ yields

$$\Psi_0( + \epsilon ) = \Psi_0( - \epsilon ) \quad (1018)$$

or

$$A = B \quad (1019)$$
On integrating the differential equation over the infinitesimal interval between \((-\epsilon, +\epsilon\)), one obtains

\[
\int_{-\epsilon}^{+\epsilon} dx \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi_0(x) - V_0 a \delta(x) \Psi_0(x) \right] = E_0 \int_{-\epsilon}^{+\epsilon} dx \Psi_0(x) \\
- \frac{\hbar^2}{2m} \frac{\partial}{\partial x} \Psi_0(x) \bigg|_{-\epsilon}^{+\epsilon} - V_0 a \Psi_0(0) = E_0 \epsilon \Psi_0(0)
\]

or in the limit \(\epsilon \to 0\)

\[+ \frac{\hbar^2}{m} \kappa A - V_0 a A = 0\]  

Hence,

\[\kappa = \frac{m a V_0}{\hbar^2}\]

thus we have

\[E_0 = -\frac{m a^2 V_0}{2 \hbar^2}\]

and the bound state wave function is given by

\[\Psi_0(x) = A \exp \left[ -\frac{m a V_0}{\hbar^2} |x| \right]\]

The magnitude of the constant \(A\) is given by the normalization condition

\[
\int_{-\infty}^{\infty} dx \ |\Psi_0(x)|^2 = 1 \\
|A|^2 \int_{-\infty}^{\infty} dx \exp \left[ -2 \frac{m a V_0}{\hbar^2} |x| \right] = 1 \\
2 |A|^2 \int_0^{\infty} dx \exp \left[ -2 \frac{m a V_0}{\hbar^2} x \right] = 1 \\
|A|^2 \frac{\hbar^2}{m a V_0} = 1
\]

Hence,

\[A = \sqrt{\frac{m a V_0}{\hbar^2}}\]

up to an arbitrary phase. The initial ground state wave function is given by

\[\Psi_0(x) = \sqrt{\frac{m a V_0}{\hbar^2}} \exp \left[ -\frac{m a V_0}{\hbar^2} |x| \right]\]
The initial state wave function $\Psi_0(x)$ can be expressed as a linear superposition of the eigenstates of the final Hamiltonian, $\hat{H}'$, $\phi_n(x)$, via

$$\Psi_0(x) = \sum_n C_n \phi_n(x)$$

(1028)

where the expansion coefficients are given by

$$C_n = \int_{-\infty}^{\infty} dx \, \phi_n^*(x) \, \Psi_0(x)$$

(1029)

The probability that a measurement of $\hat{H}'$ will result in a value for the energy of $E'_n$ is given by

$$P(n) = |C_n|^2$$

(1030)

The overlap between the initial bound state and the final bound state of potential $V'_0$, is given by

$$\int_{-\infty}^{\infty} dx \, \phi_0^*(x) \, \Psi_0(x) = 2 \frac{ma}{\hbar^2} \frac{V_0 V'_0}{V_0 + V'_0} \int_0^{\infty} dx \, \exp \left[ - \frac{ma}{\hbar^2} (V_0 + V'_0) x \right]$$

$$= 2 \frac{\sqrt{V_0 V'_0}}{V_0 + V'_0}$$

(1031)

The probability that the particle remains in the bound state, $P(0)$, is given by

$$P(0) = \left| \int_{-\infty}^{\infty} dx \, \phi_0^*(x) \, \Psi_0(x) \right|^2$$

$$= \frac{4 V_0 V'_0}{(V_0 + V'_0)^2}$$

(1032)

Thus, the probability that the particle ends up in an excited state is given by

$$P_{exc} = \sum_{n \neq 0} P(n)$$

$$= 1 - P(0)$$

$$= \frac{(V_0 - V'_0)^2}{(V_0 + V'_0)^2}$$

(1033)

since the probabilities are normalized to unity. Note that if $V_0 = V'_0$ no transitions take place.

**4.1.25 Exercise 68**

A particle moves in one dimension in a potential of the form

$$V(x) = \infty \quad \text{for} \quad x < 0$$

$$V(x) = -V_0 \, a \, \delta(x - a) \quad \text{for} \quad x > 0$$

(1034)
The potential is shown in fig(59). Find the condition that determines the bound states. What is the minimum value of $V_0$ for which a bound state appears?

4.1.26 Solution 68

We need to consider the bound state solutions of the energy eigenvalue equation

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \phi_0(x) = E_0 \phi_0(x) \quad (1035)$$

In the region when $x > a$ the bound state solution must have the form of a decaying exponential

$$\phi_0(x) = C \exp \left[ -\kappa x \right] \quad (1036)$$

where the bound state energy is

$$E = -\frac{\hbar^2 \kappa^2}{2m} \quad (1037)$$
Whereas in the region where $0 < x < a$ the wave function must have the form

$$
\phi_0(x) = A \exp[-\kappa x] + B \exp[+\kappa x]
$$

(1038)

and vanish for $x < 0$.

To satisfy the boundary condition at $x = 0$ one must have $A = -B$.

The continuity condition at $x = a$ yields

$$
A \left( \exp[-\kappa a] - \exp[+\kappa a] \right) = C \exp[-\kappa a]
$$

(1039)

and on integrating the energy eigenvalue equation in an infinitesimal region about $x = a$ to obtain the discontinuity of the first derivative in terms of the strength of the delta function potential,

$$
-\kappa C \exp[-\kappa a] - \kappa A \left( \exp[-\kappa a] + \exp[+\kappa a] \right) = -\frac{2mV_0a}{\hbar^2} C \exp[-\kappa a]
$$

(1040)

These two equations can be solved to yield

$$
\coth \kappa a = -\left( 1 - \frac{2mV_0a}{\hbar^2\kappa} \right)
$$

(1041)

The bound state only just exists if $\kappa \to 0$ in which case the above equation can be expanded in powers of $\kappa$. The solution at $\kappa \to 0$ only exists if

$$
\frac{2mV_0a^2}{\hbar^2} = 1
$$

(1042)
4.2 The One-Dimensional Harmonic Oscillator

We shall find all the energy eigenfunctions of the one-dimensional Harmonic oscillator in a systematic way. The Hamiltonian of the one-dimensional harmonic oscillator can be written as

$$\hat{H} = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{m \omega^2 x^2}{2} \right]$$

(1043)

The Harmonic Oscillator Potential

![Figure 60: The Harmonic Oscillator Potential $V(x) = \frac{1}{2} m \omega^2 x^2$.](image)

The Hamiltonian can be re-written in terms of the dimensionless variable

$$\xi = \sqrt{\frac{m \omega}{\hbar}} x$$

(1044)

Then, the Hamiltonian has the form

$$\hat{H} = \frac{\hbar \omega}{2} \left[ -\frac{\partial^2}{\partial \xi^2} + \xi^2 \right]$$

(1045)

which shows that $\hbar \omega$ provides the natural energy scale for the quantum system. The Hamiltonian operator can be expressed in terms of its classical factorization and a constant either as

$$\hat{H} = \frac{\hbar \omega}{2} \left[ \left( -\frac{\partial}{\partial \xi} + \xi \right) \left( +\frac{\partial}{\partial \xi} + \xi \right) + 1 \right]$$

(1046)
or as
\[ \hat{H} = \frac{\hbar \omega}{2} \left[ \left( + \frac{\partial}{\partial \xi} + \xi \right) \left( - \frac{\partial}{\partial \xi} + \xi \right) - 1 \right] \]  
(1047)
since the factors do not commute. In fact, the commutator of the factors is given by
\[ \left[ \left( + \frac{\partial}{\partial \xi} + \xi \right), \left( - \frac{\partial}{\partial \xi} + \xi \right) \right] = 2 \]  
(1048)

4.2.1 The Raising and Lowering Operators

Let us denote the factors by the operators \( \hat{a} \) and \( \hat{a}^\dagger \) since these factors are Hermitean conjugates. We shall also introduce a factor of \( \sqrt{2} \) into their definition
\[ \hat{a} = \frac{1}{\sqrt{2}} \left( + \frac{\partial}{\partial \xi} + \xi \right) \]
\[ \hat{a}^\dagger = \frac{1}{\sqrt{2}} \left( - \frac{\partial}{\partial \xi} + \xi \right) \]  
(1049)
to simplify the commutation relations. Thus, these operators have the commutation relations
\[ [ \hat{a}, \hat{a}^\dagger ] = + 1 \]  
(1050)

4.2.2 The Effect of the Lowering Operator

Let us consider the energy eigenvalue equation
\[ \hat{H} \Psi_n(x) = E_n \Psi_n(x) \]  
(1051)
with wave function \( \Psi_n(x) \) and energy eigenvalue \( E_n \). The Hamiltonian when expressed in terms of the new operators is just
\[ \hat{H} = \frac{\hbar \omega}{2} \left( 2 \hat{a}^\dagger \hat{a} + 1 \right) \]
\[ \hat{H} = \frac{\hbar \omega}{2} \left( 2 \hat{a} \hat{a}^\dagger - 1 \right) \]  
(1052)
The effect of the operators \( \hat{a} \) on the eigenvalue equation can be found as
\[ \hat{a} \hat{H} \Psi_n(x) = E_n \hat{a} \Psi_n(x) \]  
(1053)
but since the commutator of \( \hat{a} \) with the Hamiltonian is
\[ \hat{a} \hat{H} = \hat{a} \frac{\hbar \omega}{2} \left( 2 \hat{a}^\dagger \hat{a} + 1 \right) \]
\[ = \frac{\hbar \omega}{2} \left( 2 \hat{a}^\dagger \hat{a} + 3 \right) \hat{a} \]
\[ = \left( \hat{H} + \hbar \omega \right) \hat{a} \]  
(1054)
one finds eqn(1053) can be re-written as

\[
\left( \hat{H} + \hbar \omega \right) \hat{a} \Psi_n(x) = E_n \hat{a} \Psi_n(x) \tag{1055}
\]

Thus, on rewriting this we find

\[
\hat{H} \hat{a} \Psi_n(x) = \left( E_n - \hbar \omega \right) \hat{a} \Psi_n(x) \tag{1056}
\]

Hence, the wave function

\[
\hat{a} \Psi_n(x) \tag{1057}
\]

is an eigenfunction of the Hamiltonian with an eigenvalue of \( E_n - \hbar \omega \). Thus, the operator \( \hat{a} \) when acting on an energy eigenfunction produces another energy eigenfunction with a lower energy eigenvalue. In other words,

\[
\hat{a} \Psi_n(x) = C_n \Psi_{n-1}(x) \tag{1058}
\]

where \( C_n \) is a constant of proportionality. This property of \( \hat{a} \) justifies naming it as the lowering operator.

### 4.2.3 The Ground State

The lowest energy state has eigenvalue \( E_0 \) and, therefore, as there is no lower energy eigenfunction, one must have

\[
\hat{a} \Psi_0(x) = 0 \tag{1059}
\]

This leads to the equation for the ground state wave function

\[
\left( + \frac{\partial}{\partial \xi} + \xi \right) \Psi_0(x) = 0 \tag{1060}
\]

This has the solution

\[
\Psi_0(x) = C \exp \left[ - \frac{\xi^2}{2} \right] \tag{1061}
\]

where \( C \) is the normalization constant that still has to be determined. In terms of the original variables, the ground state wave function is found as

\[
\Psi_0(x) = C \exp \left[ - \frac{m \omega x^2}{2 \hbar} \right] \tag{1062}
\]

The normalization condition yields

\[
|C| = \left( \frac{m \omega}{\hbar \pi} \right)^{\frac{1}{4}} \tag{1063}
\]
Since the lowest energy state satisfies eqn(1059) and due to the first form of the Hamiltonian given in eqn(1052), we deduce that the lowest energy eigenvalue is $\hbar \omega$. The method implies that there exists higher-energy eigenstates that have energy eigenvalues which are larger by multiples of $\hbar \omega$, that is

$$E_n = \hbar \omega \left( n + \frac{1}{2} \right)$$  \hspace{1cm} (1064)

### 4.2.4 The Effect of The Raising Operator

The effect of the Hermitean conjugate of $\hat{a}$ can be found by considering its effect on the energy eigenvalue equation

$$\hat{a}^{\dagger} \hat{H} \Psi_n(x) = \hat{a}^{\dagger} E_n \Psi_n(x)$$  \hspace{1cm} (1065)

On using the commutation relations, one finds

$$\hat{a}^{\dagger} \hat{H} = \hat{a}^{\dagger} \frac{\hbar \omega}{2} \left( 2 \hat{a}^{\dagger} \hat{a} + 1 \right)$$

$$= \frac{\hbar \omega}{2} \left( 2 \hat{a}^{\dagger} \hat{a} - 1 \right) \hat{a}^{\dagger}$$

$$= \left( \hat{H} - \hbar \omega \right) \hat{a}^{\dagger}$$  \hspace{1cm} (1066)

so one finds that eqn(1065) becomes

$$\left( \hat{H} - \hbar \omega \right) \hat{a}^{\dagger} \Psi_n(x) = E_n \hat{a}^{\dagger} \Psi_n(x)$$  \hspace{1cm} (1067)

Thus, on re-writing the above equation, we find

$$\hat{H} \hat{a}^{\dagger} \Psi_n(x) = \left( E_n + \hbar \omega \right) \hat{a}^{\dagger} \Psi_n(x)$$  \hspace{1cm} (1068)

Hence, the wave function

$$\hat{a}^{\dagger} \Psi_n(x)$$  \hspace{1cm} (1069)

is an eigenfunction of the Hamiltonian with an eigenvalue of $E_n + \hbar \omega$, i.e. $E_{n+1}$. Thus, the operator $\hat{a}^{\dagger}$ when acting on an energy eigenfunction produces another energy eigenfunction with a higher-energy eigenvalue.

$$\hat{a}^{\dagger} \Psi_n(x) = C_{n+1}^* \Psi_{n+1}(x)$$  \hspace{1cm} (1070)

where $C_{n+1}^*$ is a constant of proportionality related to that in eqn(1058). This property of $\hat{a}^{\dagger}$ justifies naming it as the raising operator.
4.2.5 The Normalization

The constant of proportionality for the raising operator is related to the constant of proportionality for the lowering operator as can be found by considering the definition of the Hermitean conjugate of an operator

\[ \int_{-\infty}^{+\infty} dx \, \Psi_n^*(x) \hat{a} \Psi_n(x) = \left( \int_{-\infty}^{+\infty} dx \, \Psi_n^*(x) \hat{a}^\dagger \Psi_{n-1}(x) \right)^* \]  

(1071)

This implies that, with properly normalized eigenfunctions and on using the definition in eqn(1068) and its consequence eqn(1070), the coefficients of proportionality satisfy

\[ C_n = \left( C_n^* \right)^* \]  

(1072)

as expected. The constant of proportionality can be found, up to an arbitrary phase, from the energy eigenvalue equation

\[ \frac{\hbar}{2} \left( 2 \hat{a}^\dagger \hat{a} + 1 \right) \Psi_n(x) = \hbar \omega \left( n + \frac{1}{2} \right) \Psi_n(x) \]  

(1073)

Thus, on using the equations for the raising and lowering operators together with the constants of proportionality, one finds

\[ |C_n|^2 = n \]  

(1074)

Hence, on choosing a real phase for the \( C_n \), we have the equations

\[ \hat{a} \Psi_n(x) = \sqrt{n} \Psi_{n-1}(x) \]
\[ \hat{a}^\dagger \Psi_n(x) = \sqrt{n+1} \Psi_{n+1}(x) \]  

(1075)

4.2.6 The Excited States

All the energy eigenfunctions can be obtained from the ground state wave function by successive action of the raising operator, Hence, we have

\[ \Psi_1(x) = \hat{a}^\dagger \Psi_0(x) \]
\[ \Psi_1(x) = \frac{1}{\sqrt{2}} \left( - \sqrt{\frac{\hbar}{m \omega}} \frac{\partial}{\partial x} + \sqrt{\frac{m \omega}{\hbar}} x \right) \Psi_0(x) \]
\[ \Psi_1(x) = \left( \frac{m \omega}{4 \hbar \pi} \right)^{\frac{1}{4}} \left( - \sqrt{\frac{\hbar}{m \omega}} \frac{\partial}{\partial x} + \sqrt{\frac{m \omega}{\hbar}} x \right) \exp \left[ - \frac{m \omega x^2}{2 \hbar} \right] \]  

(1076)
The higher-energy eigenfunctions are given by iteration

$$
\Psi_{n+1}(x) = \frac{\hat{a}^\dagger}{\sqrt{(n+1)}} \Psi_n(x)
$$

$$
\Psi_{n+1}(x) = \frac{1}{\sqrt{2(n+1)}} \left( -\sqrt{\frac{\hbar}{m\omega}} \frac{\partial}{\partial x} + \sqrt{\frac{m\omega}{\hbar}} x \right) \Psi_n(x)
$$

(1077)

Then the $n$-th excited state wave function is given in terms of the ground state wave function $\Psi_0(x)$ by acting on it by the raising operator $n$ times

$$
\Psi_n(x) = \left( \frac{\hat{a}^\dagger}{\sqrt{n!}} \right)^n \Psi_0(x)
$$

$$
= \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}} \left( \frac{m\omega}{\hbar \pi} \right)^{\frac{n}{2}} \exp \left[ -\frac{m\omega x^2}{2\hbar} \right]
$$

$$
= \frac{1}{\sqrt{2^n n!}} \left( -\sqrt{\frac{\hbar}{m\omega}} \frac{\partial}{\partial x} + \sqrt{\frac{m\omega}{\hbar}} x \right)^n \left( \frac{m\omega}{\hbar \pi} \right)^{\frac{n}{4}} \exp \left[ -\frac{m\omega x^2}{2\hbar} \right]
$$

(1078)

Furthermore, using the operator identity

$$
\left( -\sqrt{\frac{\hbar}{m\omega}} \frac{\partial}{\partial x} + \sqrt{\frac{m\omega}{\hbar}} x \right) =
$$

$$
\equiv (-1)^n \exp \left[ +\frac{m\omega x^2}{2\hbar} \right] \sqrt{\frac{\hbar}{m\omega}} \frac{\partial}{\partial x} \exp \left[ -\frac{m\omega x^2}{2\hbar} \right]
$$

(1079)

one finds the eigenstates are given by the expression

$$
\Psi_n(x) = \frac{(-1)^n}{\sqrt{2^n n!}} \exp \left[ +\frac{m\omega x^2}{2\hbar} \right] \left( \sqrt{\frac{\hbar}{m\omega}} \frac{\partial}{\partial x} \right)^n \exp \left[ -\frac{m\omega x^2}{2\hbar} \right]
$$

$$
\times \left( \frac{m\omega}{\hbar \pi} \right)^{\frac{n}{4}} \exp \left[ -\frac{m\omega x^2}{2\hbar} \right]
$$

(1080)

The solution is recognized as involving the $n$-th order Hermite polynomial $H_n(x)$ given by

$$
H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right) = (-1)^n \exp \left[ +\frac{m\omega x^2}{\hbar} \right] \left( \sqrt{\frac{\hbar}{m\omega}} \frac{\partial}{\partial x} \right)^n \exp \left[ -\frac{m\omega x^2}{\hbar} \right]
$$

(1081)

Thus, we have found the expression for the general energy eigenfunction for the one-dimensional harmonic oscillator as

$$
\Psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left( \frac{m\omega}{\hbar \pi} \right)^{\frac{n}{4}} \exp \left[ -\frac{m\omega x^2}{2\hbar} \right] H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right)
$$

(1082)
These states are all properly normalized to unity, as the ground state wave function was properly normalized.

Figure 61: The ground state $\Psi_0(x)$ and excited state wave functions $\Psi_n(x)$ of the one-dimensional harmonic oscillator.

The quantum probability density for finding a particle with energy $E$ at position $x$ should be compared with the classical probability density if the initial position is unknown. Unlike the classical probability density, the quantum probability density shows spatial oscillations. If the spatial oscillations are averaged over, then it is seen that as the energy increases, the quantum probability density approaches the classical density.

4.2.7 Exercise 69

Find an expression for the expectation value of $x^4$, in the $n$-th excited state of the harmonic oscillator.
Figure 62: Comparison of the quantum mechanical probability densities for finding a particle at position $x$, $P(x) = |\Psi_n(x)|^2$ with the classical probability densities for $n = 4$.

4.2.8 Solution 69

The average value of $x^4$ in the $n$-th energy eigenstate of the harmonic oscillator can be found be expressing $x$ in terms of the raising and lowering operators

$$x = \sqrt{\frac{\hbar}{2m\omega}} \left( a^\dagger + a \right) \quad (1083)$$

Hence

$$\langle x^4 \rangle = \int_{-\infty}^{+\infty} dx \, \phi_n^*(x) \, x^4 \, \phi_n(x)$$

$$= \left( \frac{\hbar}{2m\omega} \right)^2 \int_{-\infty}^{+\infty} dx \, \phi_n^*(x) \, (a^\dagger + a)^4 \, \phi_n(x) \quad (1084)$$

The only non-zero terms are those involving the same number of raising and lowering operators as terms where these numbers are different can be related to the matrix elements of energy states with different values of $n$ which, because of the orthogonality of non-degenerate energy eigenstates, are zero. The non-zero
Figure 63: Comparison of the quantum mechanical probability densities for finding a particle at position $x$, $P(x) = |\Psi_n(x)|^2$ with the classical probability densities for $n = 8$.

Terms are

$$\bar{x}^4 = \left(\frac{\hbar}{2m\omega}\right)^2 \int_{-\infty}^{+\infty} dx \phi_n^*(x) \left( a^\dagger a^\dagger a a + a^\dagger a a^\dagger a + a^\dagger a a^\dagger + H.c. \right) \phi_n(x)$$

$$= \left(\frac{\hbar}{2m\omega}\right)^2 \frac{n(n-1)+nn+n(n+1)}{(n+1)n+(n+1)(n+1)+(n+2)(n+1)}$$

$$\bar{x}^4 = \left(\frac{\hbar}{2m\omega}\right)^2 3 \left( 2n^2 + 2n + 1 \right)$$

(1085)
4.2.9 Exercise 70

Show that for a harmonic oscillator in the \( n \)-th energy eigenstates, the uncertainty in the position and momentum satisfy the equation

\[
\Delta x_{\text{rms}} \Delta p_{\text{rms}} = \hbar \frac{2n + 1}{2}
\]  

(1086)

4.2.10 Solution 70

The expectation value of the \( \Delta x^2 \) is equal to the expectation value of \( x^2 \)

\[
\Delta x^2 = \frac{\hbar}{2m \omega} \int dx \phi_n^*(x) (a^\dagger + a)^2 \phi_n(x)
\]

\[
= \frac{\hbar}{2m \omega} (2n + 1)
\]

In the first line we have used the fact that the term

\[
\int dx \phi_n^*(x) (a^\dagger)^2 \phi_n(x)
\]

and the Hermitean conjugate term both vanish identically. In the second line, we have used the fact that the state \( \phi_n(x) \) is an eigenstate of the number operator \( \hat{a}^\dagger \hat{a} = \hat{n} \) with eigenvalue \( n \). Likewise

\[
\Delta p^2 = -\hbar^2 \frac{m \omega}{2} \int dx \phi_n^*(x) (a^\dagger - a)^2 \phi_n(x)
\]

\[
= \frac{\hbar m \omega}{2} (2n + 1)
\]

Combining these, we find the equality

\[
\Delta p_{\text{rms}} \Delta x_{\text{rms}} = \frac{\hbar}{2} (2n + 1)
\]  

(1088)

4.2.11 Exercise 71

A particle is moving in one dimension in a potential \( V(x) \) which is given by

\[
V(x) = \begin{cases} 
\frac{m \omega^2}{2} x^2 & x > 0 \\
\to \infty & x < 0
\end{cases}
\]  

(1089)

Find the energy eigenfunctions and eigenvalues.
4.2.12 Time Development of the Harmonic Oscillator

Given an initial condition \( \Psi(x, 0) \), one can expand this initial wave function in terms of the energy eigenstates \( \phi_n(x) \) of the harmonic oscillator via

\[
\Psi(x; 0) = \sum_n C_n \phi_n(x) \quad (1090)
\]

where the expansion coefficients may be found from

\[
C_n = \int_{-\infty}^{+\infty} dx \, \phi_n^*(x) \, \Psi(x; 0) \quad (1091)
\]

The wave function at future times \( t \) can be found from the solution of the Schrödinger equation, and as the Hamiltonian is time independent the solution can be expressed as

\[
\Psi(x; t) = \exp \left[ -i \frac{\hat{H}}{\hbar} t \right] \Psi(x; 0) \quad (1092)
\]

which gives rise to the expression for the time-dependent wave function as

\[
\Psi(x; t) = \sum_n C_n \exp \left[ -i \frac{\hat{H}}{\hbar} t \right] \phi_n(x) \quad (1093)
\]

since \( \phi_n(x) \) satisfy the energy eigenvalue equation

\[
\hat{H} \phi_n(x) = E_n \phi_n(x) \quad (1094)
\]

The motion of the particle can be viewed through examination of the average position \( \bar{x}(t) \) or momentum \( \bar{p}(t) \).

The average position is given by the expectation value

\[
\bar{x}(t) = \int_{-\infty}^{+\infty} dx \, \Psi^*(x; t) \, x \, \Psi(x; t) \quad (1095)
\]

which, on using the expression in eqn(1093), leads to

\[
\bar{x}(t) = \sum_{n,m} C^*_m C_n \exp \left[ + i \frac{(E_m - E_n)}{\hbar} t \right] \int_{-\infty}^{+\infty} dx \, \phi^*_m(x) \, x \, \phi_n(x) \quad (1096)
\]
The matrix elements of $x$ between the two energy eigenfunctions can be evaluated by expressing the $x$ in terms of the raising and lowering operators,

$$
x = \sqrt{\frac{\hbar}{m \omega}} \frac{1}{2} \left( \xi + \frac{\partial}{\partial \xi} \xi - \frac{\partial}{\partial \xi} \right)
= \sqrt{\frac{\hbar}{2 m \omega}} \left( a + a^\dagger \right) \tag{1097}
$$

Then the matrix elements can be found to be

$$
\int_{-\infty}^{+\infty} dx \, \phi_n^*(x) \, x \, \phi_n(x) = \sqrt{\frac{\hbar}{2 m \omega}} \left( \sqrt{n+1} \, \delta_{m,n+1} + \sqrt{n} \, \delta_{m,n-1} \right) \tag{1098}
$$

On substituting this expression back into eqn(1096) and performing the double summation and then using $E_{n+1} - E_n = \hbar \omega$, one finds

$$
\bar{x}(t) = \int_{-\infty}^{+\infty} dx \, \Psi^*(x; t) \, x \, \Psi(x; t)
= \sqrt{\frac{\hbar}{2 m \omega}} \sum_n \left( \sqrt{n+1} \, C_{n+1}^* C_n \exp \left[ + i \omega t \right] + \sqrt{n} \, C_{n-1}^* C_n \exp \left[ - i \omega t \right] \right)
= \sqrt{\frac{\hbar}{2 m \omega}} \sum_n \sqrt{n+1} \, \left( C_{n+1}^* C_n \exp \left[ + i \omega t \right] + C_n^* C_{n+1} \exp \left[ - i \omega t \right] \right) \tag{1099}
$$

where we have shifted the summation index by one in the second term. Since the first term is equal to the complex conjugate of the second term, the expectation value is real. This is as it must be, because $x$ is a Hermitean operator. Let us denote the expansion coefficients in terms of an amplitude and phase

$$
C_n = | C_n | \exp \left[ i \varphi_n \right] \tag{1100}
$$

then we have

$$
\bar{x}(t) = \sqrt{\frac{2 \hbar}{m \omega}} \sum_n \sqrt{n+1} \, | C_{n+1} | \, | C_n | \cos \left( \omega t + \varphi_n - \varphi_{n+1} \right) \tag{1101}
$$

Hence, the position oscillates with frequency $\omega$, just like the classical value. However, if the phase differences $\varphi_{n+1} - \varphi_n$ are randomly distributed, destructive interference may mask the oscillations.
One can evaluate the expectation value of the momentum via a similar procedure. The expectation value is given by

\[ p(t) = -i \hbar \int_{-\infty}^{+\infty} dx \left( \Psi^*(x; t) \frac{\partial}{\partial x} \Psi(x; t) \right) \]  

which yields

\[ p(t) = -i \hbar \sum_{n,m} C_m^* C_n \exp \left[ +i \left( \frac{E_m - E_n}{\hbar} \right) t \right] \int_{-\infty}^{+\infty} dx \phi_m^*(x) \frac{\partial}{\partial x} \phi_n(x) \]  

The matrix elements can be evaluated by expressing the derivative in terms of the raising and lowering operators

\[ \frac{\partial}{\partial x} = \sqrt{\frac{m \omega}{2 \hbar}} (a - a^\dagger) \]  

Hence, we have the matrix elements

\[ \int_{-\infty}^{+\infty} dx \phi_m^*(x) \frac{\partial}{\partial x} \phi_n(x) = \sqrt{\frac{m \omega}{2 \hbar}} \left( \sqrt{n} \delta_{m,n-1} - \sqrt{n+1} \delta_{m,n+1} \right) \]

On substituting the above matrix elements into the expectation value of the momentum, one finds

\[ p(t) = -\hbar \sqrt{\frac{2 m \omega}{\hbar}} \sum_n \left| C_{n+1} \right| \left| C_n \right| \sqrt{n} \sin \left( \omega t + \varphi_n - \varphi_{n+1} \right) \]

Thus, we see that the average momentum oscillates out of phase with the average position, and

\[ p(t) = m \frac{\partial}{\partial t} x(t) \]

which is just the same as the classical mechanical expression.

4.2.13 Exercise 72

Consider a harmonic oscillator in a state given by

\[ \Psi(x) = \frac{1}{\sqrt{2^s s}} \sum_{n=N-s}^{n=N+s} \exp \left[ -i \frac{n}{2} \right] \phi_n(x) \]
where $\phi_n(x)$ is the $n$-th excited state of the harmonic oscillator and $N \gg s \gg 1$. Find the time dependence of $\pi(t)$ and $p(t)$. Compare these expectation values with the classical expressions.

4.2.14 Solution 72

This type of state is a coherent state as it is a superposition of a very large number of energy eigenstates, where the exists a definite phase relation between the component states. The time dependence of the coherent states is given by

$$\Psi(x,t) = \frac{1}{\sqrt{2^s}} \sum_{n=N-s}^{n=N+s} \exp \left[-i n \varphi \right] \exp \left[-i n \omega t \right] \phi_n(x) \quad (1109)$$

As a result, the component states always have a simple phase relationship between them.

The expectation value of $\hat{x}$ is given by

$$\overline{x(t)} = \frac{1}{2^s} \sum_{n,n'} \exp \left[i \left(n' - n \right) \left( \varphi + \omega t \right) \right] \int_{-\infty}^{\infty} dx \phi_{n'}^*(x) x \phi_n(x) \quad (1110)$$

However, the operator $\hat{x}$ can be expressed in terms of the creation and annihilation operators via

$$\hat{x} = \sqrt{\frac{\hbar}{2m \omega}} \left(a^\dagger + a \right) \quad (1111)$$

Then, the matrix elements of $\hat{x}$ between the energy eigenstates $\phi_n(x)$ and $\phi_{n'}^*(x)$ can be evaluated as

$$\int_{-\infty}^{\infty} dx \phi_{n'}^*(x) x \phi_n(x) = \sqrt{\frac{\hbar}{2m \omega}} \left( \delta_{n',n+1} \sqrt{n+1} + \delta_{n',n-1} \sqrt{n} \right) \quad (1112)$$

Thus, the expectation value is calculated as

$$\overline{x(t)} = \frac{1}{2^s} \sqrt{\frac{\hbar}{2m \omega}} \sum_{n,n'} \left( \sqrt{n+1} \exp \left[i \left( \varphi + \omega t \right) \right] \delta_{n',n+1} 
+ \sqrt{n} \exp \left[-i \left( \varphi + \omega t \right) \right] \delta_{n',n-1} \right)$$

(1113)

If one only retains the terms of leading order in $\frac{1}{N}$ and $\frac{1}{s}$, one finds that the expectation value of the position is given by

$$\overline{x(t)} = \sqrt{\frac{\hbar N}{2m \omega}} \cos \left( \omega t + \varphi \right) \quad (1114)$$

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Likewise, for the expectation values of the momentum, one can show that

\[ \overline{p(t)} = -\sqrt{\frac{m \omega N}{2 \hbar}} \sin(\omega t + \varphi) \]  

(1115)

The expectation value of the momentum is related to the expectation value of the position via the classical relation

\[ \hat{p}(t) = m \frac{\partial x(t)}{\partial t} \]  

(1116)

Schrödinger\(^{12}\) determined that the coherent state

\[ \Psi_\lambda(x) = \exp\left[-\frac{1}{2}\lambda^2\right] \sum_{n=0}^{\infty} \frac{\lambda^n \exp\left[-i n \varphi\right]}{\sqrt{n!}} \phi_n(x) \]  

(1117)

is an exact eigenstate of the lowering operator. This can be seen as

\[ a \Psi_\lambda(x) = \lambda \exp\left[-i \varphi\right] \Psi_\lambda(x) \]  

(1118)

Coherent states play an important role in laser optics as they approximate classical states, containing many quanta, that have definite phases.

### 4.2.15 Hermite Polynomials

The Hermite Polynomials \( H_n(z) \) can be defined as

\[ H_n(z) = \left(-1\right)^n \exp\left[z^2\right] \frac{\partial^n}{\partial z^n} \exp\left[-z^2\right] \]  

(1119)

From this definition, we can see that they satisfy the differential equation

\[ \frac{\partial^2}{\partial z^2} H_n - 2z \frac{\partial}{\partial z} H_n + 2n H_n(z) = 0 \]  

(1120)

This is proved by evaluating the first and second derivatives of \( H_n(z) \). The first derivative is given by

\[ \frac{\partial}{\partial z} H_n = 2z \left(-1\right)^n \exp\left[z^2\right] \frac{\partial^n}{\partial z^n} \exp\left[-z^2\right] \]

\[ - \left(-1\right)^n \exp\left[z^2\right] \frac{\partial^n}{\partial z^n} 2z \exp\left[-z^2\right] \]  

(1121)

\(^{12}\)E. Schrödinger, Naturwissenschaften, 14, 664 (1926).
and the second derivative is given by
\[
\frac{\partial^2}{\partial z^2} H_n = (4 z^2 + 2)(-1)^n \exp\left[ + z^2 \right] \frac{\partial^n}{\partial z^n} \exp\left[ - z^2 \right] \\
- 8 z (-1)^n \exp\left[ + z^2 \right] \frac{\partial^n}{\partial z^n} z \exp\left[ - z^2 \right] \\
+ ( - 1 )^n \exp\left[ + z^2 \right] \frac{\partial^n}{\partial z^n} (4 z^2 - 2) \exp\left[ - z^2 \right]
\]

(1122)

The terms +2 and −2 in the round brackets cancel. On forming the combination
\[
\frac{\partial^2}{\partial z^2} H_n - 2 z \frac{\partial}{\partial z} H_n
\]
we have
\[
\frac{\partial^2}{\partial z^2} H_n - 2 z \frac{\partial}{\partial z} H_n = - 4 z (-1)^n \exp\left[ + z^2 \right] \frac{\partial^n}{\partial z^n} z \exp\left[ - z^2 \right] \\
+ ( - 1 )^n \exp\left[ + z^2 \right] \frac{\partial^n}{\partial z^n} 4 z^2 \exp\left[ - z^2 \right]
\]

(1124)

The righthand side can be simplified as
\[
= + 2 z (-1)^n \exp\left[ + z^2 \right] \frac{\partial^{n+1}}{\partial z^{n+1}} \exp\left[ - z^2 \right] \\
- ( - 1 )^n \exp\left[ + z^2 \right] \frac{\partial^n}{\partial z^n} 2 z \frac{\partial}{\partial z} \exp\left[ - z^2 \right]
\]

(1125)

which after commuting the z in the last term to the front, we have
\[
= - 2 n (-1)^n \exp\left[ + z^2 \right] \frac{\partial^n}{\partial z^n} \exp\left[ - z^2 \right]
= - 2 n H_n(z)
\]

(1126)

Thus, we have found that the Hermite polynomials satisfy the equation
\[
\frac{\partial^2}{\partial z^2} H_n - 2 z \frac{\partial}{\partial z} H_n + 2 n H_n(z) = 0
\]

(1127)

as was to be proved.

This differential equation also has an integral representation of its solution. The integral representation of the solution is given by
\[
H_n(z) = \frac{2^n}{\sqrt{n!}} \int_{-\infty}^{+\infty} du \exp\left[ - u^2 \right] \left( z + i u \right)^n
\]

(1128)
This can be shown by first evaluating the terms
\[
\frac{\partial^2}{\partial z^2} H_n(z) = n (n - 1) \frac{2^n}{\sqrt{\pi}} \int_{-\infty}^{+\infty} du \exp\left[ -u^2 \right] (z + i u)^{n-2}
\]
\[
\frac{\partial}{\partial z} H_n(z) = n \frac{2^n}{\sqrt{\pi}} \int_{-\infty}^{+\infty} du \exp\left[ -u^2 \right] (z + i u)^{n-1}
\]
(1129)
and then by forming the expression
\[
2 n H_n(z) - 2 z \frac{\partial}{\partial z} H_n(z)
\]
\[
= i n \frac{2^n}{\sqrt{\pi}} \int_{-\infty}^{+\infty} du \ 2 u \exp\left[ -u^2 \right] (z + i u)^{n-1}
\]
\[
= -i n \frac{2^n}{\sqrt{\pi}} \int_{-\infty}^{+\infty} du \left( \frac{\partial}{\partial u} \exp\left[ -u^2 \right] \right) (z + i u)^{n-1}
\]
(1130)
On integrating by parts, one finds this simplifies to
\[
= i n \frac{2^n}{\sqrt{\pi}} \int_{-\infty}^{+\infty} du \exp\left[ -u^2 \right] \frac{\partial}{\partial u} \left( z + i u \right)^{n-1}
\]
\[
= - n(n-1) \frac{2^n}{\sqrt{\pi}} \int_{-\infty}^{+\infty} du \exp\left[ -u^2 \right] (z + i u)^{n-2}
\]
\[
= - \frac{\partial^2}{\partial z^2} H_n(z)
\]
(1131)
Thus, the integral expression of eqn(1128) satisfies the differential equation
\[
\frac{\partial^2}{\partial z^2} H_n - 2 z \frac{\partial}{\partial z} H_n + 2 n H_n(z) = 0
\]
(1132)
and, therefore, is a representation of the Hermite polynomials. The integral representation can be used to yield the explicit forms of low-order Hermite polynomials. Expressions for first few lowest order Hermite polynomials \(H_n(z)\) are given in Table(2).

We can show that
\[
\frac{\partial}{\partial z} H_n(z) = 2 n H_{n-1}(z)
\]
(1133)
This is seen by examining the first derivative
\[
\frac{\partial}{\partial z} H_n = 2 z ( -1)^n \exp\left[ +z^2 \right] \frac{\partial^n}{\partial z^n} \exp\left[ -z^2 \right]
\]
\[
- ( -1)^n \exp\left[ +z^2 \right] \frac{\partial^n}{\partial z^n} 2 z \exp\left[ -z^2 \right]
\]
(1134)
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Table 2: The Lowest Order Hermite Polynomials $H_n(z)$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$H_n(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$H_0(z)$ = 1</td>
</tr>
<tr>
<td>1</td>
<td>$H_1(z)$ = 2 $z$</td>
</tr>
<tr>
<td>2</td>
<td>$H_2(z)$ = 4 $z^2$ − 2</td>
</tr>
<tr>
<td>3</td>
<td>$H_3(z)$ = 8 $z^3$ − 12 $z$</td>
</tr>
<tr>
<td>4</td>
<td>$H_4(z)$ = 16 $z^4$ − 48 $z^2$ + 12</td>
</tr>
<tr>
<td>5</td>
<td>$H_5(z)$ = 32 $z^5$ − 160 $z^3$ + 120 $z$</td>
</tr>
</tbody>
</table>

On commuting the term proportional to $z$ in the second term to the front, we have

$$
\frac{\partial}{\partial z} H_n = -2n (-1)^n \exp\left[-z^2\right] \frac{\partial^{n-1}}{\partial z^{n-1}} \exp\left[-z^2\right] = 2n H_{n-1}(z) \tag{1135}
$$

Thus, the derivative of the $n$-th order Hermite polynomial is related to the Hermite polynomial of $(n-1)$-th order.

From this relationship, we can derive the generating function for the Hermite polynomials

$$
\exp\left[-t^2 + 2tz\right] = \sum_{n=0}^{\infty} \frac{H_n(z)}{n!} t^n \tag{1136}
$$

The proof starts with examining $F(z,t)$, which is defined via

$$
F(z,t) = \sum_{n=0}^{\infty} \frac{H_n(z)}{n!} t^n \tag{1137}
$$

On taking the derivative with respect to $z$, one has

$$
\frac{\partial}{\partial z} F(z,t) = \sum_{n=0}^{\infty} \frac{\partial}{\partial z} \frac{H_n(z)}{n!} t^n = \sum_{n=0}^{\infty} 2n \frac{H_{n-1}(z)}{n!} t^n = 2 \sum_{n=0}^{\infty} \frac{H_{n-1}(z)}{(n-1)!} t^n = 2t F(z,t) \tag{1138}
$$

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The equation
\[ \frac{\partial}{\partial z} F(z,t) = 2t F(z,t) \]  
(1139)
can be integrated to yield
\[ \ln \frac{F(z,t)}{F(0,t)} = 2t z \]  
(1140)
Thus, we have
\[ F(z,t) = F(0,t) \exp \left[ 2z t \right] \]  
(1141)
We can evaluate \( F(0,t) \) from \( H_n(0) \) as
\[ F(0,t) = \sum_{n=0}^{\infty} \frac{H_n(0)}{n!} t^n \]  
(1142)
We shall re-write the expression for \( H_n(z) \) in terms of a power series and then set \( z = 0 \),
\[ H_n(z) = (-1)^n \exp \left[ +z^2 \right] \frac{\partial^n}{\partial z^n} \sum_{m} (-1)^m \frac{(z^2)^m}{m!} \]  
(1143)
The only term that remains on setting \( z = 0 \) is the term with \( n = 2m \). Hence, only the even order Hermite polynomials remain finite at \( z = 0 \). We find that these are given by
\[ H_{2m}(0) = (-1)^m \frac{(2m)!}{m!} \]  
(1144)
Thus, we have
\[ F(0,t) = \sum_{n=0}^{\infty} \frac{H_n(0)}{n!} t^n \]
\[ = \sum_{m=0}^{\infty} \frac{(-1)^m t^{2m}}{m!} \]
\[ = \exp \left[ -t^2 \right] \]  
(1145)
Hence, we obtain
\[ F(z,t) = \exp \left[ +2z t - t^2 \right] \]
\[ = \sum_{n=0}^{\infty} \frac{H_n(z)}{n!} t^n \]  
(1146)
which is the generating function expansion for the Hermite polynomials.
4.2.16 Exercise 73

The initial wave function of a particle of mass \( m \) in a harmonic potential of frequency \( \omega \) is given by

\[
\Psi(x,0) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \exp \left[ -\frac{m \omega}{2 \hbar} (x - a)^2 \right] \tag{1147}
\]

Find the probability that a measurement of the energy will give the result

\[
E_n = \hbar \omega \left( n + \frac{1}{2} \right) \tag{1148}
\]

4.2.17 Solution 73

Using the generating function expansion, we can decompose the initial wave function as

\[
\Psi(x,0) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \exp \left[ -\frac{m \omega}{2 \hbar} (x - a)^2 \right]
\]

\[
= \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \exp \left[ -\frac{m \omega}{2 \hbar} x^2 \right]
\]

\[
\times \exp \left[ -\frac{m \omega}{4 \hbar} a^2 + \frac{m \omega}{\hbar} x a \right]
\]

\[
= \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \exp \left[ -\frac{m \omega}{2 \hbar} x^2 \right]
\]

\[
\times \exp \left[ -\frac{m \omega}{4 \hbar} a^2 \right] \exp \left[ -\frac{m \omega}{4 \hbar} a^2 + \frac{2 m \omega}{\hbar} x a \right]
\]

\[
= \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \exp \left[ -\frac{m \omega}{4 \hbar} a^2 \right]
\]

\[
\times \sum_n \exp \left[ -\frac{m \omega}{2 \hbar} x^2 \right] \frac{H_n\left( \sqrt{\frac{m \omega}{\hbar}} x \right)}{n!} \left( \frac{m \omega a^2}{4 \hbar} \right)^{\frac{n}{2}}
\]

\[
= \exp \left[ -\frac{m \omega}{4 \hbar} a^2 \right] \sum_n \frac{\phi_n(x)}{\sqrt{n!}} \left( \frac{m \omega a^2}{2 \hbar} \right)^{\frac{n}{2}} \tag{1149}
\]

where \( \phi_n(x) \) is the \( n \)-th energy eigenfunction given by

\[
\phi_n(x) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \exp \left[ -\frac{m \omega}{2 \hbar} x^2 \right] H_n\left( \sqrt{\frac{m \omega}{\hbar}} x \right) \tag{1150}
\]
Thus, as the probability $P(n)$ is given by the square of the expansion coefficient, we have

$$P(n) = \left( \frac{m \omega a^2}{2 \hbar} \right)^n \frac{1}{n!} \exp \left[ - \frac{m \omega}{2 \hbar} a^2 \right] \tag{1151}$$

4.2.18 Exercise 74

Find the time dependence of the state which has the initial wave function

$$\Psi(x, 0) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \exp \left[ - \frac{m \omega}{2 \hbar} \left( x - a \right)^2 \right] \tag{1152}$$

and, hence, find the time dependence of the probability density $P(x, t)$ of finding the particle at position $x$.

4.2.19 Solution 74

From the previous example, we have the expansion of the initial wave function in terms of energy eigenstates,

$$\Psi(x, 0) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \exp \left[ - \frac{m \omega}{2 \hbar} \left( x - a \right)^2 \right] \tag{1153}$$

The time dependence of the wave function is then found from the time dependence of the energy eigenstates

$$\Psi(x, t) = \exp \left[ - i \frac{\hat{H} t}{\hbar} \right] \Psi(x, 0) = \exp \left[ - i \frac{\omega t}{2} \right] \exp \left[ - \frac{m \omega}{4 \hbar} a^2 \right] \times \sum_n \exp \left[ - i n \omega t \right] \frac{\phi_n(x)}{\sqrt{n!}} \left( \frac{m \omega a^2}{2 \hbar} \right)^{\frac{n}{2}} \tag{1154}$$

which can be re-summed to yield

$$\Psi(x, t) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \exp \left[ - i \frac{\omega t}{2} \right] \exp \left[ - \frac{m \omega}{2 \hbar} x^2 \right] \tag{1155}$$
\[ \times \exp \left[ - \frac{m \omega}{4 \hbar} a^2 \left( 1 + e^{-2i\omega t} \right) + \frac{m \omega}{\hbar} x a e^{-i\omega t} \right] \]  

\text{(1155)}

Hence, we find the probability density \( P(x, t) \) as

\[
P(x, t) = |\Psi(x, t)|^2 = \left( \frac{m \omega}{\pi \hbar} \right)^\frac{1}{2} \exp \left[ - \frac{m \omega}{\hbar} (x - a \cos \omega t)^2 \right] \text{(1156)}
\]

Hence we see that the state, which was initially displaced from the equilibrium state by a distance \( a \), performs oscillations of amplitude \( a \) and frequency \( \omega \) just like a classical particle in the same potential.

\[ \text{4.2.20 The Completeness Condition} \]

As the Hamiltonian operator for the harmonic oscillator is a Hermitean operator, the energy eigenfunctions form a complete set. The completeness condition for the harmonic oscillator energy eigenfunctions can be proved by using the integral representation and the generating function. We take the generating function

\[
F(x, t) = \exp \left[ + 2x t - t^2 \right]
\]

\[
= \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^n \text{(1157)}
\]

then let \( t = y + iu \), so

\[
\exp \left[ + 2x y - y^2 \right] \exp \left[ 2i(x - y)u + u^2 \right] = \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} (y + iu)^n \text{(1158)}
\]

On multiplying this equation by \( \exp \left[ - u^2 \right] \) and then integrating over \( u \) from \(-\infty\) to \(+\infty\), we find

\[
\int_{-\infty}^{\infty} du \exp \left[ + 2x y - y^2 \right] \exp \left[ 2i(x - y)u \right] = \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} \int_{-\infty}^{\infty} du \exp \left[ - u^2 \right] (y + iu)^n \text{(1159)}
\]
so we have

\[
\pi \exp \left[ + 2x y - y^2 \right] \delta(x - y) = \frac{\sqrt{\pi}}{2^n} \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} H_n(y) \quad (1160)
\]

The above equation can be rearranged to yield

\[
\delta(x - y) = \sum_{n=0}^{\infty} \frac{1}{2^n n! \sqrt{\pi}} \exp \left[ - \frac{x^2}{2} \right] H_n(x) \exp \left[ - \frac{y^2}{2} \right] H_n(y)
\quad (1161)
\]

On identifying the normalized energy eigenfunctions \( \phi_n(x) \) with the product of the exponential and the Hermite polynomials, one finds the completeness relation for the energy eigenfunctions of the Hermitian Hamilton operator

\[
\delta(x - y) = \sum_n \phi_n^*(x) \phi_n(y) \quad (1162)
\]

The completeness condition allows an arbitrary function to be expanded in terms of the energy eigenstates.

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4.3 Dual-symmetry

Let us assume that we know the ground state solution of the energy eigenvalue equation for a particle moving in one dimension in the presence of a specific potential \( V(x) \). Let the ground state energy be denoted by \( E_0 \) and the ground state wave function be denoted by \( \phi_0(x) \). Using these definitions, the energy eigenvalue equation has the form

\[
\hat{H} \phi_0(x) = E_0 \phi_0(x)
\]

Alternatively, we can identify \( \hat{H} - E_0 \) with an operator

\[
\hat{H} - E_0 = \hbar^2 \frac{\partial^2}{\partial x^2} + \{ \hat{A}, \hat{A}^\dagger \}
\]

This (energy-shifted) Hamiltonian of eqn(1164) can be factorized as the product of a pair of Hermitean conjugate operators. The first operator is defined by

\[
\hat{A} = \frac{\hbar}{\sqrt{2m}} \left[ \frac{\partial}{\partial x} - \frac{\phi_0''(x)}{\phi_0(x)} \right]
\]

and its Hermitean conjugate is then found to be

\[
\hat{A}^\dagger = \frac{\hbar}{\sqrt{2m}} \left[ - \frac{\partial}{\partial x} - \frac{\phi_0'(x)}{\phi_0(x)} \right]
\]

The Hamiltonian (up to the definition of the ground state energy) is given by the product

\[
\hat{H} - E_0 = \hat{A}^\dagger \hat{A}
\]

The pair of Hermitean conjugate operators have a commutation relation given by

\[
[ \hat{A}, \hat{A}^\dagger ] = 2 \hbar \frac{\partial}{\partial x} \left[ \left( \frac{\phi_0'(x)}{\phi_0(x)} \right)^2 - \frac{\phi_0''(x)}{\phi_0(x)} \right]
\]

For the case of the Harmonic Oscillator, \( \hat{A} \) and \( \hat{A}^\dagger \) respectively are proportional to the lowering and raising operators, and their commutator is merely the constant \( \hbar \omega \).

The dual partner \( \hat{H}_d \) of the Hamiltonian \( \hat{H} \) is given by the product of the pair of operators taken in the reverse order

\[
\hat{H}_d = \hat{A}^\dagger \hat{A}
\]

The dual potential \( V_d(x) \) is defined in terms of the dual Hamiltonian. The dual potential is found to be

\[
V_d(x) = V(x) - E_0 + [ \hat{A}, \hat{A}^\dagger ]
\]

\[
= V(x) - E_0 - \frac{\hbar^2}{m} \frac{\partial}{\partial x} \left( \frac{\phi_0'(x)}{\phi_0(x)} \right)
\]
The pair of potentials $V(x)$ and $V_d(x)$ are dual partner potentials. For the Harmonic Oscillator, the potential and the dual potential are the same except for a constant shift of the energy.

In general, $V_d(x)$ and $V(x)$ have the same energy level spectrum, $E_n - E_0 = E_{n'}^d$. The exceptional case is the zero energy eigenvalue for the ground state of $V(x)$, and this exception occurs since the operator $\hat{A}$ annihilates the ground state. The equality between the shifted eigenvalues is proved by noting that, if

$$\hat{H} \phi_n = (E_n - E_0) \phi_n$$

then

$$\hat{H}_d \left( \hat{A} \phi_n \right) = \hat{A} \hat{A}^\dagger \left( \hat{A} \phi_n \right)$$

$$= \hat{A} \left( \hat{H} \phi_n \right)$$

$$= (E_n - E_0) \left( \hat{A} \phi_n \right)$$

Hence, $E_{n'}^d = (E_n - E_0)$, unless $\hat{A} \phi_n = 0$. Likewise, one can establish the inverse relationship between the eigenstates of $\hat{H}_d$ with the eigenstates of $\hat{H}$. That is, if $\phi_n^d(x)$ is an eigenstate of $\hat{H}_d$ with eigenvalue $E_{n'}^d$, then $\hat{A}^\dagger \phi_n^d(x)$ is an eigenstate of $\hat{H}$ with eigenvalue $E_n$. Thus, $\hat{A}$ and $\hat{A}^\dagger$ connect states of different Hamiltonians that have the same energies.

**Duality and the Infinite Square Well**

The infinite square well has an infinite number of bound states with energy eigenvalues given by

$$E_n = \frac{\hbar^2}{2m} \left( \frac{\pi n}{L} \right)^2$$

and energy eigenfunctions are given by

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n \pi x}{L} \right)$$

where $n$ is a positive integer, excluding zero. Since the logarithmic derivative of the ground state wave function is given by

$$\left( \frac{\phi'_1(x)}{\phi_1(x)} \right) = \left( \frac{\pi}{L} \right) \cot \left( \frac{\pi x}{L} \right)$$

the dual partner potential is found to be

$$V_d(x) = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 \left[ \csc^2 \left( \frac{\pi x}{L} \right) - 1 \right]$$
The dual energy eigenstates are given, up to an arbitrary multiplicative constant, by

$$
\phi_n^d(x) \propto \hat{A} \phi_n(x) \\
\propto \left[ \frac{\partial}{\partial x} - \frac{\pi}{L} \cot \left( \frac{\pi x}{L} \right) \right] \sin \left( \frac{n \pi x}{L} \right) \\
\propto n \cos \left( \frac{n \pi x}{L} \right) - \cos \left( \frac{\pi x}{L} \right) \left[ \sin \left( \frac{n \pi x}{L} \right) \right] (1177)
$$

where $\phi_1^d(x)$ and $E_1^d$ are absent.
Figure 65: The potential $V^d(x)$ dual to the infinite square well potential. The energy eigenvalues are marked by the dashed horizontal lines.

4.4 Bargmann Potentials

Bargmann potentials are an interesting class of one-dimensional potentials. Bargmann potentials have the very unusual property that they are reflectionless potentials, which means that a plane wave incident on the potential does not produce a reflected wave. The potential produces bound states and does have an effect on the states with $E > 0$ in that the transmitted wave experiences a phase shift relative to the incident wave.

We shall consider solutions of the family of energy eigenvalue equations governed by the integer parameter $n$. The eigenvalue equation is given by

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi_{\alpha,n}(x) - V_0 n \left( n + 1 \right) \text{sech}^2 \left( \frac{x}{\xi} \right) \Psi_{\alpha,n}(x) = E_{\alpha} \Psi_{\alpha,n}(x)$$

(1178)

where the length scale $\xi$ is given by

$$\xi^2 = \frac{\hbar^2}{2m V_0}$$

(1179)
Figure 66: The lowest two energy eigenstates $\phi^d_n(x)$ of the dual potential.

For $n = 0$, the Bargmann energy eigenvalue equation reduces to the free particle problem. The general solution of the free particle problem is simply

$$\Psi_{\alpha,0}(x) = A \exp \left[ + i k x \right] + B \exp \left[ - i k x \right]$$

(1180)

where the energy eigenvalue is given by

$$E_{\alpha,0} = \frac{\hbar^2 k^2}{2 m}$$

(1181)

We can relate the general scattering solution for arbitrary $n$ to the general solution for the free particle problem (where $n = 0$) by an iterative method. This relation involves dual-symmetry. We shall show that

$$\Psi_{\alpha,n}(x) = \left[ \xi \frac{\partial}{\partial x} - n \tanh \left( \frac{x}{\xi} \right) \right] \Psi_{\alpha,n-1}(x)$$

(1182)

First let us change variable from $x$ to the dimensionless variable $z = \frac{x}{\xi}$. Then the Bargmann equation takes the form

$$\frac{\partial^2}{\partial z^2} \Phi_{\alpha,n}(z) + n (n + 1) \text{sech}^2 z \Phi_{\alpha,n}(z) = -\frac{2 m E_\alpha \xi^2}{\hbar^2} \Phi_{\alpha,n}(z)$$

(1183)
Figure 67: Bargmann potentials, $V_n(x)$ for various values of $n$.

Let us assume that $\Phi_{\alpha,n-1}(z)$ satisfies the Bargmann equation of order $n-1$. Then on pre-multiplying the eigenvalue equation by

$$\hat{M}_n = \left[ \frac{\partial}{\partial z} - n \tanh z \right]$$

we have

$$\left[ \frac{\partial}{\partial z} - n \tanh z \right] \left[ \frac{\partial^2}{\partial z^2} \Phi_{\alpha,n-1}(z) + n \left( n - 1 \right) \text{sech}^2 z \Phi_{\alpha,n-1}(z) \right] = -\frac{2mE_\alpha}{\hbar^2} \left[ \frac{\partial}{\partial z} - n \tanh z \right] \Phi_{\alpha,n-1}(z)$$

The Hamiltonian $\hat{H}_n$ depends on $n$ via

$$\hat{H}_n = -\frac{\hbar^2}{2m\xi^2} \left[ \frac{\partial^2}{\partial z^2} + n \left( n + 1 \right) \text{sech}^2 z \right]$$

On commuting $\hat{M}_n$ with $\hat{H}_{n-1}$, we obtain

$$\hat{M}_n \hat{H}_{n-1} = \hat{H}_{n-1} \hat{M}_n - n \frac{\hbar^2}{m\xi^2} \text{sech}^2 z \left[ \frac{\partial}{\partial z} - n \tanh z \right]$$

$$= \hat{H}_n \hat{M}_n$$

(1187)
Thus, we find that
\[ \hat{H}_n \hat{M}_n \Phi_{\alpha,n-1} = E_{\alpha} \hat{M}_n \Phi_{\alpha,n-1} \] (1188)

This shows that the wave function
\[ \Phi_{\alpha,n}(z) = \hat{M}_n \Phi_{\alpha,n-1}(z) = \left[ \frac{\partial}{\partial z} - n \tanh z \right] \Phi_{\alpha,n-1}(z) \] (1189)
is an eigenfunction of \( \hat{H}_n \) with the same eigenvalue \( E_{\alpha} \).

### 4.4.1 Exercise 75
Show that the raising operator \( \hat{M}_n \) satisfies the relation
\[ \hat{M}_n \hat{H}_{n-1} = \hat{H}_n \hat{M}_n \] (1190)

### 4.4.2 Solution 75
In dimensionless units, the raising operator is given by
\[ \hat{M}_n = \frac{\partial}{\partial z} - n \tanh z \] (1191)

and the Hamiltonian \( \hat{H}_n \) containing the \( n \)-th order Bargmann potential can be put into the form
\[ \hat{H}_n = -\left( \frac{\hbar^2}{2 m \xi^2} \right) \left[ \frac{\partial^2}{\partial z^2} + n (n + 1) \sech^2 z \right] \] (1192)

The identity can be proved by starting with the product \( \hat{M}_n \hat{H}_{n-1} \) and re-writing it as
\[ \hat{M}_n \hat{H}_{n-1} = \hat{H}_{n-1} \hat{M}_n + [ \hat{M}_n , \hat{H}_{n-1} ] \] (1193)

The commutator can be evaluated as
\[ [ \hat{M}_n , \hat{H}_{n-1} ] = -\left( \frac{\hbar^2}{2 m \xi^2} \right) \left[ \frac{\partial}{\partial z} , n (n - 1) \sech^2 z \right] + \left( \frac{\hbar^2}{2 m \xi^2} \right) n [ \tanh z , \frac{\partial^2}{\partial z^2} ] \]
\[
= 2n(n-1) \left( \frac{\hbar^2}{2m \xi^2} \right) \text{sech}^2 z \tanh z - n \left( \frac{\hbar^2}{2m \xi^2} \right) \left[ \frac{\partial^2}{\partial z^2} \right] \text{tanh} z
\]
\[
= \left( \frac{\hbar^2}{2m \xi^2} \right) 2n(n-1) \text{sech}^2 z \tanh z
\]
\[
- n \left( \frac{\hbar^2}{2m \xi^2} \right) \frac{\partial}{\partial z} \left[ \text{tanh} z \right] - n \left( \frac{\hbar^2}{2m \xi^2} \right) \left[ \frac{\partial}{\partial z} \right] \text{tanh} z
\]
\[
= 2n(n-1) \left( \frac{\hbar^2}{2m \xi^2} \right) \text{sech}^2 z \tanh z
\]
\[
- n \left( \frac{\hbar^2}{2m \xi^2} \right) \frac{\partial}{\partial z} \text{sech}^2 z - n \left( \frac{\hbar^2}{2m \xi^2} \right) \text{sech}^2 z \frac{\partial}{\partial z}
\]
\[
= 2n^2 \left( \frac{\hbar^2}{2m \xi^2} \right) \text{sech}^2 z \tanh z - 2n \left( \frac{\hbar^2}{2m \xi^2} \right) \text{sech}^2 z \frac{\partial}{\partial z}
\]
\[
= -2n \left( \frac{\hbar^2}{2m \xi^2} \right) \text{sech}^2 z \left[ \frac{\partial}{\partial z} - n \text{tanh} z \right]
\]
\[
= -2n \left( \frac{\hbar^2}{2m \xi^2} \right) \text{sech}^2 z \hat{M}_n \tag{1194}
\]

Inserting this in the expression (1193), one finds
\[
\hat{M}_n \hat{H}_{n-1} = \hat{H}_{n-1} \hat{M}_n - 2n \left( \frac{\hbar^2}{2m \xi^2} \right) \text{sech}^2 z \hat{M}_n
\]
\[
= \hat{H}_n \hat{M}_n \tag{1195}
\]
which proves the identity.

Starting from \( n = 0 \), one can generate all the scattering states by iteration,
\[
\Phi_{k,n}(z) = \hat{M}_n \hat{M}_{n-1} \ldots \hat{M}_2 \hat{M}_1 \Phi_{k,0}(z) \tag{1196}
\]

Let us note that at \( z \to +\infty \) the solution takes the asymptotic form
\[
\Phi_{k,n}(z) = A \exp \left[ +i k z \right] \prod_{m=1}^{m=n} \left( +i k - m \right)
\]
\[
+ B \exp \left[ -i k z \right] \prod_{m=1}^{m=n} \left( -i k - m \right) \tag{1197}
\]

whereas at \( z \to -\infty \) the solution takes the form
\[
\Phi_{k,n}(z) = A \exp \left[ +i k z \right] \prod_{m=1}^{m=n} \left( +i k + m \right)
\]
\[
+ B \exp \left[ -i k z \right] \prod_{m=1}^{m=n} \left( -i k + m \right) \tag{1198}
\]
On setting $B = 0$, a case which corresponds to an incident beam with momentum $p = \hbar k$, we see that there is no reflected beam and the transmitted beam has a phase which is different from that of the incident beam. The change of phase $2 \delta(k)$ is calculated from

$$\delta(k) = \sum_{m=1}^{m=n} \tan^{-1} \left( \frac{k}{m} \right)$$

(1199)

The phase shift $\delta(k)$ varies as $k$ is varied. The total variation of the phase shift

Figure 68: The $k$ dependence of the phase shift $\delta(k)$ for the scattering states of the $n = 4$ Bargmann potential.

is defined as

$$\delta(\infty) - \delta(0)$$

(1200)

and is equal to $n \frac{\pi}{2}$. The total change in the phase shift is related to the number of bound states of the equation through Levinson’s theorem\(^{13}\).

On increasing $n$ by unity, the number of bound states of the Bargmann increases by unity. Thus, the Bargmann equation of order $n$ has $n$ bound states. The lowest energy bound state is given by the un-normalized wave function

$$\Phi_{n,n}(z) = \text{sech}^n z$$

(1201)

Raising Operators for the Bargmann Potentials

Figure 69: A graphical description of the raising operators for the Bargmann equations. The raising operators $M_n$ transform the solutions of the $(n-1)$-th Bargmann potential to solutions of the $n$-th potential, but with the same energy eigenvalue.

and has a bound state energy given by

$$E_n = -\frac{\hbar^2}{2m\xi^2} n^2$$

(1202)

Then the higher energy bound states $\Phi_{m,n}(z)$ can be created from the corresponding bound states $\Phi_{m,m}(z)$ which have energies $E_m = -\frac{\hbar^2}{2m\xi^2} m^2$. The higher-energy bound states are found by operating on $\Phi_{m,m}(z)$ with the sequentially ordered product of operators $\hat{M}_n \hat{M}_{n-1} \ldots \hat{M}_{n'} \ldots \hat{M}_{m+2} \hat{M}_{m+1}$ (where $n \geq n' \geq m+1$). Thus, for example, the second lowest energy (un-normalized) eigenfunction of the $n$-th order Bargmann equation is

$$\Phi_{n-1,n}(z) = \hat{M}_n \Phi_{n-1,n-1}(z)$$

$$= \left[ \frac{\partial}{\partial z} - n \tanh z \right] \text{sech}^{n-1} z$$

$$= - (2n-1) \text{sech}^{n-1} z \tanh z$$

(1203)

which has the energy eigenvalue

$$E_{n-1} = -\frac{\hbar^2}{2m\xi^2} (n-1)^2$$

(1204)
4.4.3 Exercise 76
Find the eigenfunctions and eigenvalues of the Bargmann equation with index $n = 2$. Also show that the bound states are orthogonal to the scattering states.

Figure 70: The Bargmann potential for $n = 2$. There are two bound states and the bound state energies are denoted by horizontal lines.

4.4.4 Solution 76
In terms of the dimensionless variable $z$, lowest energy bound state of the $n$-th Bargmann potential has the wave function

$$\phi_{n,n}(z) = C \, \text{sech}^n z \quad (1205)$$

and the dimensionless energy eigenvalue is $E_n = -n^2$. The higher energy bound state is found by using the raising operator $M_n$ acting on the bound
states of the \((n - 1)\)-th Bargmann potential, i.e.,
\[
\phi_{m,n}(z) = \hat{M}_n \phi_{m,n-1}(z)
\] (1206)

The resulting bound state \(\phi_{m,n}(z)\) has energy \(E_m\). In this manner, we find that
\[
\phi_{n-1,n}(z) = \hat{M}_n \phi_{n-1,n-1}(z) = [\frac{\partial}{\partial z} - n \tanh z \sech^{n-1}z] = -(2n - 1) \sech^{n-1}z \tanh z
\] (1207)

The eigenfunction \(\phi_{n-1,n}(z)\) corresponds to the energy eigenvalue \(E_{n-1} = -(n - 1)^2\). Thus, for \(n = 2\), the two bound states are given by
\[
\phi_2(z) = \sech^2 z
\]
\[
\phi_1(z) = \sech z \tanh z
\] (1208)

The bound state wave functions are shown in fig(71).

Figure 71: The bound states of Bargmann potential for \(n = 2\). For \(n = 2\) there are two bound states, the two bound state wave functions are denoted by \(\Psi_0(x)\) and \(\Psi_1(x)\).
The scattering states are given by $\phi_k(z)$ which can be determined from the scattering states of the $n = 0$ potential, by using the raising operator twice. The scattering states for $n = 2$ are given by

$$\phi_k(z) = \hat{M}_2 \hat{M}_1 \left( A \exp \left[ + i k z \right] + B \exp \left[ - i k z \right] \right)$$

$$= \left[ \frac{\partial}{\partial z} - 2 \tanh z \right] \left[ \frac{\partial}{\partial z} - \tanh z \right] \left( A \exp \left[ + i k z \right] + B \exp \left[ - i k z \right] \right)$$

$$= \left( 2 - k^2 - 3 i k \tanh z - 3 \sech^2 z \right) A \exp \left[ + i k z \right]$$

$$+ \left( 2 - k^2 + 3 i k \tanh z - 3 \sech^2 z \right) B \exp \left[ - i k z \right]$$

(1209)

Note that on analytically continuing from $k$ to $i \kappa$, one finds that the asymptotic exponentially growing term, for both positive and negative $z$, has a vanishing coefficient in the asymptotic limit if $\kappa$ is equal to either 2 or 1. The solutions for these special values of $\kappa$ correspond to the bound states that we have already found.

It remains to show that the bound states are orthogonal to the scattering states. That is, we have to show that

$$\int_{-\infty}^{+\infty} dz \phi_m(z) \phi_k(z) = 0$$

(1210)

For the lowest bound state where $m = 2$, this requires that coefficients of $A$ and $B$ vanish separately. These both vanish if the integral

$$\int_{0}^{\infty} dz \cos k z \left( 2 - k^2 - 3 \sech^2 z \right) \sech^2 z - 3 i k \int_{0}^{\infty} dz \sin k z \tanh z \sech^2 z$$

also vanishes. On integrating the second term by parts, we establish that the two terms can be combined as

$$= \int_{0}^{\infty} dz \cos k z \left( 2 + \frac{1}{2} k^2 - 3 \sech^2 z \right) \sech^2 z$$

(1212)

As the integrals are evaluated as

$$\int_{0}^{\infty} dz \cos k z \sech^2 z = \frac{\pi k}{2 \sinh \frac{\pi k}{2}}$$

(1213)

and

$$\int_{0}^{\infty} dz \cos k z \sech^4 z = \frac{1}{3!} \frac{\pi k}{\sinh \frac{\pi k}{2}} \left( 4 + k^2 \right)$$

(1214)
The overlap matrix element vanishes. The orthogonality of the scattering states and the \( m = 1 \) bound state is treated similarly.

4.4.5 Exercise 77

Find the normalization for the two lowest energy bound states of the Bargmann potential for arbitrary \( n \).

4.4.6 Solution 77

The lowest energy solution of the \( n \)-th order Bargmann eigenvalue equation

\[
- \frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{n(n+1)}{\xi^2} \text{sech}^2 \left( \frac{x}{\xi} \right) \right] \phi_m(x) = E_m \phi_m(x) \tag{1215}
\]

is seen to be

\[
\phi_n(x) = A \text{sech}^n \left( \frac{x}{\xi} \right) \tag{1216}
\]

This can be most easily seen by changing to the scaled variable

\[
z = \frac{x}{\xi} \tag{1217}
\]

so the eigenvalue equation becomes

\[
\left[ \frac{\partial^2}{\partial z^2} + n(n+1) \right] \phi_n(z \xi) = - \frac{2m \xi^2}{\hbar^2} E \phi_n(z \xi) \tag{1218}
\]

The function \( \phi_n(z \xi) \) is an eigenfunction, as can be seen by direct substitution of

\[
\phi_n(z \xi) = A \text{sech}^n z \tag{1219}
\]

into the eigenvalue equation and then by noting that

\[
\frac{\partial^2}{\partial z^2} \text{sech}^n z = n(n+1) \text{sech}^n z \tanh^2 z - n \text{sech}^n z
\]

\[
= n^2 \text{sech}^n z - n(n+1) \text{sech}^{(n+2)} z \tag{1220}
\]

Thus, \( \text{sech}^n z \) is a bound state with the bound state energy given by

\[
E_n = - \frac{\hbar^2}{2m \xi^2} n^2 \tag{1221}
\]
Hence, the second bound state $\phi_{n-1}$ can be found by applying $\hat{M}_n$ on $\text{sech}^{n-1}z$.

$$\phi_{n-1}(z) \propto \left[ \frac{\partial}{\partial z} - n \tanh z \right] \text{sech}^{n-1}z$$

(1222)

which leads to the identification of

$$\phi_{n-1} = B \text{sech}^{n-1}z \tanh z$$

(1223)

as the bound state with energy eigenvalue

$$E_{n-1} = -\frac{\hbar^2}{2m\xi^2} (n - 1)^2$$

(1224)

The magnitude of the normalization constant $A$ can be determined from

$$1 = |A|^2 \int_{-\infty}^{\infty} dx \text{sech}^{2n}z$$

$$= |A|^2 \xi \int_{-\infty}^{\infty} dz \text{sech}^{2n}z$$

(1225)

The integration can be evaluated by integration by parts

$$\int_{-\infty}^{\infty} dz \text{sech}^{2n}dz = \int_{-\infty}^{\infty} dz \text{sech}^{2n-2}z \frac{\partial}{\partial z} \tanh z$$

$$= \text{sech}^{2(n-1)}z \tanh z \bigg|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dz \tanh z \frac{\partial}{\partial z} \text{sech}^{2(n-1)}z$$

(1226)

The boundary term is zero for $n \geq 2$ and for $n = 1$ the boundary term is just 2. Since,

$$\frac{\partial}{\partial z} \text{sech}^{2(n-1)}z = -2 \left( n - 1 \right) \text{sech}^{2(n-1)}z \tanh z$$

(1227)

and

$$\tanh^2 z = 1 - \text{sech}^2 z$$

(1228)

one has the recursion relation

$$\int_{-\infty}^{\infty} dz \text{sech}^{2n}dz = \frac{2(n-1)}{(2n-1)} \int_{-\infty}^{\infty} dz \text{sech}^{2(n-1)}z$$

$$= \frac{2^n(n-1)!}{(2n-1)!!}$$

(1229)

for $n \geq 1$. Thus, the normalized wave function for the lowest energy bound state is given by

$$\phi_n(x) = \sqrt{\frac{(2n-1)!!}{\xi 2^n(n-1)!}} \text{sech}^n \left( \frac{x}{\xi} \right)$$

(1230)
The normalization of the next lowest-energy bound state is found from

\[
1 = |B|^2 \xi \int_{-\infty}^{\infty} dz \sech^{2(n-1)} z \tanh^2 z \\
= |B|^2 \xi \left( \int_{-\infty}^{\infty} dz \sech^{2(n-1)} z - \int_{-\infty}^{\infty} dz \sech^{2n} z \right) \\
= |B|^2 \xi \left( \frac{2(n-1)}{(2n-3)!!} - \frac{2^n (n-1)!!}{(2n-1)!!} \right) \\
= |B|^2 \xi \left( \frac{2(n-1)}{(2n-1)!!} \right) 
\]

(1231)

Thus, the normalized bound state wave function is given by

\[
\phi_{n-1}(x) = \sqrt{\frac{(2n-1)!!}{\xi 2^{n-1} (n-2)!}} \sech^n \left( \frac{x}{\xi} \right) \tanh \left( \frac{x}{\xi} \right) 
\]

(1232)
4.5 Orbital Angular Momentum

In three dimensions, the orbital angular momentum operator is a pseudo-vector and is defined by the vector product

\[ \hat{L} = \hat{r} \wedge \hat{p} \]  

therefore, it can be decomposed in terms of Cartesian unit vectors via

\[ \hat{L} = \hat{e}_x \hat{L}_x + \hat{e}_y \hat{L}_y + \hat{e}_z \hat{L}_z \]  

where the components are given by the expressions

\[
\begin{align*}
\hat{L}_x &= \hat{y} \hat{p}_z - \hat{z} \hat{p}_y \\
\hat{L}_y &= \hat{z} \hat{p}_x - \hat{x} \hat{p}_z \\
\hat{L}_z &= \hat{x} \hat{p}_y - \hat{y} \hat{p}_x
\end{align*}
\]

From the commutation relations between position and momentum operators, one finds that the components of the angular momentum operator satisfy the following type of commutation relations with the components of the position and momentum

\[
\begin{align*}
[\hat{L}_x, \hat{y}] &= i \hbar \hat{z} \\
[\hat{L}_x, \hat{p}_y] &= i \hbar \hat{p}_z \\
[\hat{L}_x, \hat{x}] &= 0 \\
[\hat{L}_x, \hat{p}_x] &= 0
\end{align*}
\]

The above expressions can be used together with the rules for the commutators of sums and products of operators, to prove that

\[
\begin{align*}
[\hat{L}_x, \hat{L}_y] &= i \hbar \hat{L}_z \\
[\hat{L}_y, \hat{L}_z] &= i \hbar \hat{L}_x \\
[\hat{L}_z, \hat{L}_x] &= i \hbar \hat{L}_y
\end{align*}
\]

Since the components of the orbital angular momentum operators do not commute, the uncertainty principle asserts that, in general, it is not possible to find an a simultaneous eigenstate of more than one component. Since the angular momentum operators satisfy the above commutation relations, they provide an example of a Lie algebra. 

\[ \text{[The operators of a Lie algebra satisfy commutation relations of the form]}
\]

\[ \left[ \hat{A}_i, \hat{A}_j \right] = \sum_k C_{i,j}^{k} \hat{A}_k \]

The set of operators \( \hat{A}_i \) which form a Lie algebra are linearly related to the infinitesimal generators of transformation groups, known as Lie Groups. In the case of orbital angular momentum, the Lie group is the group of three-dimensional rotations. It is also noteworthy
The commutation relations between the various components of the angular momentum can be evaluated through

\[
\begin{align*}
[\hat{L}_x, \hat{L}_y] &= [\hat{L}_x, z \hat{p}_x] - [\hat{L}_x, x \hat{p}_z] \\
&= [\hat{L}_x, z] \hat{p}_x + z [\hat{L}_x, \hat{p}_x] - [\hat{L}_x, x] \hat{p}_z - x [\hat{L}_x, \hat{p}_z] \\
&= -i \hbar y \hat{p}_x + i \hbar x \hat{p}_y \\
&= i \hbar \hat{L}_z
\end{align*}
\]

(1238)

The others can be obtained by cyclic permutations, corresponding to the different choices of Cartesian coordinate axes.

The operator expressing the squared magnitude of the angular momentum vector follows from the operators representing the Cartesian components and the Pythagorean theorem

\[
\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2
\]

(1239)

That is, the squared magnitude of the angular momentum is merely the sum of the squares of the operator components. The magnitude of \( L^2 \) is a scalar quantity. It can be proved that

\[
\begin{align*}
[\hat{L}_x, \hat{L}^2] &= 0 \\
[\hat{L}_y, \hat{L}^2] &= 0 \\
[\hat{L}_z, \hat{L}^2] &= 0
\end{align*}
\]

(1240)

Thus, it is possible to find simultaneous eigenfunctions of any one component of the angular momentum and the magnitude squared.

The commutation relation between the \( z \) component of the angular momentum \( \hat{L}_z \) and the magnitude of the angular momentum \( \hat{L}^2 \) is proved by considering

\[
[\hat{L}_z, \hat{L}^2] = [\hat{L}_z, \hat{L}_x^2] + [\hat{L}_z, \hat{L}_y^2] + [\hat{L}_z, \hat{L}_z^2]
\]

(1241)

that the set of commutation relations between the angular momentum operators and any vector quantity with components \( \hat{v}_i \) satisfy commutation relations of the form

\[
[\hat{L}_i, \hat{v}_j] = i \hbar \sum_k \epsilon_{i,j,k} \hat{v}_k
\]

where \( \epsilon_{i,j,k} \) is the Levi-Civita symbol. The Levi-Civita symbol is defined as

\[
\epsilon_{i,j,k} = \begin{cases} 
1 & \text{if } i,j,k \text{ is a cyclic permutation of } 1,2,3 \\
-1 & \text{if } i,j,k \text{ is not a cyclic permutation of } 1,2,3 \\
0 & \text{otherwise}
\end{cases}
\]

The above commutation relations imply that all vectors transform in the same way under the set of rotation operations.
which becomes
\[
[ \hat{L}_z, \hat{L}_x^2 ] = [ \hat{L}_z, \hat{L}_x^2 ] + [ \hat{L}_z, \hat{L}_y^2 ]
\]
\[
= [ \hat{L}_z, \hat{L}_x ] \hat{L}_x + [ \hat{L}_z, \hat{L}_x ] \hat{L}_x + [ \hat{L}_z, \hat{L}_y ] \hat{L}_y + \hat{L}_y [ \hat{L}_z, \hat{L}_y ]
\]
\[
= i \hbar \left( \hat{L}_y \hat{L}_x + \hat{L}_x \hat{L}_y \right) - i \hbar \left( \hat{L}_x \hat{L}_y + \hat{L}_y \hat{L}_x \right)
\]
\[
= 0 \quad (1242)
\]
Thus, \( \hat{L}_z \) and \( \hat{L}_x^2 \) commute. By invariance under the permutation of the coordinate axes, the commutators of \( \hat{L}_x^2 \) with the other components of \( \hat{L} \) are also found to be zero.

\begin{subsection}{4.5.1 Exercise 78}
Find the expression for the operator \( L^2 \) in terms of the Cartesian components of the position and derivatives w.r.t position. Express your final result entirely in terms of invariant quantities, such as scalar products.
\end{subsection}

\begin{subsection}{4.5.2 Solution 78}
The components of the angular momentum can be written in terms of the Levi-Civita symbol \( \epsilon_{i,j,k} \) as
\[
L_k = -i \hbar \sum_{i,j} \epsilon_{i,j,k} x_i \frac{\partial}{\partial x_j} \quad (1243)
\]
where
\[
\epsilon_{i,j,k} = 1 \quad (1244)
\]
if \( i, j, k \) are an even permutation of the indices 1, 2, and 3, and
\[
\epsilon_{i,j,k} = -1 \quad (1245)
\]
if \( i, j, k \) are an odd permutation of the indices 1, 2, and 3, and
\[
\epsilon_{i,j,k} = 0 \quad (1246)
\]
if any index is repeated.
The magnitude of the angular momentum is given by

\[ \hat{L}^2 = \sum_k \hat{L}_k^2 \]

\[ = -\hbar^2 \sum_k \epsilon_{i,j,k} x_i \frac{\partial}{\partial x_j} \sum_l \epsilon_{l,m,k} x_l \frac{\partial}{\partial x_m} \]

(1247)

But on using the identity

\[ \sum_k \epsilon_{i,j,k} \epsilon_{l,m,k} = \delta_{i,l} \delta_{j,m} - \delta_{i,m} \delta_{j,l} \]

(1248)

one obtains

\[ \hat{L}^2 = -\hbar^2 \sum_{i,j} \left( x_i \frac{\partial}{\partial x_j} x_i \frac{\partial}{\partial x_j} - x_i \frac{\partial}{\partial x_j} x_j \frac{\partial}{\partial x_i} \right) \]

\[ = -\hbar^2 \sum_{i,j} \left( x_i x_i \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_j} + x_i \frac{\partial x_i}{\partial x_j} \frac{\partial}{\partial x_j} \right. \]

\[ - x_i x_j \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_i} - x_i \frac{\partial x_j}{\partial x_j} \frac{\partial}{\partial x_i} \]

\[ = -\hbar^2 \sum_{i,j} \left( x_i^2 \frac{\partial^2}{\partial x_j^2} + x_i \delta_{i,j} \frac{\partial}{\partial x_j} \right) \]

\[ - x_i x_j \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_i} - x_i \frac{\partial}{\partial x_i} \] (1249)

Thus, we have

\[ \hat{L}^2 = -\hbar^2 \left( \sum_i x_i^2 \sum_j \frac{\partial^2}{\partial x_j^2} + \sum_i x_i \frac{\partial}{\partial x_i} \right. \]

\[ - \sum_{i,j} x_i x_j \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_i} - 3 \sum_i x_i \frac{\partial}{\partial x_i} \] (1250)

Hence, the magnitude of the angular momentum can be written as

\[ \hat{L}^2 = -\hbar^2 \left( \sum_i x_i^2 \sum_j \frac{\partial^2}{\partial x_j^2} + \sum_i x_i \frac{\partial}{\partial x_i} \right. \]

\[ - \sum_{i,j} x_i x_j \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_i} - 3 \sum_i x_i \frac{\partial}{\partial x_i} \]

\[ = -\hbar^2 \left( \sum_i x_i^2 \sum_j \frac{\partial^2}{\partial x_j^2} - \sum_{i,j} x_i x_j \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_i} - 2 \sum_i x_i \frac{\partial}{\partial x_i} \right) \] (1251)
which can be expressed as

$$\hat{L}^2 = -\hbar^2 \left( \sum_i x_i^2 \sum_j \frac{\partial^2}{\partial x_j^2} - \sum_{i,j} x_j \frac{\partial}{\partial x_j} x_i \frac{\partial}{\partial x_i} - 1 \sum_i x_i \frac{\partial}{\partial x_i} \right)$$

(1252)

When put in vector notation, the magnitude of the angular momentum becomes

$$\hat{L}^2 = -\hbar^2 \left( \mathbf{r}^2 \nabla^2 - (\mathbf{r} \cdot \nabla)^2 - (\mathbf{r} \cdot \nabla) \right)$$

(1253)

which is seen to be a scalar operator.

4.5.3 Exercise 79

Show that the following functions are eigenfunctions of $\hat{L}_z$ and $\hat{L}^2$ and find the corresponding eigenvalues.

$$\Psi_0(r) = g_0(r)$$
$$\Psi_1(r) = z g_1(r)$$
$$\Psi_2(r) = (x + iy) g_2(r)$$
$$\Psi_3(r) = (x - iy) g_3(r)$$
$$\Psi_4(r) = (3z^2 - r^2) g_4(r)$$
$$\Psi_5(r) = (x + iy)^2 g_5(r)$$
$$\Psi_6(r) = (x - iy)^2 g_6(r)$$
$$\Psi_7(r) = z (x + iy) g_7(r)$$
$$\Psi_8(r) = z (x - iy) g_8(r)$$

(1254)

where the functions $g_n(r)$ are arbitrary functions of the radial distance.

The Cartesian components of the angular momentum operators can be expressed in terms of spherical polar coordinates. The Cartesian components are found to be given by the expressions

$$\hat{L}_x = -i \hbar \left( -\sin \varphi \frac{\partial}{\partial \theta} - \cos \varphi \cot \theta \frac{\partial}{\partial \varphi} \right)$$
$$\hat{L}_y = -i \hbar \left( +\cos \varphi \frac{\partial}{\partial \theta} - \sin \varphi \cot \theta \frac{\partial}{\partial \varphi} \right)$$
$$\hat{L}_z = -i \hbar \frac{\partial}{\partial \varphi}$$

(1255)
and these components can be shown to satisfy the same commutation relations that were derived from a purely Cartesian formulation.

We shall commence the derivation of eqns(1255) by expressing the angular momentum in terms of the unit vectors of the polar coordinate system. The orbital angular momentum operator is expressed as

\[ \hat{\mathbf{L}} = \mathbf{r} \wedge \hat{\mathbf{p}} = -i \hbar \mathbf{r} \wedge \nabla \] (1256)

and on using the representation

\[ \nabla = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \] (1257)

one finds

\[ \hat{\mathbf{L}} = -i \hbar \mathbf{r} \left( \hat{e}_r \wedge \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_r \wedge \hat{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \]

\[ = -i \hbar \left( \hat{e}_\varphi \frac{\partial}{\partial \theta} - \hat{e}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \right) \] (1258)

In the last line we have used the fact that the unit vectors \( \hat{e}_r, \hat{e}_\theta \) and \( \hat{e}_\varphi \) form an orthogonal coordinate system. Furthermore, as

\[ \hat{\mathbf{r}} = \mathbf{r} \]

\[ = r \cos \theta \hat{e}_z + r \sin \theta \left( \sin \varphi \hat{e}_y + \cos \varphi \hat{e}_x \right) \] (1259)

one can express the spherical polar coordinate unit vectors in terms of the Cartesian unit vectors by using the definition of the unit vectors

\[ \hat{e}_r = \frac{\partial}{\partial r} \mathbf{r} \]

\[ = \cos \theta \hat{e}_z + \sin \theta \left( \sin \varphi \hat{e}_y + \cos \varphi \hat{e}_x \right) \]

\[ \hat{e}_\theta = \frac{1}{r} \frac{\partial}{\partial \theta} \mathbf{r} \]

\[ = -\sin \theta \hat{e}_z + \cos \theta \left( \sin \varphi \hat{e}_y + \cos \varphi \hat{e}_x \right) \]

\[ \hat{e}_\varphi = \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \mathbf{r} \]

\[ = \left( \cos \varphi \hat{e}_y - \sin \varphi \hat{e}_x \right) \] (1260)

On substituting the above expressions for the unit vectors into the equation for the angular momentum vector \( \hat{\mathbf{L}} \) in eqn(1258), the angular momentum is found
in the form

\[
\hat{L} = -i\hbar \left( -\hat{e}_x \sin \varphi \frac{\partial}{\partial \theta} + \hat{e}_y \cos \varphi \frac{\partial}{\partial \theta} - \hat{e}_x \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} - \hat{e}_y \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} + \hat{e}_z \frac{\partial}{\partial \varphi} \right) \quad (1261)
\]

which has three components given by the expressions of eqn(1255).

The square of the angular momentum \(\hat{L}^2\) is given by

\[
\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right] \quad (1262)
\]

### 4.5.4 Simultaneous Eigenfunctions.

In spherical polar coordinates, the angular momentum operators act on the wave functions \(\Psi(r, \theta, \varphi)\), but since \(r\) does not appear in the operators, it is redundant. The simultaneous eigenfunctions of the pair of operators \(\hat{L}_z\) and \(\hat{L}^2\) are functions of \(\theta\) and \(\varphi\) alone, and are written as \(Y_{lm}(\theta, \varphi)\). These eigenfunctions satisfy the pair of eigenvalue equations,

\[
\hat{L}^2 Y_{lm}(\theta, \varphi) = -\hbar^2 \left[ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right] Y_{lm}(\theta, \varphi)
= \lambda_l Y_{lm}(\theta, \varphi) \quad (1263)
\]

\[
\hat{L}_z Y_{lm}(\theta, \varphi) = -i\hbar \frac{\partial}{\partial \varphi} Y_{lm}(\theta, \varphi)
= \mu Y_{lm}(\theta, \varphi) \quad (1264)
\]

where \(\lambda_l\) is the eigenvalue of \(\hat{L}^2\) and \(\mu\) is the eigenvalue of \(\hat{L}_z\). The eigenfunctions \(Y_{lm}(\theta, \varphi)\) are usually factorized according to

\[
Y_{lm}(\theta, \varphi) = \Theta_{lm}(\theta) \Phi_m(\varphi) \quad (1265)
\]

From the form of the \(\hat{L}_z\) operator as a derivative w.r.t. \(\varphi\), one can easily find that the \(\varphi\) dependence of \(Y_{lm}(\theta, \varphi)\) must be given by

\[
Y_{lm}(\theta, \varphi) = \Theta_{lm}(\theta) \left( \frac{1}{2\pi} \right)^\frac{1}{2} \exp \left[ i \frac{\mu \varphi}{\hbar} \right] \quad (1266)
\]

The modulus of the wave function is single valued, as it must represent a unique probability density for each point in space. Therefore, we expect that the wave
function at the point \((r, \theta, \varphi)\) must have the same values at \((r, \theta, \varphi + 2\pi)\) since this represents the same point. In this case, we have

\[
\exp \left[ i \frac{\mu \varphi}{\hbar} \right] = \exp \left[ i \frac{\mu (\varphi + 2\pi)}{\hbar} \right] \tag{1267}
\]

which is satisfied if \(\mu = \hbar m\) for any positive or negative integer \(m\).

Classically, the magnitude of a component of the angular momentum should be smaller than the magnitude of the pseudo-vector \(\vec{L}\). From this observation, one expects that an inequality should exist between the eigenvalues of \(\lambda_l\) and \(m \hbar\). The maximum value of \(m\) will be denoted by \(l\). Later, we shall show that the eigenvalue \(\lambda_l\) is related to \(l\) via \(\lambda_l = \hbar^2 l (l + 1)\).

This suggests a picture of the orbital angular momentum eigenstates as being states where \(\vec{L}\) has a definite magnitude \(\sqrt{\lambda_l}\) and a definite \(z\) component \(m \hbar\). The picture is that in which the vector \(\vec{L}\) has a definite \(z\) component and magnitude, but has an uncertain direction due to precession around the \(z\) axis.

![Figure 72: A semi-classical picture of a state with angular momentum \(l\) and \(z\) component \(m\). The picture of the angular momentum is a vector of length \(\hbar \sqrt{l(l+1)}\) which has a projection \(\hbar m\) along the \(z\) axis. The angular momentum vector can be thought of as precessing around the \(z\) axis, so that the \(x\) and \(y\) components are indeterminate.](image-url)
4.5.5 The Raising and Lowering Operators

Two useful operators are given by the raising and lowering operators, \( \hat{L}_+ \) and \( \hat{L}_- \) defined by

\[
\hat{L}_+ = \hat{L}_x + i \hat{L}_y \\
\hat{L}_- = \hat{L}_x - i \hat{L}_y
\]

(1268)

The operators \( \hat{L}_+ \) and \( \hat{L}_- \) are Hermitean conjugates. These operators also commute with \( \hat{L}_2 \).

\[
[ \hat{L}_2, \hat{L}_+ ] = [ \hat{L}_2, \hat{L}_- ] = 0
\]

(1269)

as both \( \hat{L}_x \) and \( \hat{L}_y \) commute with \( \hat{L}_2 \).

In spherical polar coordinates, the raising and lowering operators are given by

\[
\hat{L}_+ = + \hbar \exp \left[ + i \varphi \right] \left( \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \\
\hat{L}_- = - \hbar \exp \left[ - i \varphi \right] \left( \frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \varphi} \right)
\]

(1270)

The raising and lowering operators satisfy the commutation relations

\[
[ \hat{L}_z, \hat{L}_+ ] = + \hbar \hat{L}_+ \\
[ \hat{L}_z, \hat{L}_- ] = - \hbar \hat{L}_- \\
[ \hat{L}_+, \hat{L}_- ] = 2 \hbar \hat{L}_z
\]

(1271)

On operating with the commutators \( [ \hat{L}_2, \hat{L}_\pm ] \) on the eigenfunctions of \( \hat{L}_2 \), one finds

\[
\hat{L}_\pm \hat{L}_\pm Y^l_m(\theta, \varphi) = \hat{L}_\pm \hat{L}_2 Y^l_m(\theta, \varphi) = \lambda_l \hat{L}_\pm Y^l_m(\theta, \varphi)
\]

(1272)

and recognizes that \( \hat{L}_\pm Y^l_m(\theta, \varphi) \) is also an eigenfunction of \( \hat{L}_2 \) with the same eigenvalue \( \lambda_l \) as found for \( Y^l_m(\theta, \varphi) \). Thus, \( \hat{L}_\pm \) acting on an eigenfunction of the magnitude of the orbital angular momentum does not change the eigenvalue \( \lambda_l \).

On operating with the commutator \( [ \hat{L}_z, \hat{L}_\pm ] = \pm \hbar \hat{L}_\pm \) on the eigenfunctions \( Y^l_m(\theta, \varphi) \), one finds

\[
\hat{L}_z \hat{L}_\pm Y^l_m(\theta, \varphi) = \left( \hat{L}_\pm \hat{L}_z \pm \hbar \hat{L}_\pm \right) Y^l_m(\theta, \varphi) \\
= \left( m \hbar \pm \hbar \right) \hat{L}_\pm Y^l_m(\theta, \varphi)
\]

(1273)
Thus, the raising and lowering operators when acting on a simultaneous eigenfunction of $\hat{L}_z$ and $\hat{L}_x$ produce other simultaneous eigenfunctions with $\hat{L}_z$ eigenvalues that are either raised or lowered by $\hbar$. The action of $\hat{L}_\pm$ on the eigenfunction $Y^l_m(\theta,\varphi)$ is to produce a function proportional to $Y^l_{m\pm 1}(\theta,\varphi)$. Thus, we have

$$\hat{L}_\pm Y^l_m(\theta,\varphi) = C_\pm(l,m) Y^l_{m\pm 1}(\theta,\varphi) \quad (1274)$$

The constants of proportionality, $C_\pm(l,m)$, have yet to be determined.

### 4.5.6 The Eigenvalues and Degeneracy

First we shall note the two equalities,

$$\begin{align*}
\hat{L}_- \hat{L}_+ & = \hat{L}_2 - \hat{L}_z^2 - \hbar \hat{L}_z \\
\hat{L}_+ \hat{L}_- & = \hat{L}_2 - \hat{L}_z^2 + \hbar \hat{L}_z
\end{align*} \quad (1275)$$

We shall first consider the effect of the raising operator. On operating $\hat{L}_- \hat{L}_+$ on the eigenfunction $Y^l_m(\theta,\varphi)$, on using the first equality of eqn(1275), one finds

$$\begin{align*}
\hat{L}_- \hat{L}_+ Y^l_m(\theta,\varphi) & = \left( \hat{L}_2 - \hat{L}_z^2 - \hbar \hat{L}_z \right) Y^l_m(\theta,\varphi) \\
& = \left( \lambda_l - \hbar^2 m^2 - \hbar^2 m \right) Y^l_m(\theta,\varphi) \quad (1276)
\end{align*}$$

If the value of $m$ is the maximum value $l$, then we have

$$\hat{L}_+ Y^l_l(\theta,\varphi) = 0 \quad (1277)$$

and so, on substituting $m = l$ in the previous equation, we find

$$\lambda_l = \hbar^2 l \left( l + 1 \right) \quad (1278)$$

Thus, we have found the eigenvalue of the square of the angular momentum in terms of the maximum eigenvalue of the $z$ component of the angular momentum operator.

Now we shall determine explicit expressions for the products of the coefficients $C_\pm(l,m)$. On using the properties of the raising and lowering operators given by eqn(1274), one finds

$$\hat{L}_- \hat{L}_+ Y^l_m(\theta,\varphi) = C_-(l,m+1) C_+(l,m) Y^l_m(\theta,\varphi) \quad (1279)$$

but we also have

$$\hat{L}_- \hat{L}_+ Y^l_m(\theta,\varphi) = \left( \lambda_l - \hbar^2 m^2 - \hbar^2 m \right) Y^l_m(\theta,\varphi) \quad (1280)$$

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Therefore, we can determine the products of the coefficient \( C_{\pm}(l,m) \) by equating the above two expressions and then by substituting the expression for \( \lambda_l \). Thus, we find

\[
C_-(l,m + 1) C_+(l,m) = \lambda_l - \hbar^2 \left( m^2 + m \right) = \hbar^2 \left( l \left( l + 1 \right) - m^2 - m \right) \tag{1281}
\]

The effect of the lowering operator is found by considering the other equality, and considering the minimum value of \( l \). On operating \( \hat{L}_+ \) and \( \hat{L}_- \) on the eigenfunction \( Y^l_m(\theta,\varphi) \) and on using the second equality of eqn(1275), one finds

\[
\hat{L}_+ \hat{L}_- Y^l_m(\theta,\varphi) = \left( \hat{L}^2 - \hat{L}_z^2 + \hbar \hat{L}_z \right) Y^l_m(\theta,\varphi) = \hbar^2 \left( l \left( l + 1 \right) - m^2 + m \right) Y^l_m(\theta,\varphi) \tag{1282}
\]

If \( m \) is the minimum value \( l' \), then we have

\[
\hat{L}_- Y^l_m(\theta,\varphi) = 0 \tag{1283}
\]

therefore

\[
\hbar^2 \left( l \left( l + 1 \right) - l'^2 + l' \right) = 0 \tag{1284}
\]

so we find that the minimum value of \( m \) is given by \( l' = -l \). Thus, the possible values of \( m \) run through the set of numbers \(-l, -(l-1), -(l-2), \ldots, (l-2), (l-1), l\), which includes 0. There are \((2l + 1)\) different eigenfunctions of \( m \) for fixed \( l \). Thus, the eigenvalues of \( \hat{L}^2 \) corresponding to the value \( l \) have a degeneracy of \((2l + 1)\). Since we have proved that the eigenvalues \( m \) for the \( z \) component of the orbital angular momentum are integer, we note that \( l \) must also be an integer.

### 4.5.7 The Effect of the Raising Operators.

The coefficients \( C_{\pm}(l,m) \) are found by noting that as \( \hat{L}_+ \) and \( \hat{L}_- \) are Hermitean conjugates

\[
\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\varphi \ Y^l_{m+1}(\theta,\varphi)^* \hat{L}_+ Y^l_m(\theta,\varphi) = C_+(l,m) = \left( \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\varphi \ Y^l_m(\theta,\varphi)^* \hat{L}_- Y^l_{m+1}(\theta,\varphi) \right)^* = C_-(l,m + 1) \tag{1285}
\]
Thus, we have
\[ | C_+ (l, m) |^2 = \hbar^2 \left( (l + 1) - m \left( m + 1 \right) \right) \]
\[ = \hbar^2 \left( l + m \right) \left( l + m + 1 \right) \tag{1286} \]

and, by considering the lowering operator, one finds the analogous equation
\[ | C_- (l, m) |^2 = \hbar^2 \left( (l + 1) - m \left( m - 1 \right) \right) \]
\[ = \hbar^2 \left( l + m \right) \left( l - m + 1 \right) \tag{1287} \]

Thus, the effect of the raising and lowering operators are given by
\[ \hat{L}_+ Y^l_m(\theta, \varphi) = \hbar \sqrt{(l - m) \left( l + m + 1 \right)} Y^l_{m+1}(\theta, \varphi) \]
\[ \hat{L}_- Y^l_m(\theta, \varphi) = \hbar \sqrt{(l + m) \left( l - m + 1 \right)} Y^l_{m-1}(\theta, \varphi) \tag{1288} \]

where we have chosen the phase of the constants to be zero.

### 4.5.8 Explicit Expressions for the Eigenfunctions

Explicit expressions for the simultaneous eigenfunctions \( Y^l_m(\theta, \varphi) \) can be found starting from the effect of the raising operator on the state with maximum \( m \), i.e. \( m = l \). This results in the equation
\[ \hat{L}_+ Y^l_l(\theta, \varphi) = 0 \tag{1289} \]

which has the explicit form
\[ \hbar \exp \left[ + i \varphi \right] \left( \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) Y^l_l(\theta, \varphi) = 0 \tag{1290} \]

As the eigenfunction has a \( \varphi \) dependence of \( \exp \left[ i l \varphi \right] \), and as the eigenfunction is factorized as
\[ Y^l_m(\theta, \varphi) = \Theta^l_m(\theta) \left( \frac{1}{2 \pi} \right)^\frac{1}{2} \exp \left[ i m \varphi \right] \tag{1291} \]

one finds
\[ \frac{\partial}{\partial \theta} \Theta^l_l(\theta) = l \cot \theta \Theta^l_l(\theta) \tag{1292} \]

This equation can be integrated to yield
\[ \Theta^l_l(\theta) = B^l_l \sin l \theta \tag{1293} \]

where \( B^l_l \) is a constant of proportionality. The magnitude of \( B^l_l \) is determined by the normalization condition
\[ | B^l_l |^2 \int_0^\pi d\theta \sin \theta \sin 2l \theta = 1 \tag{1294} \]
Thus, the magnitude of the normalization is found as

$$ |B_{l}^{i}| = \left( \frac{(2l+1)!}{2^{2l+1} (l!)^2} \right)^{\frac{1}{2}} $$

(1295)

The normalized eigenfunction $Y_{l}^{i}(\theta, \varphi)$ is found as

$$ Y_{l}^{i}(\theta, \varphi) = \left( \frac{1}{4\pi} \frac{(2l+1)!}{2^{2l} (l!)^2} \right)^{\frac{1}{2}} \sin l \theta \exp \left[ i l \varphi \right] $$

(1296)

up to an arbitrary constant phase.

The lowering operator acting on the state with minimum $m$, i.e. $m = -l$, results in the equation

$$ \hat{\mathbf{L}}_{-} Y_{l}^{i}(\theta, \varphi) = 0 $$

(1297)

which has the explicit form

$$ \hbar \exp \left[ -i \varphi \right] \left( -\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) Y_{l}^{i}(\theta, \varphi) = 0 $$

(1298)

As the eigenfunction has a $\varphi$ dependence of $\exp[-i l \varphi]$, and as the eigenfunction is factorized as

$$ Y_{m}^{i}(\theta, \varphi) = \Theta_{m}^{i}(\theta) \left( \frac{1}{2\pi} \right)^{\frac{1}{2}} \exp \left[ i m \varphi \right] $$

(1299)

one finds

$$ \frac{\partial}{\partial \theta} \Theta_{m}^{i}(\theta) = l \cot \theta \Theta_{-l}^{i}(\theta) $$

(1300)

which can be integrated to yield

$$ \Theta_{-l}^{i}(\theta) = B_{-l}^{i} \sin l \theta $$

(1301)

where $B_{-l}^{i}$ is a constant of proportionality. The magnitude of $B_{-l}^{i}$ is determined by the normalization condition

$$ |B_{-l}^{i}|^2 \int_{0}^{\pi} d\theta \sin \theta \sin 2l \theta = 1 $$

(1302)

Thus, the magnitude of the normalization is found as

$$ |B_{-l}^{i}| = \left( \frac{(2l+1)!}{2^{2l+1} (l!)^2} \right)^{\frac{1}{2}} $$

(1303)

The normalized eigenfunction $Y_{-l}^{i}(\theta, \varphi)$ is found as

$$ Y_{-l}^{i}(\theta, \varphi) = \left( \frac{1}{4\pi} \frac{(2l+1)!}{2^{2l} (l!)^2} \right)^{\frac{1}{2}} \sin l \theta \exp \left[ -i l \varphi \right] $$

(1304)
up to an arbitrary constant phase.

The eigenfunctions corresponding to larger values of $m$ can be found by successive operation with the raising operators,

$$\exp \left[ + i \varphi \right] \left( \frac{\partial}{\partial \theta} + i \frac{\partial}{\partial \varphi} \cot \theta \right) Y^l_m(\theta, \varphi) = \sqrt{ (l - m) (l + m + 1) } Y^l_{m+1}(\theta, \varphi)$$

Thus, on factorizing the eigenfunctions, we have

$$\left( + \frac{\partial}{\partial \theta} - m \cot \theta \right) \Theta^l_m(\theta) = \sqrt{ (l - m) (l + m + 1) } \Theta^l_{m+1}(\theta)$$

$$\sin^m \theta \frac{1}{\sin^m \theta} \Theta^l_m(\theta) = \sqrt{ (l - m) (l + m + 1) } \Theta^l_{m+1}(\theta)$$

Starting with $m = -l$, after $l + m$ iterations, one finds

$$\Theta^l_m(\theta) = \frac{(-1)^{l+m}}{2^l l!} \left[ \frac{(2l + 1) (l - m)!}{2 (l + m)!} \right]^{\frac{l}{2}} \sin^m \theta \left[ \frac{\partial}{\partial \cos \theta} \right]^{l+m} \sin^{2l} \theta$$

Thus, the spherical harmonics are given by

$$Y^l_m(\theta) = \frac{(-1)^{l+m}}{2^l l!} \left[ \frac{(2l + 1) (l - m)!}{4 \pi (l + m)!} \right]^{\frac{l}{2}} \times$$

$$\times \sin^m \theta \left[ \frac{\partial}{\partial \cos \theta} \right]^{l+m} \sin^{2l} \theta \exp \left[ i m \varphi \right]$$

These eigenfunctions are normalized via

$$\int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta \ | Y^l_m(\theta, \varphi) |^2 = 1$$

The eigenfunction for positive $m$ and negative $m$ are related via

$$Y^l_{-m}(\theta, \varphi) = (-1)^m Y^l_m(\theta, \varphi)^*$$

The spherical harmonics also satisfy eigenvalue equation for $\hat{\mathbf{L}}^2$. This can be seen explicitly from the representation in spherical polar coordinates

$$-\hbar^2 \left[ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right] Y^l_m(\theta, \varphi) = \hbar^2 l (l + 1) Y^l_m(\theta, \varphi)$$
which on factorizing the eigenfunctions into polar and azimuthal parts, yields

\[ \left[ + \frac{m^2}{\sin^2 \theta} - \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right] \Theta_m^l(\theta) = l (l + 1) \Theta_m^l(\theta) \quad (1312) \]

which identifies \( \Theta_m^l(\theta) \) with the associated Legendre Polynomials \( P_m^l(\cos \theta) \).

This identification proceeds through changing variables \( x = \cos \theta \), so one finds

\[ \frac{\partial}{\partial x} \left[ \left( 1 - x^2 \right) \frac{\partial \Theta}{\partial x} \right] - \frac{m^2}{1 - x^2} \Theta = -l (l + 1) \Theta \quad (1313) \]

which can then be put into the standard form

\[ \left( 1 - x^2 \right) \frac{\partial^2 \Theta}{\partial x^2} - 2 x \frac{\partial \Theta}{\partial x} - \frac{m^2}{1 - x^2} \Theta = -l (l + 1) \Theta \quad (1314) \]

The spherical harmonics are given in terms of the associated Legendre Polynomials via

\[ Y_m^l(\theta, \varphi) = \sqrt{\frac{2 l + 1}{4 \pi} \frac{(l - m)!}{(l + m)!}} \left( -1 \right)^m P_m^l(\cos \theta) \exp \left[ i m \varphi \right] \quad (1315) \]

4.5.9 Legendre Polynomials

The generating function \( F(z, t) \) for the Legendre polynomials has an expansion given by

\[ F(z, t) = \frac{1}{\sqrt{1 + t^2 - 2 z t}} = \sum_{l=0}^{\infty} t^l P_l(z) \quad (1316) \]

for \( t < 1 \).

The Legendre polynomials satisfy recurrence relations, which can be derived from the generating function expansion. The first is obtained by differentiating the generating function with respect to \( t \)

\[ \left( \frac{\partial F(z, t)}{\partial t} \right) = \frac{(z - t)}{(1 + t^2 - 2 z t)^{1/2}} = \sum_{l=0}^{\infty} t^{l-1} P_l(z) \quad (1317) \]

After multiplying the above equation with a factor of \( (1 + t^2 - 2 z t) \) and then substituting the generating function expansion, one obtains the relation

\[ (1 + t^2 - 2 z t) \sum_{l=0}^{\infty} t^{l-1} P_l(z) = (z - t) \sum_{l=0}^{\infty} t^l P_l(z) \quad (1318) \]
Figure 73: Since the spherical harmonics $Y^l_m(\theta, \varphi)$ only depend on $\varphi$ through a phase factor, their $\theta$ dependence can be conveniently represented by a polar plot. In a polar plot, points on a curve are represented by the radial and angular coordinates $\left( |Y^l_m(\theta, \varphi)|^2, \theta \right)$.

On equating like powers of $t$, one has

$$ (l + 1) P_{l+1}(z) - (2l + 1) z P_l(z) + l P_{l-1}(z) = 0 \quad (1319) $$

A second recurrence relation can be found by differentiating the generating function expansion with respect to $z$

$$ \left( \frac{\partial F(z, t)}{\partial z} \right) = \frac{t}{(1 + t^2 - 2zt)^2} = \sum_{l=0}^{\infty} t^l P'_l(z) \quad (1320) $$

On multiplying by $(1 + t^2 - 2zt)$ and then substituting the generating function expansion, one obtains

$$ t \sum_l t^l P_l(z) = (1 + t^2 - 2zt) \sum_l t^l P'_l(z) \quad (1321) $$

which yields the relation

$$ P'_{l+1}(z) + P''_{l-1}(z) = 2z P'_l(z) + P_l(z) \quad (1322) $$

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involving the derivatives of the polynomials.

Numerous other relations can be obtained from the above recurrence relations. If we take the derivative of the first recurrence relation, eqn(1319), then we have

\[(l + 1) P'_{l+1}(z) - (2l + 1)z P'_l(z) + l P'_{l-1}(z) = (2l + 1) P_l(z)\] (1323)

The term proportional to $z P'_l(z)$ can be eliminated from the above equation. This is achieved by multiplying eqn(1323) by two and then subtracting $(2l + 1)$ times eqn(1322), which leads to

\[P'_{l-1}(z) - P'_{l+1}(z) = -(2l + 1) P_l(z)\] (1324)

A more useful set of equations can be obtained by relating the Legendre polynomials of one order to the next. For example, adding eqn(1322) and eqn(1324) one eliminates $P'_{l+1}(z)$

\[P'_{l-1}(z) = z P'_l(z) - l P_l(z)\] (1325)

On subtracting the same pair of the equations, one has

\[P'_{l+1}(z) = (l + 1) P_l(z) + z P'_l(z)\] (1326)

Another pair of equations can be obtained from eqn(1325) and eqn(1326) by shifting the index of eqn(1325) from $l - 1$ to $l$ and then eliminating the term proportional to $P'_{l+1}(z)$, leading to the equation

\[(1 - z^2) P'_l(z) = (l + 1) \left[ z P_l(z) - P_{l+1}(z) \right]\] (1327)

Another recurrence relation can be derived from the above equation by using eqn(1319) to eliminate the term proportional to $(l + 1) P_{l+1}(z)$. This process results in

\[(1 - z^2) P'_l(z) = l P_{l-1}(z) - l z P_l(z)\] (1328)

From these relations we can find the differential equation for the Legendre polynomials $P_l(z)$. By differentiating eqn(1328), one obtains an equation involving $P''_{l-1}(z)$ which can be eliminated using eqn(1325). This procedure leads to Legendre’s equation

\[(1 - z^2) P''_l(z) - 2z P'_l(z) = -l (l + 1) P_l(z)\] (1329)
On setting \( z = \cos \theta \), the differential equation takes the form

\[
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} P_l(\cos \theta) \right) + l(l+1) P_l(\cos \theta) = 0 \tag{1330}
\]

This is recognized as the eigenvalue equation for the total angular momentum, in the case where there is a simultaneous zero eigenvalue for the \( z \) component of the angular momentum, \( m = 0 \). In the general case, where \( m \neq 0 \), the simultaneous eigenfunctions were denoted by \( \Theta^l_m(\theta) \). For finite \( m \), the \( \theta \) dependence of the angular momentum eigenvalues is expressed in terms of the associated Legendre polynomials.

### 4.5.10 Associated Legendre Functions

The Associated Legendre functions, \( P^l_m(z) \) for positive \( m \), are defined as

\[
P^l_m(z) = (1 - z^2)^{\frac{m}{2}} \frac{\partial^m}{\partial z^m} P_l(z) \tag{1331}
\]

Clearly, the associated Legendre function with \( m = 0 \) is identical with the Legendre polynomial. Furthermore, since \( P_l(z) \) is a polynomial of order \( l \), the associated Legendre functions vanish for \( m > l \).

The associated Legendre functions satisfy a differential equation obtained by differentiating Legendre’s equation \( m \) times. This leads to

\[
(1 - z^2) v'' - 2z(m + 1)v' + (l - m)(l + m + 1)v = 0 \tag{1332}
\]

where

\[
v = \frac{\partial^m}{\partial z^m} P_l(z) \tag{1333}
\]

The associated Legendre function \( P^l_m(z) \) and \( v \) are related via

\[
v = \frac{1}{(1 - z^2)^{\frac{m}{2}}} P^l_m(z) \tag{1334}
\]

The first and second derivatives of \( v \) are evaluated as

\[
v' = m \frac{1}{1 - z^2} v + \frac{1}{(1 - z^2)^{\frac{m}{2}}} \frac{\partial}{\partial z} P^l_m(z) \tag{1335}
\]

and

\[
v'' = m \left[ (m + 2) \frac{z^2}{(1 - z^2)^2} v + \frac{1}{1 - z^2} v \right] + \frac{2mz}{1 - z^2} \frac{1}{(1 - z^2)^{\frac{m}{2}}} \frac{\partial}{\partial z} P^l_m(z) + \frac{1}{(1 - z^2)^{\frac{m}{2}}} \frac{\partial^2}{\partial z^2} P^l_m(z) \tag{1336}
\]
Substitution of the expressions for \( v, v' \) and \( v'' \) into eqn(1332) leads to

\[
(1 - z^2) \frac{\partial^2}{\partial z^2} P_m^l(z) - 2z \frac{\partial}{\partial z} P_m^l(z) + \left[ l(l+1) - \frac{m^2}{1 - z^2} \right] P_m^l(z) = 0
\]

which is the differential equation satisfied by the associated Legendre functions. On changing variables from \( z \) to \( \cos \theta \), one finds that the associated Legendre polynomials satisfy

\[
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} P_m^l(\cos \theta) \right) + \left[ l(l+1) - \frac{m^2}{\sin^2 \theta} \right] P_m^l(\cos \theta) = 0
\]

The above equation occurs as part of eigenvalue equation for the magnitude of the orbital angular momentum, when the \( \phi \) dependence has been separated out by the introduction of the quantum number \( m \) corresponding to the \( z \) component of the orbital angular momentum. The normalized part of the wave function which depends on the polar angle \( \theta \) is given by

\[
\Theta_m^l(\theta) = \sqrt{\frac{(2l + 1)(l - m)!}{(l + m)!}} P_m^l(\cos \theta)
\]

which involves the associated Legendre function in the variable \( \cos \theta \).

4.5.11 Spherical Harmonics

Explicit expressions for the first few spherical harmonics \( Y_m^l(\theta, \phi) \) are given in Tables(3-4). The spherical harmonics are normalized so that

\[
\int_0^{2\pi} d\phi \int_0^\pi d\theta \ Y_m^{l*}(\theta, \phi) \ Y_m^l(\theta, \phi) = \delta_{l,l'} \delta_{m,m'}
\]
Table 3: The Lowest Order Spherical Harmonics $Y_{lm}^l(\theta, \varphi)$.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$m$</th>
<th>$Y_{lm}^l(\theta, \varphi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$Y_{00}^0(\theta, \varphi)$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$Y_{00}^1(\theta, \varphi)$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1$</td>
<td>$Y_{\pm 1}^1(\theta, \varphi)$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$Y_{00}^2(\theta, \varphi)$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1$</td>
<td>$Y_{\pm 1}^2(\theta, \varphi)$</td>
</tr>
<tr>
<td></td>
<td>$\pm 2$</td>
<td>$Y_{\pm 2}^2(\theta, \varphi)$</td>
</tr>
</tbody>
</table>

Table 4: The Spherical Harmonics with $l = 3$, $Y_{lm}^3(\theta, \varphi)$.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$m$</th>
<th>$Y_{lm}^3(\theta, \varphi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>$Y_{00}^3(\theta, \varphi)$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1$</td>
<td>$Y_{\pm 1}^3(\theta, \varphi)$</td>
</tr>
<tr>
<td></td>
<td>$\pm 2$</td>
<td>$Y_{\pm 2}^3(\theta, \varphi)$</td>
</tr>
<tr>
<td></td>
<td>$\pm 3$</td>
<td>$Y_{\pm 3}^3(\theta, \varphi)$</td>
</tr>
</tbody>
</table>
Figure 74: The angular dependence of the squared modulus of the spherical harmonic $|Y_0^0(\theta, \varphi)|^2$. Since the spherical harmonic does not depend on $(\theta, \varphi)$ via the exponential term $\exp[im\varphi]$, the angular distribution is spherically symmetric. The $\theta$ dependence for $l = 0$ is shown as a polar plot.
Figure 75: The angular dependence of the squared modulus of the spherical harmonics $|Y^l_m(\theta, \varphi)|^2$. Since the spherical harmonics only depend on $\varphi$ via the exponential term $\exp[i \, m \, \varphi]$, the probability density is independent of $\varphi$. The angular dependence is solely determined by the associated Legendre functions $\Theta^l_m(\theta)$. The $\theta$ dependence for $l = 1$, $m = \pm 1$, 0 are shown as polar plots.
Under inversion $\mathbf{r} \rightarrow -\mathbf{r}$, then as $\varphi \rightarrow \varphi + \pi$ and $\theta \rightarrow \pi - \theta$, one finds that the spherical harmonics transform as

$$Y^l_m(\theta, \varphi) \rightarrow Y^l_m(\pi - \theta, \pi + \varphi) \rightarrow (-1)^l Y^l_m(\theta, \varphi) \quad (1341)$$

Thus, all orbital angular momentum wave functions with the same value of $l$ must have the same parity.

The spherical harmonics are simultaneous eigenstates of two Hermitean operators, therefore, they form a complete set. The completeness relation in the space of $(\theta, \varphi)$ can be expressed as

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y^l_m(\theta', \varphi')^* Y^l_m(\theta, \varphi) = \delta(\hat{\mathbf{r}}' - \hat{\mathbf{r}}) \quad (1342)$$

where the delta function expresses the condition that the directions $\hat{\mathbf{r}}$ and $\hat{\mathbf{r}}'$ must be the same.

4.5.12 Exercise 80

Calculate the vector probability current density $j(r, \theta, \varphi)$ for a wave function of the form

$$\Psi(r, \theta, \varphi) = f(r) Y^l_m(\theta, \varphi) \quad (1343)$$

which has an orbital angular momentum of $l = 1$, for the various eigenvalues of the $z$ component of the angular momentum, $m$, if $f(r)$ is a real function.

4.5.13 Solution 80

The velocity is expressed as

$$\mathbf{v} = \frac{\hat{p}}{m_e} = -i \frac{\hbar}{m_e} \nabla \quad (1344)$$

The gradient is written as

$$\nabla = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \quad (1345)$$
Figure 76: The angular dependence of the squared modulus of the spherical harmonics $|Y_{lm}(\theta, \phi)|^2$. Since the spherical harmonics only depend on $\phi$ via the exponential term $\exp[i m \phi]$, the probability density is independent of $\phi$. The angular dependence is solely determined by the associated Legendre functions $\Theta_{lm}(\theta)$. The $\theta$ dependence for $l = 2$, $m = \pm 2, \pm 1, 0$ are shown as polar plots.
Figure 77: The angular dependence of the squared modulus of the spherical harmonics \( |Y_{l}^{m}(\theta, \varphi)|^2 \). Since the spherical harmonics only depend on \( \varphi \) via the exponential term \( \exp[im \varphi] \), the probability density is independent of \( \varphi \). The angular dependence is solely determined by the associated Legendre functions \( \Theta_{l}^{m}(\theta) \). The \( \theta \) dependence for \( l = 3, m = \pm 3, \pm 2, \pm 1, 0 \) are shown as polar plots. The probability density is peaked up in the equatorial plane \( \theta = \frac{\pi}{2} \) for \( m = \pm l \).
Inversion

Figure 78: In spherical polar coordinates, the inversion or parity operator produces the transformation $\varphi \rightarrow \varphi + \pi$ and $\theta \rightarrow \pi - \theta$.

The probability current density is expressed in terms of the wave function $\Psi(r, t)$ as the imaginary part of a vector quantity

$$
\mathbf{j}(r, t) = \frac{\hbar}{m_e} \Im \left[ \Psi^*(r, t) \nabla \Psi(r, t) \right]
$$

which in the case of a pure energy eigenvalue is time independent. In spherical polar coordinates, the probability current is expressed as

$$
\mathbf{j}(r, t) = \hat{e}_r \frac{\hbar}{2m_e} i \left( \Psi^*(r) \frac{\partial}{\partial r} \Psi(r) - \Psi(r) \frac{\partial}{\partial r} \Psi^*(r) \right)
$$

$$
+ \hat{e}_\theta \frac{\hbar}{2m_e} r \left( \Psi^*(r) \frac{\partial}{\partial \theta} \Psi(r) - \Psi(r) \frac{\partial}{\partial \theta} \Psi^*(r) \right)
$$

$$
+ \hat{e}_\varphi \frac{\hbar}{2m_e} i r \sin \theta \left( \Psi^*(r) \frac{\partial}{\partial \varphi} \Psi(r) - \Psi(r) \frac{\partial}{\partial \varphi} \Psi^*(r) \right)
$$

On expressing the wave function as

$$
\Psi(r) = g(r) \Theta_l^m(\theta) \exp \left[ i m \varphi \right]
$$
where both \( g(r) \) and the associated Legendre functions \( \Theta^l_m(\theta) \) are real, one obtains

\[
\hat{\mathbf{j}}(\mathbf{r}, t) = \hat{\mathbf{e}}_\varphi \frac{\hbar m}{m_e r \sin \theta} \left( g(r) \Theta^l_m(\theta) \right)^2
\]

\[
= \hat{\mathbf{e}}_\varphi \frac{\hbar m}{m_e r \sin \theta} \left| \Psi(r) \right|^2
\]

(1349)

where \( m \) is the azimuthal or magnetic quantum number. Hence, if the state is an eigenstate of the \( z \) component of the angular momentum, the probability current orbits around the atom in orbits parallel to the \( x - y \) plane.

### 4.5.14 Exercise 81

In the dipole approximation, the average power radiated when the hydrogen atom decays from the \( n, l \) th excited state to the \( n', l' \) th excited state is given by

\[
P_{n,l,n',l'} = \frac{4 \omega^4 \varepsilon^2}{3} \int d^3\mathbf{r} \phi^*_{n',l',m'}(\mathbf{r}) \mathbf{r} \phi_{n,l,m}(\mathbf{r})^2
\]

(1350)

By considering the angular integration, show that the only non-zero matrix elements occur when the angular momentum quantum numbers \( l \) and \( m \) for the two states are related via

\[
\Delta l = l' - l = \pm 1 \\
\Delta m = m' - m = 0, \pm 1
\]

(1351)

These are the selection rules for dipole radiation. From conservation of angular momentum, and since \( \Delta l = \pm 1 \), one sees that the photon must have spin one. The photon has a spin which is an integer multiple of \( \hbar \) and, therefore, it is a boson. This contrasts with particles which have spins that are half-odd integer multiples of \( \hbar \), such as the electron which has \( \frac{1}{2} \hbar \), that are fermions\(^{15}\). Transitions which do not satisfy the dipole selection rules are forbidden. Generally, forbidden transitions still can occur, but require going beyond the dipole approximation and have intensities which are lower by factors of the order of magnitude \( \frac{a_0^2}{\lambda^2} \) where \( a_0 \) is the Bohr radius and \( \lambda \) is the wave length of light.

\(^{15}\)The relationship between spin and statistics was first discussed by W. Pauli in the article, Physical Review, 58, 716 (1940).
Figure 79: The energy levels for Hydrogen (with $4 \geq l$). The energies are plotted in units of Rydbergs. Some of the transitions allowed by the electric dipole selection rule are shown.

### 4.5.15 Solution 81

The vector $\mathbf{r}$ is expressed in terms of the Cartesian unit vectors through

$$\mathbf{r} = r \left( \cos \theta \hat{e}_z + \sin \theta \left( \sin \varphi \hat{e}_y + \cos \varphi \hat{e}_x \right) \right)$$  \hspace{1cm} (1352)

and substituted into the matrix elements. To evaluate the angular integrations, we start by finding the two recurrence relations

$$(2l + 1) \cos \theta P^l_m(\cos \theta) = (l + m) P^{l-1}_m(\cos \theta) + (l - m + 1) P^{l+1}_m(\cos \theta)$$

$$(2l + 1) \sin \theta P^l_m(\cos \theta) = P^{l-1}_{m+1}(\cos \theta) + P^{l+1}_{m+1}(\cos \theta)$$  \hspace{1cm} (1353)

and then show that

$$\cos \theta Y^l_m(\theta, \varphi) =$$

$$= \left( \frac{(l - m + 1) (l + m + 1)}{(2l + 1) (2l + 3)} \right)^{\frac{1}{2}} Y^{l+1}_m + \left( \frac{(l - m) (l + m)}{(2l - 1) (2l + 1)} \right)^{\frac{1}{2}} Y^{l-1}_m$$

$$\exp \left[ + i \varphi \right] \sin \theta Y^l_m(\theta, \varphi) =$$

303
\[
\frac{(l + m + 1)(l + m + 2)}{(2l + 1)(2l + 3)} \frac{1}{2} Y_{m+1}^{l+1} + \frac{(l - m)(l - m - 1)}{(2l - 1)(2l + 1)} \frac{1}{2} Y_{m+1}^{l-1} + \frac{(l + m)(l + m - 1)}{(2l - 1)(2l + 1)} \frac{1}{2} Y_{m-1}^{l+1} + \frac{(l - m)(l - m + 1)}{(2l + 1)(2l + 3)} \frac{1}{2} Y_{m-1}^{l-1}
\]

(1355)

\[
\exp \left[ -i \varphi \right] \sin \theta Y_{m}^{l}(\theta, \varphi) =
\]

(1356)

The expected result then follows immediately from the orthogonality of the spherical harmonics.

4.5.16 Exercise 82

Consider the commutation relations

\[
[ \hat{L}_z, x ] = + i \hbar y \\
[ \hat{L}_z, y ] = - i \hbar x \\
[ \hat{L}_z, z ] = 0
\]

(1357)

Take the matrix elements of the commutator involving \( z \) between states with angular momentum \((l', m')\) and \((l, m)\) and use the eigenvalue equation to show that

\[
( m - m' ) \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta Y_{m'}^{l'}(\theta, \varphi)^* \cos \theta Y_{m}^{l}(\theta, \varphi) = 0
\]

(1358)

Likewise, by considering the commutation rules involving \( x \) and \( y \), show that they can be combined to yield

\[
( m - m')^2 \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta Y_{m'}^{l'}(\theta, \varphi)^* \sin \theta \cos \varphi Y_{m}^{l}(\theta, \varphi)
\]

\[
= \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta Y_{m'}^{l'}(\theta, \varphi)^* \sin \theta \cos \varphi Y_{m}^{l}(\theta, \varphi)
\]

(1359)

Hence, deduce the selection rule that the matrix element

\[
\int d^3 \mathbf{r} \phi_{n', l', m'}^{*}(\mathbf{r}) \mathbf{r} \cdot \mathbf{L} \cdot \phi_{n, l, m}(\mathbf{r}) = 0
\]

(1360)

vanishes unless \( m' - m = \pm 1 \) or \( m' - m = 0 \).
Following a similar procedure with the double commutator\(^{16}\)

\[
[ \hat{L}^2 , [ \hat{L}^2 , \hat{r} ] ] = 2 \hbar^2 \left( \hat{r} \hat{L}^2 + \hat{L}^2 \hat{r} \right)
\]

(1362)
deduce that the matrix elements

\[
\int d^3 \vec{r} \phi^*_{n',l',m'}(\vec{r}) \hat{r} \phi_{n,l,m}(\vec{r})
\]

(1363)
are only non-zero if \(l\) and \(l'\) satisfy the equation

\[
\left( (l' + l + 1)^2 - 1 \right) \left( (l' - l)^2 - 1 \right) = 0
\]

(1364)
Since the first factor is always positive (unless \(l' = l = 0\)), the electric dipole selection rule becomes \(l' - l = \pm 1\).

---

### 4.5.17 Solution 82

The selection rules for the \(z\)-component of the electron’s orbital angular momentum can be proved by considering the commutation relations

\[
[ \hat{L}_z , x ] = i \hbar y \\
[ \hat{L}_z , y ] = -i \hbar x \\
[ \hat{L}_z , z ] = 0
\]

(1365)
On taking the matrix elements between states with definite \(z\)-components of the angular momenta, one finds

\[
< n'l'm' | [ \hat{L}_z , x ] | nlm > = i \hbar < n'l'm' | y | nlm > \\
< n'l'm' | [ \hat{L}_z , y ] | nlm > = -i \hbar < n'l'm' | x | nlm > \\
< n'l'm' | [ \hat{L}_z , z ] | nlm > = 0
\]

(1366)
which reduce to

\[
( m' - m ) < n'l'm' | x | nlm > = i < n'l'm' | y | nlm > \\
( m' - m ) < n'l'm' | y | nlm > = -i < n'l'm' | x | nlm > \\
( m' - m ) < n'l'm' | z | nlm > = 0
\]

(1367)
\(^{16}\)As was shown by Dirac (P. A. M. Dirac, Proc. Roy. Soc. A111, 251 (1926)), this double commutation relation is a specific example of the more general relation

\[
[ \hat{J}^2 , [ \hat{J}^2 , \hat{A} ] ] = 2 \hbar^2 \left( \hat{A} \hat{J}^2 + \hat{J}^2 \hat{A} \right) - 4 \hbar^2 ( \hat{A} \cdot \hat{\hat{J}} ) \hat{\hat{J}}
\]

(1361)
valid for any arbitrary vector operator \(\hat{A}\).
From the last equation, it follows that either \( m' = m \) or that

\[
< n' l' m' | z | nlm > = 0
\]  
(1368)

On combining the first two equations, one finds that

\[
( m' - m )^2 < n' l' m' | x | nlm > = \left( m' - m \right) < n' l' m' | y | nlm > = < n' l' m' | x | nlm >
\]  
(1369)

This equation is solved by requiring that either

\[
( m' - m )^2 = 1
\]  
(1370)

or

\[
< n' l' m' | x | nlm > = 0
\]  
(1371)

Hence, we have derived the selection rules \( \Delta m = \pm 1, 0 \).

The selection rules for the magnitude of the electrons orbital angular momentum are found by considering the double commutator

\[
[ \hat{L}^2, [ \hat{L}^2, \mathbf{r} ] ] = 2 \hbar^2 \left( \mathbf{r} \hat{L}^2 + \hat{L}^2 \mathbf{r} \right)
\]  
(1372)

On taking the matrix elements of this equation between eigenstates of the magnitude of the orbital angular momentum, one finds

\[
\hbar^4 \left( l' ( l' + 1 ) - l ( l + 1 ) \right)^2 < n' l' m' | \mathbf{r} | nlm > = \left( l' ( l' + 1 ) + l ( l + 1 ) \right) < n' l' m' | \mathbf{r} | nlm >
\]  
(1373)

Hence, either

\[
< n' l' m' | nlm > = 0
\]  
(1374)

or

\[
\left( ( l' + l + 1 )^2 - 1 \right) \left( ( l' - l )^2 - 1 \right) = 0
\]  
(1375)

Since the first factor is always positive for non-zero \( l \) and \( l' \), the electric dipole selection rule becomes \( \Delta l = \pm 1 \).

### 4.5.18 The Addition Theorem

The addition theorem for spherical harmonics states that

\[
P_l( \cos \gamma ) = \frac{4 \pi}{2 l + 1} \sum_{m=-l}^{m=l} Y^l_m(\theta_1, \varphi_1) Y^l_m(\theta_2, \varphi_2)^*
\]  
(1376)
where $\gamma$ is the angle between the directions $(\theta_1, \varphi_1)$ and $(\theta_2, \varphi_2)$, i.e.,

$$\cos \gamma = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos (\varphi_1 - \varphi_2)$$  \hspace{1cm} (1377)

We shall assume that we can expand $P_l(\cos \gamma)$ as a Laplace series

$$P_l(\cos \gamma) = \sum_{m_1} a_{lm_1} Y_{m_1}^l(\theta_1, \varphi_1)$$  \hspace{1cm} (1378)

where

$$a_{lm_1} = \int d\Omega_1 P_l(\cos \gamma) Y_{m_1}^l(\theta_1, \varphi_1)$$  \hspace{1cm} (1379)

But, on noting that the associated Legendre polynomials are the same as the Legendre polynomials when $m = 0$ and on using eqn(1315), one obtains

$$P_l(\cos \gamma) = \left(\frac{4 \pi}{2l + 1}\right)^{\frac{1}{2}} Y_0^l(\gamma, 0)$$  \hspace{1cm} (1380)

The choice of the azimuthal angle as 0 is irrelevant, as $m = 0$. Hence, we have

$$a_{lm_1} = \left(\frac{4 \pi}{2l + 1}\right)^{\frac{1}{2}} \int d\Omega_1 Y_0^l(\gamma, 0) Y_{m_1}^l(\theta_1, \varphi_1)^*$$  \hspace{1cm} (1381)

The choice of the orientation of the axes is irrelevant, as the integration over $d\Omega_1$ runs over all $4\pi$ solid angle. We shall choose the direction $(\theta_2, \varphi_2)$ as our polar axis. In this case, we need to re-express the spherical harmonic $Y_{m_1}^l(\theta_1, \varphi_1)$ in terms of our new variable of integration

$$Y_{m_1}^l(\theta_1, \varphi_1)^* = \sum_{m_2} b_{m_2}^l Y_{m_2}^l(\gamma, 0)^*$$  \hspace{1cm} (1382)

where, as we are dealing with an eigenfunction of the scalar magnitude of the angular momentum with eigenvalue governed by $l$, the eigenvalue $l$ is completely unaltered by a different choice of Cartesian coordinates. Thus,

$$a_{m_1}^l = \left(\frac{4 \pi}{2l + 1}\right)^{\frac{1}{2}} \sum_{m_2} \int d\Omega_1 Y_0^l(\gamma, 0) b_{m_2}^l Y_{m_2}^l(\gamma, 0)^*$$

$$= \left(\frac{4 \pi}{2l + 1}\right)^{\frac{1}{2}} \sum_{m_2} b_{m_2}^l \delta_{m_2,0}$$

$$= \left(\frac{4 \pi}{2l + 1}\right)^{\frac{1}{2}} b_0^l$$  \hspace{1cm} (1383)

where we have used the orthogonality property of the spherical harmonics.

Therefore, we see that the coefficients $a_{m_1}^l$ which appear in the Laplace expansion are related to only one non-zero coefficient $b_0^l$ in their expansion given
by eqn(1382). The coefficient $b_0^*$ can be obtained directly when $\gamma = 0$ as the expansion only contains the one term
\[ Y_{m_2}^l(\theta_1, \varphi_1)^* = b_0^* Y_0^0(0,0)^* = b_0^* \left( \frac{2l + 1}{4\pi} \right)^{\frac{1}{2}} \] (1384)
since the spherical harmonics with $m \neq 0$ vanish when $\gamma = 0$. In the above equation the variables $(\theta_1, \varphi_1)$ take on the fixed numerical values $(\theta_2, \varphi_2)$, because $\gamma \equiv 0$. Hence,
\[ b_0^* = \left( \frac{4\pi}{2l + 1} \right)^{\frac{1}{2}} Y_{m_2}^l(\theta_2, \varphi_2)^* \] (1385)
Inserting this into eqn(1383), we have
\[ a_{m_1}^l = \left( \frac{4\pi}{2l + 1} \right)^{\frac{1}{2}} Y_{m_2}^l(\theta_2, \varphi_2)^* \] (1386)
On substituting the coefficient $a_{m_1}^l$, back into the Laplace series expansion, one has
\[ P_l(\cos \gamma) = \frac{4\pi}{2l + 1} \sum_{m_1 = -l}^{m_1 = l} Y_{m_2}^l(\theta_1, \varphi_1) Y_{m_1}^l(\theta_2, \varphi_2)^* \] (1387)
This concludes the proof of the Addition Theorem for Spherical Harmonics.

4.5.19 Finite-Dimensional Representations

One can find a representation of the angular momentum operators $\hat{L}_i$ within the manifold of eigenstates of $\hat{L}_z^2$ with the eigenvalue $\lambda_l$. The states are to be represented by column vectors. Since the eigenvalues are $(2l + 1)$ fold degenerate, the space is spanned by unit column vectors with $(2l + 1)$ rows. Any arbitrary column vector can be expressed as a linear superposition of the $(2l + 1)$ basis column vectors. The angular momentum operators act on the states, and transform the states into other states. The rules of transformation correspond to the laws of matrix multiplication, in which the operators are $(2l + 1) \times (2l + 1)$ dimensional square matrices. For convenience, the basis states may be taken to be the $(2l + 1)$ eigenstates of $\hat{L}_z$. For definiteness, we shall restrict our discussion to $l = 1$. The three basis eigenstates may be represented by the unit column vectors;
\[ Y_1^1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \] (1388)
with eigenvalue $+\hbar$,
\[ Y_0^1 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \] (1389)
with eigenvalue 0, and
\[
Y_{-1}^l = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}
\] (1390)
with eigenvalue \( -\hbar \). Any arbitrary state \( \Psi \) with eigenvalue \( \lambda_l \) can be expressed as the linear superposition of the basis states via
\[
\Psi = \sum_{m=-1}^{m=1} \Psi_m Y_m^l
\] (1391)
in which \( \Psi_m \) are the expansion coefficients. This equation can be expressed more concretely as
\[
\begin{pmatrix} \Psi_1 \\ \Psi_0 \\ \Psi_{-1} \end{pmatrix} = \Psi_1 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \Psi_0 \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + \Psi_{-1} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}
\] (1392)
The inner product of two states \( \Psi \) and \( \Phi \) is defined to be a complex number, obtained via
\[
\Phi^\dagger \Psi = \sum_{m=-1}^{m=1} \Phi_m^* \Psi_m
\] (1393)
The inner product is a generalization of the scalar product to arbitrary dimensional (in this case \( 2l + 1 \) dimensional) column matrices with complex components. It involves a row vector \( \Phi^\dagger \) which is the complex conjugate and transpose of the column vector \( \Phi \). In general, it is convenient to label the components of the basis vectors by an abstract index \( i \), instead of the quantum number \( m \) which corresponds to the \( z \) component of angular momentum. We shall use this more general labelling below. The inner product is just the result of the matrix multiplication of the row matrix \( \Phi^\dagger \) with the column matrix \( \Psi \), i.e.,
\[
\Phi^\dagger \Psi = \begin{pmatrix} \Phi_1^* & \Phi_2^* & \Phi_3^* \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \end{pmatrix}
\] (1394)
where we are labelling the three components of our states \( \Phi \) and \( \Psi \) by the index \( i \). We shall assume that our states \( \Psi \) are normalized to unity, that is, we require
\[
\Psi^\dagger \Psi = \sum_{i=1}^{i=3} \Psi_i^* \Psi_i = 1
\] (1395)
This just corresponds to the condition that the sum over all possibilities yields a probability of unity.

The effect of an operator \( \hat{A} \) on a state \( \Psi \) transforms it into another state \( \Phi \), according to the laws of matrix multiplication
\[
\Phi = \hat{A} \Psi
\] (1396)
where \( \hat{A} \) is a three by three matrix. More concretely, the action of the operator is given by
\[
\begin{pmatrix}
\Phi_1 \\
\Phi_2 \\
\Phi_3 
\end{pmatrix} =
\begin{pmatrix}
A_{1,1} & A_{1,2} & A_{1,3} \\
A_{2,1} & A_{2,2} & A_{2,3} \\
A_{3,1} & A_{3,2} & A_{3,3}
\end{pmatrix}
\begin{pmatrix}
\Psi_1 \\
\Psi_2 \\
\Psi_3 
\end{pmatrix}
\]\n(1397)
which results in the state \( \Phi \) having the components
\[
\Phi_i = \sum_{j=1}^{3} A_{i,j} \Psi_j
\]\n(1398)

The operator \( \hat{A} \) is specified by specifying the matrix elements \( A_{i,j} \). Operators represented by matrices can be compounded by the laws of matrix addition and multiplication. Matrix multiplication is generally non-commutative, and is suitable for representing non-commuting operators.

The Hermitian conjugate of the operator is defined by the equation
\[
\left( \Phi^\dagger \hat{A} \Psi \right)^* = \Psi^\dagger \hat{A}^\dagger \Phi
\]\n(1399)
which must be true for any arbitrary states \( \Phi \) and \( \Psi \). From this, one can see that the Hermitian conjugate of a matrix is just the complex conjugate of the transposed matrix. Thus, if the matrix \( \hat{A} \) has matrix elements \( A_{i,j} \), then the Hermitian conjugate \( \hat{A}^\dagger \) has matrix elements given by \( A_{j,i}^* \). A Hermitian matrix is defined to be a matrix for which \( \hat{A} = \hat{A}^\dagger \).

Since the basis states are eigenfunctions of the operator \( \hat{L}_z \), one has
\[
\hat{L}_z \ Y_{m}^l = m \hbar \ Y_{m}^l
\]\n(1400)
The three linear equations can be trivially interpreted as a matrix equation, in which the operator \( \hat{L}_z \) is diagonal in the chosen basis. Thus, one can represent the operator \( \hat{L}_z \) by the diagonal three by three matrix
\[
\hat{L}_z = \hbar \begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]\n(1401)
where the diagonal matrix elements are just the eigenvalues of \( \hat{L}_z \). The effect of the raising operator \( \hat{L}_+ \) on the basis states is to raise the angular momentum according to the law
\[
\hat{L}_+ \ Y_{m}^l = \hbar \sqrt{ (l - m)(l + m + 1) } \ Y_{m+1}^l
\]\n(1402)
Since the effect of \( \hat{L}_+ \) on the state with maximal \( m \), \( m = +1 \), is to produce zero, one has one trivial and two non-trivial algebraic equations, which can be
used to represent the raising operator as

\[ \hat{L}_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \]  \hspace{1cm} (1403)

Likewise, from considering the equation

\[ \hat{L}_- Y^l_m = \hbar \sqrt{(l + m)(l - m + 1)} Y^l_{m-1} \]  \hspace{1cm} (1404)

one can construct a representation of the lowering operator as

\[ \hat{L}_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix} \]  \hspace{1cm} (1405)

The \( x \) and \( y \) components of the angular momentum are found from the definitions

\[ \hat{L}_\pm = \hat{L}_x \pm i \hat{L}_y \]  \hspace{1cm} (1406)

as

\[ \hat{L}_x = \frac{1}{2} ( \hat{L}_+ + \hat{L}_- ) \]  \hspace{1cm} (1407)

and

\[ \hat{L}_y = \frac{1}{2i} ( \hat{L}_+ - \hat{L}_- ) \]  \hspace{1cm} (1408)

From which, one has

\[ \hat{L}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \]  \hspace{1cm} (1409)

and

\[ \hat{L}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \]  \hspace{1cm} (1410)

It can be shown that these matrices, when compounded according to the laws of matrix multiplication and addition, satisfy the commutation relations

\[ [ \hat{L}_i, \hat{L}_j ] = i \hbar \sum_k \epsilon_{i,j,k} \hat{L}_k \]  \hspace{1cm} (1411)

where \( \epsilon_{i,j,k} \) is the anti-symmetric Levi-Civita symbol. The anti-symmetric Levi-Civita symbol is defined so that \( \epsilon_{i,j,k} = 1 \) if \( i, j, k \) correspond to an even number of permutations of \( x, y, z \), or is \(-1\), if \( i, j, k \) corresponds to an odd permutation of \( x, y, z \). Otherwise, \( \epsilon_{i,j,k} = 0 \), when one or more index is repeated. Furthermore, since the Hermitian conjugate of the operator just corresponds to the complex conjugate of the transposed matrix, we see that the components \( \hat{L}_k \) not only satisfy the angular momentum commutation relations, but are also
Hermitean operators.

It can then be easily shown that the operator

\[ \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \]  

(1412)
is a diagonal matrix, with non-zero matrix elements \( \lambda_l = 1 \left( 1 + 1 \right) \hbar^2 \). This is as expected, since the basis states are all eigenstates of the magnitude of the angular momentum. Hence, we have

\[ \hat{L}^2 = 2 \hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]  

(1413)

Since the operator corresponding to the magnitude of the angular momentum is proportional to the unit operator, it commutes with all the components of the angular momentum \( \hat{L}_i \). The operator \( \hat{L}^2 \) is sometimes referred to as a Casimir operator.

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**4.5.20 Exercise 83**

Evaluate the commutators of the three by three matrices representing the components of the angular momentum, and show that they satisfy the commutation relations, such as,

\[ [ \hat{L}_x, \hat{L}_y ] = i \hbar \hat{L}_z \]  

(1414)

Also evaluate the matrix corresponding to the square of the angular momentum \( \hat{L}^2 \) and show that it commutes with the various components of \( \hat{L} \), and find the eigenvalues of \( \hat{L}^2 \).

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**4.5.21 Exercise 84**

Find the eigenvalues and eigenvectors of the component of the angular momentum along the unit vector \( \hat{\eta} \), where

\[ \hat{\eta} = \sin \theta \cos \varphi \hat{e}_x + \sin \theta \sin \varphi \hat{e}_y + \cos \theta \hat{e}_z \]  

(1415)

Work in the space of \( l = 1 \) with the basis in which \( \hat{L}_z \) is diagonal.

Hence, find the unitary matrix \( \hat{U}_\hat{e}(\theta) \) which produces a rotation of the states through an angle \( \theta \), about the axis

\[ \hat{e} = - \sin \varphi \hat{e}_x + \cos \varphi \hat{e}_y \]  

(1416)
The operator \( \hat{U}(\theta) \) should bring the eigenstates of \( \hat{L}_z \) into coincidence with the eigenstates of \( \hat{L}_\eta \). It is also required that \( \hat{U}(\theta) \) does not transform the eigenstates of \( \hat{L}_\eta \).

4.5.22 Solution 84

We seek the eigenvalues and eigenfunctions of the operator

\[
\eta \cdot \hat{L} = \sin \theta \cos \varphi \hat{L}_x + \sin \theta \sin \varphi \hat{L}_y + \cos \theta \hat{L}_z
\]

which has the matrix representation

\[
\eta \cdot \hat{L} = \hbar \begin{pmatrix}
\cos \theta & \frac{1}{\sqrt{2}} \sin \theta \exp[-i \varphi] & 0 \\
\frac{1}{\sqrt{2}} \sin \theta \exp[i \varphi] & 0 & \frac{1}{\sqrt{2}} \sin \theta \exp[-i \varphi] \\
0 & \frac{1}{\sqrt{2}} \sin \theta \exp[-i \varphi] & -\cos \theta
\end{pmatrix}
\]

in the basis where \( \hat{L}_z \) is diagonal. The eigenvalues \( \mu \hbar \) are determined from the secular equation

\[
0 = \begin{vmatrix}
\cos \theta - \mu & \frac{1}{\sqrt{2}} \sin \theta \exp[-i \varphi] & 0 \\
\frac{1}{\sqrt{2}} \sin \theta \exp[i \varphi] & -\mu & \frac{1}{\sqrt{2}} \sin \theta \exp[-i \varphi] \\
0 & \frac{1}{\sqrt{2}} \sin \theta \exp[-i \varphi] & -\cos \theta - \mu
\end{vmatrix}
\]

and, thus, are found to be \( \mu = 0, \pm \hbar \). The eigenfunction \( Y_\mu^\eta \) corresponding to the eigenvalue \( \mu \), are denoted by

\[
Y_\mu^\eta = \begin{pmatrix}
\alpha_\mu^\eta \\
\beta_\mu^\eta \\
\gamma_\mu^\eta
\end{pmatrix}
\]

The components of the \( \mu = 0 \) eigenfunction are found from the eigenvalue equation

\[
\begin{pmatrix}
0 \\
0 \\
0
\end{pmatrix} = \begin{pmatrix}
\sqrt{2} \cos \theta & \sin \theta \exp[-i \varphi] & 0 \\
\sin \theta \exp[i \varphi] & 0 & \sin \theta \exp[-i \varphi] \\
0 & \sin \theta \exp[i \varphi] & -\sqrt{2} \cos \theta
\end{pmatrix} \begin{pmatrix}
\alpha_0^\eta \\
\beta_0^\eta \\
\gamma_0^\eta
\end{pmatrix}
\]

Thus, the normalized eigenfunction of the operator in eqn(1417) corresponding to the zero eigenvalue is found as

\[
Y_0^\eta = \frac{1}{\sqrt{2}} \begin{pmatrix}
-\sin \theta \exp[-i \varphi] \\
\sqrt{2} \cos \theta \\
\sin \theta \exp[i \varphi]
\end{pmatrix}
\]
Likewise, one finds the eigenfunction corresponding to $\mu = +1$ is given by

$$Y^\eta_1 = \frac{1}{2} \begin{pmatrix} (1 + \cos \theta) \exp[-i \varphi] \\ \sqrt{2} \sin \theta \\ (1 - \cos \theta) \exp[i \varphi] \end{pmatrix}$$

and the eigenfunction corresponding to $\mu = -1$ is found as

$$Y^{-\eta}_1 = \frac{1}{2} \begin{pmatrix} (1 - \cos \theta) \exp[-i \varphi] \\ -\sqrt{2} \sin \theta \\ (1 + \cos \theta) \exp[i \varphi] \end{pmatrix}$$

The phases of the eigenfunctions are completely arbitrary.

The required rotation is about an axis in the plane perpendicular to the unit vectors $\hat{e}_z$ and $\hat{e}_\eta$. Since the rotation is specified by three parameters (the axis of the rotation and the angle of rotation), the transformation matrix contains three parameters that have to be determined. The rotation matrix $\hat{U}_\eta(\theta)$ is partly determined from its action on the eigenstates of $\hat{L}_z$

$$Y^\eta_\mu = \hat{U}_\eta(\theta) Y^z_\mu$$

There is also the subsidiary requirement that the component of the spins along the rotation axis are unaffected, which means that the eigenstates of $\hat{L}_\eta$ should be mapped onto themselves. Thus, we have

$$\begin{pmatrix} \alpha^\eta_\mu \\ \beta^\eta_\mu \\ \gamma^\eta_\mu \end{pmatrix} = \frac{1}{2} \begin{pmatrix} (1 + \cos \theta) \exp[-i \varphi] - \sqrt{2} \sin \theta \exp[-i \varphi] \\ \sqrt{2} \sin \theta \\ (1 - \cos \theta) \exp[i \varphi] \end{pmatrix} \begin{pmatrix} (1 - \cos \theta) \exp[-i \varphi] \\ 2 \cos \theta \\ -\sqrt{2} \sin \theta \end{pmatrix}$$

$$\times \begin{pmatrix} \alpha^z_\mu \\ \beta^z_\mu \\ \gamma^z_\mu \end{pmatrix}$$

The columns of the transformation matrix $\hat{U}_\eta(\varphi)$ are the eigenvectors that we have just found. The phases of the columns can be altered to fit our requirement that a state with angular momentum directed along the axis of rotation $\hat{e}_\eta$ remains unchanged (apart from an over all phase factor). The phase factors of the $Y^\eta_\mu$ are chosen as $\exp[i \mu \varphi]$ so that the diagonal elements of the unitary transformation are real\footnote{The change of phase can be understood as being the result of a rotation through $\varphi$ about the $\hat{\eta}$ axis}. This choice of phase factors produces the desired rotation since the eigenstates of $\hat{L}_\eta$ are unchanged by it. More precisely, under
this transformation, the eigenstates of \( \hat{L}_e \) only change by a \( \theta \) dependent phase factor. Also, with the above choice of phase, the eigenstates \( Y_i^m \) are completely unaffected by the transformation, if the angle of rotation \( \theta \) is set to zero.

The above result can be re-written as follows. On recognizing that the component of the angular momentum operator parallel to the axis of rotation is given by

\[
\left( \hat{e} \cdot \hat{L} \right) = \frac{\hbar}{\sqrt{2}} \begin{pmatrix}
0 & -i \exp[-i \varphi] & 0 \\
-i \exp[i \varphi] & 0 & -i \exp[i \varphi] \\
i \exp[i \varphi] & i \exp[-i \varphi] & 0
\end{pmatrix}
\]

and that the square is given by

\[
\left( \hat{e} \cdot \hat{L} \right)^2 = \frac{\hbar^2}{2} \begin{pmatrix}
1 & 0 & -\exp[-2i \varphi] \\
0 & 2 & 0 \\
-\exp[+2i \varphi] & 0 & 1
\end{pmatrix}
\]

we find that the rotation operator may be written in the form

\[
\hat{U}_e(\theta) = \hat{1} + \left( \cos \theta - 1 \right) \left( \frac{\hat{e} \cdot \hat{L}}{\hbar} \right)^2 - i \sin \theta \left( \frac{\hat{e} \cdot \hat{L}}{\hbar} \right)
\]

This is an example of Cayley’s theorem, as the rotation about the axis \( \hat{e} \) can be written as the exponential of a matrix

\[
\hat{U}_e(\theta) = \exp \left[ -\frac{i}{\hbar} \theta \left( \hat{e} \cdot \hat{L} \right) \right]
\]

The angular momentum operator corresponding to larger \( l \) values can also be constructed by the same method, but with a larger number of basis states. In particular, one requires \( (2l + 1) \) basis states to span the space with total angular momentum \( l \). In fact, almost any operator can be represented by a \( N \times N \) square matrix acting on a \( N \)-dimensional column vector, however, this is only useful for bases where the dimension \( N \) is finite.

4.5.23 The Laplacian Operator

The magnitude of the angular momentum can be expressed in terms of the Laplacian by using the vector identity

\[
\left( A \wedge B \right) \cdot \left( C \wedge D \right) = \left( A \cdot C \right) \left( B \cdot D \right) - \left( A \cdot D \right) \left( B \cdot C \right)
\]
which, for our operators, can be adapted as

\[ \hat{L}^2 = (\hat{r} \wedge \hat{p}) \cdot (\hat{r} \wedge \hat{p}) \]

\[ = - (\hat{r} \wedge \hat{p}) \cdot (\hat{p} \wedge \hat{r}) \]

\[ = - \hat{r} \cdot \left[ \hat{p} \cdot (\hat{p} \cdot \hat{r}) - \hat{p}^2 \hat{r} \right] \]  

(1432)

In manipulating the expression for the square of the angular momentum, one has to carefully respect the ordering of \( \hat{r} \) and \( \hat{p} \). In the second line we have used the identity

\[ \hat{r} \wedge \hat{p} = - \hat{p} \wedge \hat{r} \]  

(1433)

which is valid because the different components of the position and angular momentum commute. The last term in eqn(1432) can be written in terms of \( r^2 \hat{p}^2 \) by using the commutator

\[ [\hat{r}, \hat{p}^2] = 2i \hbar \hat{p} \]  

(1434)

Also the first term in eqn(1432) can be re-written by using the commutator

\[ \hat{p} \cdot \hat{r} - \hat{r} \cdot \hat{p} = -3i \hbar \]  

(1435)

in the last factor. Hence, we obtain

\[ \hat{L}^2 = r^2 \hat{p}^2 + i \hbar \hat{r} \cdot \hat{p} - (\hat{r} \cdot \hat{p}) (\hat{r} \cdot \hat{p}) \]  

(1436)

The term \( \hat{r} \cdot \hat{p} \) is evaluated as

\[ \hat{r} \cdot \hat{p} = -i \hbar \frac{\partial}{\partial r} \]  

(1437)

Putting these together, we find that the square of the angular momentum is given by

\[ \hat{L}^2 = r^2 \hat{p}^2 + \hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \]  

(1438)

Thus, we find that the Laplacian operator is expressed in terms of the angular momentum by

\[ \hat{\nabla}^2 = \frac{\hat{L}^2}{r^2} - \frac{\hbar^2}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \]  

(1439)

This results in the usual expression for the kinetic energy in spherical polar coordinates

\[ \hat{T} = \frac{\hat{p}^2}{2m} \]

\[ = \frac{\hat{L}^2}{2m} - \frac{\hbar^2}{2m r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \]  

(1440)
4.5.24 An Excursion into $d$-Dimensional Space

As angular momentum is associated with a rotation in a two-dimensional plane and since in $d$ dimensions there is no unique normal to a two-dimensional plane, the angular momentum is not a vector. The angular momentum is a two-form and has $d(d-1)/2$ components that are labelled by two indices denoting the plane of rotation. In a Cartesian coordinate system, the components of $\hat{L}_{j,k}$ are defined via

$$\hat{L}_{j,k} = -i \hbar \left( x_j \frac{\partial}{\partial x_k} - x_k \frac{\partial}{\partial x_j} \right)$$

(1441)

The quantity $\hat{L}_{j,k}$ is antisymmetric in the indices $j$ and $k$. The square of the angular momentum no longer has a simple geometric significance, but is still defined as the operator

$$\hat{L}^2 = \sum_{j>k} d \hat{L}_{j,k}^2$$

$$= -\hbar^2 \sum_{j>k} \left( x_j \frac{\partial}{\partial x_k} - x_k \frac{\partial}{\partial x_j} \right)^2$$

(1442)

The above form can be expanded as

$$\hat{L}^2 = -\hbar^2 \sum_{j,k} \left( x_j^2 \frac{\partial^2}{\partial x_k^2} - x_j x_k \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_k} \right) + (d-1) \hbar^2 \sum_{j=1}^d x_j \frac{\partial}{\partial x_j}$$

$$= r^2 \hat{p}^2 + \hbar^2 \sum_{j,k} x_j x_k \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_k} + (d-1) \hbar^2 \sum_{j=1}^d x_j \frac{\partial}{\partial x_j}$$

(1443)

where the radius is defined by the $d$-dimensional version of the Pythagorean theorem

$$r^2 = \sum_{j=1}^d x_j^2$$

(1444)

A point in a $d$-dimensional space can be described by hyper-spherical polar coordinates involving the hyper-radius $r$ and $(d-1)$ angle variables $(\theta_1, \ldots, \theta_{d-1})$. The hyper-spherical polar coordinates are related to the Cartesian coordinates via the set of equations

$$x_d = r \cos \theta_{d-1}$$

$$x_{d-1} = r \sin \theta_{d-1} \cos \theta_{d-2}$$

$$x_{d-2} = r \sin \theta_{d-1} \sin \theta_{d-2} \cos \theta_{d-3}$$

$$\vdots \vdots \vdots$$

$$x_2 = r \sin \theta_{d-1} \sin \theta_{d-2} \ldots \sin \theta_2 \cos \theta_1$$

$$x_1 = r \sin \theta_{d-1} \sin \theta_{d-2} \ldots \sin \theta_2 \sin \theta_1$$

(1445)

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18 In three dimensions, the angular momentum is an antisymmetric second rank tensor that is only masquerading as a vector.
The set of equations can be written symbolically as

\[ x_j = r f_j(\{\theta_i\}) \quad (1446) \]

Hence, we can evaluate the partial derivative w.r.t. \( r \) as

\[
\left( \frac{\partial}{\partial r} \right)_{\{\theta_i\}} = \sum_j \left( \frac{\partial x_j}{\partial r} \right)_{\{\theta_i\}} \frac{\partial}{\partial x_j} = \sum_j \left( f_j(\{\theta_i\}) \right) \frac{\partial}{\partial x_j} = \sum_j \left( \frac{x_j}{r} \right) \frac{\partial}{\partial x_j} \quad (1447)
\]

and the second derivative is evaluated as

\[
\left( \frac{\partial^2}{\partial r^2} \right)_{\{\theta_i\}} = \sum_{j,k} \left( \frac{\partial x_j}{\partial r} \right)_{\{\theta_i\}} \frac{\partial}{\partial x_j} \left( \frac{\partial x_k}{\partial r} \right)_{\{\theta_i\}} \frac{\partial}{\partial x_k} = \sum_{j,k} \left( f_j(\{\theta_i\}) \right) \left( f_k(\{\theta_i\}) \right) \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_k} = \sum_{j,k} x_j x_k \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_k} \quad (1448)
\]

Hence, we find that the magnitude of the angular momentum is related to the magnitude the momentum and some radial derivatives

\[
\widehat{L}^2 = r^2 \widehat{p}^2 + \hbar^2 r^2 \frac{\partial^2}{\partial r^2} + (d - 1) \hbar^2 r \frac{\partial}{\partial r} \quad (1449)
\]

or

\[
\widehat{p}^2 = - \hbar^2 \frac{1}{r^{d-1}} \frac{\partial}{\partial r} \left( r^{d-1} \frac{\partial}{\partial r} \right) + \frac{\widehat{L}^2}{r^2} \quad (1450)
\]

This equation can be used to express the kinetic energy in terms of the angular momentum in situations where there is spherical symmetry. The above identity reduces to the usual expression found when \( d = 3 \).

The eigenvalues of the angular momentum are the hyper-spherical harmonics. Harmonic functions \( h_{\nu}^{\lambda} \) are defined as homogeneous polynomials of order \( \lambda \) (homogeneous polynomials in the Cartesian coordinates) that satisfy Laplace’s equation

\[
\nabla^2 h_{\nu}^{\lambda} = 0 \quad (1451)
\]

The hyper-spherical harmonics \( Y_{\mu}^{\lambda} \) with angular momentum \( \lambda \) can be expressed in terms of the complete set of harmonic functions of order \( \lambda \) via

\[
r^{\lambda} Y_{\mu}^{\lambda} = \sum_{\nu} C_{\mu,\nu} h_{\nu}^{\lambda} \quad (1452)
\]
where the $C_{\mu,\nu}$ are expansion coefficients. The above equation implies that the hyper-spherical harmonics only depend on the direction of the vector $\mathbf{z}$. Operating with $\hat{p}^2$ on $r^\lambda Y_\mu^\lambda$ yields

$$\hat{p}^2 r^\lambda Y_\mu^\lambda = 0$$ (1453)

since $r^\lambda Y_\mu^\lambda$ is a combination of harmonic functions. Furthermore, the above equation together with eqn(1450) implies that

$$\left[ -\hbar^2 \frac{1}{r^{d-1}} \frac{\partial}{\partial r} \left( r^{d-1} \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{r^2} \right] r^\lambda Y_\mu^\lambda = 0$$ (1454)

Since the $Y_\mu^\lambda$ only depend on the set of angles $\{\theta_i\}$ and do not depend on $r$, we find that the above equation reduces to

$$\hat{L}^2 Y_\mu^\lambda = \hbar^2 \lambda ( \lambda + d - 2 ) Y_\mu^\lambda$$ (1455)

Thus, the hyper-spherical harmonics $Y_\mu^\lambda$ are eigenfunctions $\hat{L}^2$ and the eigenvalues are $\hbar^2 \lambda ( \lambda + d - 2 )$. The eigenvalue equation reduces to the standard eigenvalue equation in three dimensions.

### 4.5.25 Exercise 85

Show that the radial momentum $p_r$, which in classical mechanics is defined by

$$p_r = \frac{1}{r} \left( \mathbf{r} \cdot \mathbf{p} \right)$$ (1456)

must be represented by the symmetrized form

$$p_r = \frac{1}{2} \left[ \frac{1}{r} \left( \mathbf{r} \cdot \mathbf{p} \right) + \left( \mathbf{p} \cdot \mathbf{r} \right) \frac{1}{r} \right]$$ (1457)

in order to yield the Hermitian operator

$$\hat{p}_r = -i \hbar \left( \frac{\partial}{\partial r} + \frac{1}{r} \right)$$ (1458)

Show that in $d$ dimensions this leads to the expression

$$\hat{p}_r = -i \hbar \left( \frac{\partial}{\partial r} + \frac{d - 1}{2r} \right)$$ (1459)

which is a Hermitian operator.

---

19 The expansion coefficients $C_{\mu,\nu}$ are dependent on the choice of the set of basis functions $h^\lambda_\mu$, the choice of the set of quantum numbers $\mu$ and an overall phase factor.
4.5.26 Solution 85

The quantum operator corresponding to the un-symmetrized form of the classical radial momentum is found from

\[ \frac{1}{r} \left( \hat{r} \cdot \hat{\mathbf{p}} \right) = \frac{1}{r} \left( r\hat{e}_r \cdot \hat{\mathbf{p}} \right) = -i \hbar \frac{1}{r} \left( r\hat{e}_r \cdot \nabla \right) = -i \hbar \frac{1}{r} \left( r \frac{\partial}{\partial r} \right) = -i \hbar \frac{\partial}{\partial r} \]

(1460)

where we have used the expression for \( \nabla \) in \( d \)-dimensional spherical polar coordinates

\[ \nabla = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_{\theta_1} \frac{1}{r} \frac{\partial}{\partial \theta_1} + \hat{e}_{\theta_2} \frac{1}{r \sin \theta_1} \frac{\partial}{\partial \theta_2} + \ldots + \hat{e}_{\theta_d} \frac{1}{r \sin \theta_1 \ldots \sin \theta_{d-2}} \frac{\partial}{\partial \theta_{d-1}} \]

(1461)

In this expression, we have introduced the unit vectors \( \hat{e}_{\theta_i} \) in the orthogonal directions defined by

\[ \hat{e}_{\theta_i} = \frac{1}{h_i} \frac{\partial}{\partial \theta_i} \hat{e}_r \]

(1462)

and the product \( h_i \) of the dimensionless angular factors

\[ h_i = \prod_{j=1}^{i-1} \left( \sin \theta_j \right) \]

(1463)

This operator is not Hermitean, as can be seen by constructing the Hermitean conjugate. The Hermitean conjugate is evaluated by considering the effect of the matrix elements with two different arbitrary but normalizable radial wave functions \( R_n(r) \) and \( R_m(r) \),

\[ \int_0^\infty dr\ r^{d-1} R^*_m(r) \left( -i \hbar \frac{\partial}{\partial r} \right) R_n(r) \]

(1464)

The factor \( r^{d-1} \) represents the \( r \) dependence of the surface area of a \( d \)-dimensional sphere, and \( dr\ r^{d-1} \) is proportional to the volume of an infinitesimal shell of thickness \( dr \). By integration by parts, and using the fact that the wave functions are normalizable to eliminate the boundary terms, one obtains the result

\[ = \int_0^\infty dr\ R_n(r) \left( +i \hbar \frac{\partial}{\partial r} \right) r^{d-1} R^*_m(r) \]
\[
= \int_0^\infty dr \ r^{d-1} R_m(r) \left( + i \hbar \frac{\partial}{\partial r} + i \hbar \frac{d - 1}{r} \right) R_m^*(r)
\]  

(1465)

On using the definition of the Hermitean conjugate, one identifies the Hermitean conjugate operator as
\[
\left( \frac{1}{r} \left( r \hat{e}_r \cdot \hat{\rho} \right) \right)^\dagger = -i \hbar \left( \frac{\partial}{\partial r} + \frac{d - 1}{r} \right)
\]  

(1466)

The symmetric partner
\[
(\hat{p} \cdot \hat{r}) \frac{1}{r}
\]

is quantized as
\[
\left( \hat{p} \cdot \hat{r} \right) \frac{1}{r} = -i \hbar \left( \sum_i r \hat{e}_r \right) \frac{1}{r}
\]
\[
= -i \hbar \left( \sum_i \hat{e}_r \right)
\]
\[
= -i \hbar \frac{\partial}{\partial r} - i \hbar \sum_{i=1}^{d-1} \frac{1}{r h_i} \hat{e}_{\theta_i} \cdot \left( \frac{\partial}{\partial \theta_i} \hat{e}_r \right)
\]  

(1468)

The factor of \( r \) cancels with \( \frac{1}{r} \) in the second line, as the differential operator acts on both factors. In the last line, we have utilized the identity
\[
\frac{\partial}{\partial r} \hat{e}_r = 0
\]  

(1469)

The derivative of the unit vector \( \hat{e}_r \) with respect to the angle \( \theta_i \) is evaluated as
\[
\frac{\partial \hat{e}_r}{\partial \theta_i} = h_i \hat{e}_{\theta_i}
\]  

(1470)

As the unit vectors are orthogonal, one has
\[
(\hat{p} \cdot \hat{r}) \frac{1}{r} = -i \hbar \frac{\partial}{\partial r} - i \hbar \sum_{i=1}^{d-1} \frac{1}{r h_i} \hat{e}_{\theta_i} \cdot \left( \frac{\partial}{\partial \theta_i} \hat{e}_r \right)
\]
\[
= -i \hbar \frac{\partial}{\partial r} - i \hbar \sum_{i=1}^{d-1} \frac{1}{r h_i} \hat{e}_{\theta_i} \cdot \sum_{j=1}^{d-1} h_j \hat{e}_{\theta_j}
\]
\[
= -i \hbar \frac{\partial}{\partial r} - i \hbar \sum_{i=1}^{d-1} \frac{1}{r h_i} \sum_{j=1}^{d-1} h_j \delta_{i-j}
\]
\[
= -i \hbar \frac{\partial}{\partial r} - i \hbar \sum_{i=1}^{d-1} \frac{1}{r}
\]
\[
= -i \hbar \frac{\partial}{\partial r} - i \hbar \frac{d - 1}{r}
\]  

(1471)
Hence, the quantized symmetric partner is equal to the Hermitean conjugate.

The Hermitean operator corresponding to the radial component of the momentum is given by the Hermitean part of the operator

\[
\hat{p}_r = \frac{1}{2} \left[ \frac{1}{r} (\hat{r} \cdot \hat{p}) + \left( \frac{1}{r} (\hat{r} \cdot \hat{p}) \right)^\dagger \right] = \frac{1}{2} \left[ \frac{1}{r} (\hat{r} \cdot \hat{p}) + (\hat{p} \cdot \hat{r}) \frac{1}{r} \right] - i \hbar \left[ \frac{\partial}{\partial r} + \frac{d - 1}{2r} \right] \tag{1472}
\]
4.6 Spherically Symmetric Potentials

The Hamiltonian for a particle of mass $m$ and charge $q$ moving in a spherically symmetric potential is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + q \phi(r)$$  \hspace{1cm} (1473)

where the potential $\phi(r)$ only depends on the radial coordinate $r$ and is independent of $(\theta, \varphi)$. Since the Hamiltonian commutes with the orbital angular momentum operator,

$$[ \hat{H}, \hat{L}_z ] = 0$$ \hspace{1cm} (1474)

and, therefore, also commutes with the magnitude

$$[ \hat{H}, \hat{L}^2 ] = 0$$ \hspace{1cm} (1475)

one may find simultaneous eigenfunctions of $\hat{H}$, $\hat{L}_z$ and $\hat{L}^2$. These eigenfunctions must be of the separable form

$$\Psi_{E,l,m}(r) = R_{E,l}(r) Y_m^l(\theta, \varphi)$$ \hspace{1cm} (1476)

Thus, the energy eigenvalue equation becomes

$$\left[ -\frac{\hbar^2}{2m r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hbar^2 l (l + 1)}{2m r^2} + q \phi(r) \right] R_{E,l}(r) = E R_{E,l}(r)$$ \hspace{1cm} (1477)

After substituting eqn(1476) in the above equation, and after using the fact that $Y_m^l(\theta, \varphi)$ is an eigenstate of $\hat{L}^2$, with eigenvalue $\hbar^2 l (l + 1)$, one finds that the spherical harmonic is a common factor that can be cancelled. The radial part of the wave function must satisfy the radial equation

$$\left[ -\frac{\hbar^2}{2m r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hbar^2 l (l + 1)}{2m r^2} + q \phi(r) \right] R_{E,l}(r) = E R_{E,l}(r)$$ \hspace{1cm} (1478)

This is an ordinary differential equation, instead of a partial differential equation, in which the centrifugal potential appears as an addition to the electrostatic potential. The radial equation is independent of the azimuthal quantum number $m$, and hence, so are the radial eigenfunctions and eigenvalues.

4.6.1 Exercise 86

A particle of mass $m$ moves in a three-dimensional spherically symmetric potential $V(r)$ which vanishes at $r \to \infty$. It has an eigenstate which is given by

$$\Phi(\tau) = C r^s \exp \left[ -\alpha r \right] \sin \theta \exp \left[ i l \varphi \right]$$ \hspace{1cm} (1479)
Figure 80: The effective radial potential $V_{\text{eff}}(r)$ is the sum of the potential $V(r)$ and the centrifugal potential.

What are the values of the angular momentum and energy quantum numbers for this state? Find the potential $V(r)$.

### 4.6.2 Solution 86

The state is an eigenstate of angular momentum with $l = l$ and $m = l$. The energy eigenvalue and the potential can be determined from

$$
\left[ V(r) - E \right] \Phi(\mathbf{r}) = \frac{\hbar^2}{2m} \nabla^2 \Phi(\mathbf{r})
$$

where

$$
\nabla^2 \Phi(\mathbf{r}) = \left[ \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{l(l + 1)}{r^2} \right] C r^s \exp \left[ -\alpha r \right] \sin^l \theta \exp \left[ i l \varphi \right] 
$$

$$
= \left[ \alpha^2 - 2 \alpha \frac{(1 + s)}{r} + \frac{s(s + 1) - l(l + 1)}{r^2} \right] \Phi(\mathbf{r})
$$

(1481)
Thus, at \( r \to \infty \) where \( V(r) \to 0 \), we find

\[
E = -\frac{\hbar^2 \alpha^2}{2m}
\]

and

\[
V(r) = \frac{\hbar^2}{2m} \left[ \frac{(s - l)(s + l + 1)}{r^2} - \frac{2\alpha(1 + s)}{r} \right]
\]

### 4.6.3 The Free Particle

The free particle corresponds to the case of a vanishing electrostatic potential \( \phi(r) = 0 \). The time-independent Schrödinger equation for the free particle separates in spherical polar coordinates. The radial wave function is given by the solution of

\[
\left[ -\frac{\hbar^2}{2m r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hbar^2 l(l + 1)}{2m r^2} \right] R_{E,l}(r) = E R_{E,l}(r)
\]

where, with \( \hbar k = \sqrt{2mE} \), becomes

\[
\left[ -\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{l(l + 1)}{r^2} \right] R_{E,l}(r) = k^2 R_{E,l}(r)
\]

It is also useful to introduce a dimensionless variable \( \rho = k r \) to obtain the scaled equation

\[
\left[ -\frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial}{\partial \rho} \right) + \frac{l(l + 1)}{\rho^2} \right] R_{E,l}(\rho/k) = R_{E,l}(\rho/k)
\]

This differential equation reduces to Bessel’s equation. This can be seen by making the transformation

\[
R_{E,l}(r) = \frac{y_l(\rho)}{\sqrt{\rho}}
\]

which leads to

\[
\frac{d^2 y_l}{d \rho^2} + \frac{1}{\rho} \frac{d y_l}{d \rho} + \left( 1 - \frac{(l + \frac{1}{2})^2}{\rho^2} \right) y_l = 0
\]

This is Bessel’s equation for half-integer indices, and the solutions we seek are proportional to the Bessel functions \( J_{l+\frac{1}{2}}(\rho) \). The Bessel functions are finite at
the origin $\rho = 0$. The solutions for $R_{E,l}$ are, therefore, known as the spherical Bessel functions

$$R_{E,l}(r) = j_l(\rho) = \sqrt{\frac{\pi}{2}} \frac{J_{\frac{1}{2}}(\rho)}{\sqrt{\rho}}$$ (1489)

Equation (1486) actually has two independent solutions $j_l(z)$ and $\eta_l(z)$ which are the spherical Bessel functions and the spherical Neumann functions. For values of $\rho$ close to the origin, the solutions have leading terms in the power series expansion which vary as

$$R_l(r) \propto \rho^\alpha + O(\rho^{\alpha+2})$$ (1490)

where $\alpha$ has to be determined. On substituting the leading term into the differential equation, and noting that the term of order unity can be neglected compared with the centrifugal barrier near $r = 0$, one finds that the differential equation reduces to

$$\left( - \alpha ( \alpha + 1 ) + l ( l + 1 ) \right) \rho^{\alpha-2} + O(\rho^\alpha) = 0$$ (1491)

for small $\rho$. The values of $\alpha$, for which this is satisfied, satisfy a quadratic equation and are given by either of the solutions $\alpha = l$ or $\alpha = - ( l + 1 )$. The spherical Bessel functions $j_l(\rho)$ vary as $\rho^l$ close to the origin, which is a consequence of the high centrifugal barrier that prevents classical particles with fixed $l$ approaching the origin. The spherical Neumann functions $\eta_l(\rho)$ vary as $\rho^{-(l+1)}$ as $\rho \to 0$. The spherical Neumann functions are to be discarded as $r^2 | R_{E,l}(r) |^2 dr$ is proportional to the probability of finding a particle in the interval $dr$ at a radial distance $r$. The inclusion of the spherical Neumann functions would lead to the probability diverging like $r^{-2l}$ as $r \to 0$. Therefore, the spherical Neumann functions represent unphysical solutions near the origin.

Since the spherical Bessel functions and spherical Neumann functions play an important role in the description of scattering by short ranged potentials, we shall digress to examine the general properties of these functions in more detail.

The solution of equation (1486) with $\alpha = l$, is the spherical Bessel function $j_l(z)$, and can be written as

$$j_l(z) = D_l z^l \int_{-1}^{+1} ds \exp[i s z] \left( 1 - s^2 \right)^l$$ (1492)

where the usual normalization is given as

$$D_l = \frac{1}{2^{l+1} l!}$$ (1493)

It can be shown that $j_l(z)$ satisfies the differential equation for $R_{l,E}$ by direct substitution. We first need to evaluate the various derivatives in the equation.
The first derivative of $j_l(z)$ is given by
\[
\frac{\partial}{\partial z} j_l(z) = D l z^{l-1} \int_{-1}^{+1} ds \ exp[i s z] (1 - s^2)^l + D i z^l \int_{-1}^{+1} ds \ exp[i s z] s (1 - s^2)^l \quad (1494)
\]
and the second derivative is given by
\[
\frac{\partial^2}{\partial z^2} j_l(z) = D l (l - 1) z^{l-2} \int_{-1}^{+1} ds \ exp[i s z] (1 - s^2)^l + D 2 i l z^{l-1} \int_{-1}^{+1} ds \ exp[i s z] s (1 - s^2)^l - D z^l \int_{-1}^{+1} ds \ exp[i s z] s^2 (1 - s^2)^l \quad (1495)
\]
On substituting in the differential equation number (1486) and collecting like terms, after some cancellations, we find
\[
\frac{\partial^2}{\partial z^2} j_l(z) + 2 \frac{\partial}{\partial z} j_l(z) + \left(1 - \frac{l (l + 1)}{z^2}\right) j_l(z) = D 2 i (l + 1) z^{l-1} \int_{-1}^{+1} ds \ exp[i s z] s (1 - s^2)^l + D z^l \int_{-1}^{+1} ds \ exp[i s z] (1 - s^2)^{l+1} = -D i z^{l-1} \int_{-1}^{+1} ds \ exp[i s z] \frac{d}{ds} (1 - s^2)^{l+1} + D z^l \int_{-1}^{+1} ds \ exp[i s z] (1 - s^2)^{l+1} \quad (1496)
\]
In the last expression, we have rewritten the integrand in the first term as a differential with respect to $s$. On integrating by parts in the first term, and noting the boundary term is zero, we find that the right hand side of the differential equation is given by
\[
= -D z^l \int_{-1}^{+1} ds \ exp[i s z] (1 - s^2)^{l+1} + D z^l \int_{-1}^{+1} ds \ exp[i s z] (1 - s^2)^{l+1} = 0 \quad (1497)
\]
Thus, $j_l(z)$ satisfies the radial differential equation.
From the above integral representation expression for, $j_l$ and its derivative, we can easily verify that the recursion relation
\[
j_{l+1}(z) = \frac{l}{z} j_l(z) - \frac{\partial}{\partial z} j_l(z)
\] (1498)
holds true. A second useful recursion relation that can be derived is
\[
(2l + 1) \frac{\partial}{\partial z} j_l(z) = lj_{l-1}(z) - (l + 1) j_{l+1}(z)
\] (1499)

A second solution $\eta_l(z)$ is given by the integral
\[
\eta_l(z) = C \frac{1}{z^{l+1}} \int_{-1}^{1} ds \exp[i s z] \frac{1}{(1 - s^2)^{l+1}}
\] (1500)
since the differential equation is invariant under the transformation $l \to -(l + 1)$.

From the integral expressions for $j_l(z)$ and $\eta_l(z)$, one can show that the spherical Bessel functions are regular at the origin
\[
\lim_{z \to 0} j_l(z) \sim \frac{2^l l!}{(2l + 1)!} z^l
\] (1501)
while the spherical Neumann functions are divergent at the origin,
\[
\lim_{z \to 0} \eta_l(z) \sim -\frac{(2l)!}{2^l l!} z^{-(l+1)}
\] (1502)

The asymptotic large $z$ variation of the spherical Bessel function is found from the integral representation
\[
j_l(z) = \frac{z^l}{2^{l+1} l!} \int_{-1}^{1} ds \exp[i s z] (1 - s^2)^l
\] (1503)
by integrating by parts $l$ times. Each integration by parts reduces the power of the monomial in $z$ in front of the integral by unity, yielding
\[
j_l(z) = \frac{z^l}{2^{l+1} l!} \int_{-1}^{1} ds \exp[i s z] \left( \frac{d}{ds} \right)^l (1 - s^2)^l
\] (1504)
since the boundary terms all vanish. The vanishing of the boundary terms occurs as there are more factors of $(1 - s^2)$ than there are derivatives with respect to $s$. However, on further integration by parts, the higher order derivatives remain non-zero at the boundaries $s = \pm 1$. Repeated integration by parts yields an
expansion where the non-zero terms are ordered in increasing powers of \( z^{-1} \). The first non-zero term in the asymptotic expansion is given by

\[
j_l(z) \sim -\frac{j_{l+1}}{2^{l+1} l! z} \exp i s z \left( \frac{d}{ds} \right)^l \left( 1 - s^2 \right)^{\frac{l}{2}} + O(z^{-2}) \tag{1505}\]

Thus, the leading term in the asymptotic large \( z \) expansion is given by

\[
\lim_{z \to \infty} j_l(z) \sim \cos \left[ \frac{z - (l + 1) \pi}{2} \right] \tag{1506}\]

The asymptotic expansion for the spherical Neumann function is given by an analogous expression which is most easily found from eqn(1506) via the substitution \( l \rightarrow -(l + 1) \), and is given by

\[
\lim_{z \to \infty} \eta_l(z) \sim \sin \left[ \frac{z - (l + 1) \pi}{2} \right] \tag{1507}\]

The explicit forms of the first few spherical Bessel and Neumann functions are given in Table(5).

The eigenfunctions for the free particle have to be square integrable over any finite volume of space, as the integral of the modulus squared of the wave function represents the probability that a particle is found in the volume. Since only the spherical Bessel functions are integrable over the region near the origin, they can represent physical wave functions near the origin. The spherical Neumann functions have to be discarded near the origin.

The orthogonality condition for the spherical Bessel functions is given by

\[
\int_0^\infty dr \, r^2 \, j_l(kr) \, j_l(k'r) = \frac{\pi}{2} \frac{\delta(k - k')}{k^2} \tag{1508}\]

The normalization condition corresponds to the continuous eigenvalue spectrum associated with the delocalized wave functions. As the wave functions are proportional to the spherical harmonics, they are orthogonal for different values of \( l \). Therefore, we only require that the Bessel functions with the same values of \( l \) but different energy eigenvalues are orthogonal.

The solution of the free particle energy eigenvalue equation, with angular momentum \( l \), also has uses in cases where there is a spherically symmetric potential \( \phi(r) \) which is short ranged. In this case, the energy eigenvalue equation can be separated into radial and angular parts

\[
\Psi(r, \theta, \varphi) = R_{t,k}(r) \, Y^l_m(\theta, \varphi) \tag{1509}\]

since the potential is spherically symmetric. The wave functions of the spatially extended states with energy eigenvalues \( E_k > 0 \) have asymptotic large \( r \)
Table 5: The Spherical Bessel $j_l(z)$ and Neumann $\eta_l(z)$ Functions.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$j_l(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l = 0$</td>
<td>$j_0(z) = \frac{\sin z}{z}$</td>
</tr>
<tr>
<td>$l = 1$</td>
<td>$j_1(z) = \frac{\sin z - z \cos z}{z^2}$</td>
</tr>
<tr>
<td>$l = 2$</td>
<td>$j_2(z) = \frac{(3 - z^2) \sin z - 3z \cos z}{z^3}$</td>
</tr>
<tr>
<td>$l = 3$</td>
<td>$j_3(z) = \frac{(15 - 6z^2) \sin z - (15z - z^3) \cos z}{z^4}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$l$</th>
<th>$\eta_l(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l = 0$</td>
<td>$\eta_0(z) = -\frac{\cos z}{z}$</td>
</tr>
<tr>
<td>$l = 1$</td>
<td>$\eta_1(z) = -\frac{\cos z + z \sin z}{z^2}$</td>
</tr>
<tr>
<td>$l = 2$</td>
<td>$\eta_2(z) = -\frac{(3 - z^2) \cos z + 3z \sin z}{z^3}$</td>
</tr>
<tr>
<td>$l = 3$</td>
<td>$\eta_3(z) = -\frac{(15 - 6z^2) \cos z + (15z - z^3) \sin z}{z^4}$</td>
</tr>
</tbody>
</table>
limits which are expressible as linear superpositions of the spherical Bessel and Neumann functions, since $\phi(r) \approx 0$ in this region. Thus,

$$R_{l,k}(r) = A_l j_l(kr) + B_l \eta_l(kr)$$  \hfill (1510)

The ratio of the amplitude of the two terms contains information about the short ranged potential, and is usually expressed in terms of the phase shift $\delta_l(k)$,

$$\frac{B_l}{A_l} = - \tan \delta_l(k)$$  \hfill (1511)

On using this definition of the phase shift, and the asymptotic large $r$ forms of the spherical Bessel and Neumann functions, one finds that the asymptotic form of the radial wave function is given by

$$R_{l,k}(r) \sim \frac{A_l}{\cos \delta_l(k)} \frac{\sin \left( kr - \frac{l \pi}{2} + \delta_l(k) \right)}{kr}$$  \hfill (1512)

Hence, the large $r$ form of the radial wave function resembles that of a free particle. The main difference is that the phase of the radial oscillations is shifted by $\delta_l(k)$.

The normalization of the extended states, for an arbitrary short ranged potential, can be inferred from the asymptotic large $r$ behavior. This can be

$$\text{Figure 81: The spherical Bessel functions } j_l(z) \text{ as a function of } z \text{ for various } l.$$
Figure 82: The spherical Neumann functions $\eta_l(z)$ as a function of $z$ for various $l$. The spherical Neumann functions diverge at the origin.

shown by re-writing radial part of the energy eigenvalue equation in the alternate form

$$\frac{1}{r} \frac{\partial^2}{\partial r^2} \left( r R_{l,k}(r) \right) + \frac{2 m E}{\hbar^2} R_{l,k}(r) = \left[ \frac{l (l + 1)}{r^2} + \frac{2m q \phi(r)}{\hbar^2} \right] R_{l,k}(r)$$

(1513)

A generalized continuity equation can be derived from the time-independent Schrödinger equation. The continuity equation has the form

$$\left( k^2 - k'^2 \right) \int_0^R dr \ r^2 R_{l,k'}^*(r) R_{l,k}(r) =$$

$$= - \left[ r R_{l,k'}^*(r) \frac{\partial}{\partial r} r R_{l,k}(r) - r R_{l,k'} \frac{\partial}{\partial r} r R_{l,k}^* \right]_0^R$$

(1514)

We note that as $r \to 0$, $R_{l,k}(r)$ vanishes for non-zero $l$. Hence, the normalization is governed solely by the asymptotic behavior. As previously mentioned, the radial wave function has the asymptotic large $r$ form

$$R_{l,k}(r) \sim \frac{1}{r} \sin \left( k r - \frac{l \pi}{2} + \delta_l(k) \right)$$

(1515)

where $\delta_l(k)$ is the phase shift and $k^2 = \frac{2m E}{\hbar^2}$. Then, on substituting the
asymptotic form in the expression for the normalization, one finds

\[ \int_0^R dr \, r^2 R^*_l,k'(r) \, R^l,k(r) = \]

\[ = \frac{1}{k'^2 - k^2} \left[ k \sin \left( k' R - \frac{l \pi}{2} + \delta_l(k') \right) \cos \left( k R - \frac{l \pi}{2} + \delta_l(k) \right) \right. \]

\[ - k' \sin \left( k R - \frac{l \pi}{2} + \delta_l(k) \right) \cos \left( k' R - \frac{l \pi}{2} + \delta_l(k') \right) \left. \right] \]

(1516)

The above expression can be re-written in the form

\[ = \frac{\pi}{2} \left[ \sin \left( \frac{(k' - k) R + \delta_l(k') - \delta_l(k)}{k' - k} \right) \right. \]

\[ + \left. \sin \left( \frac{(k' + k) R + \delta_l(k') + \delta_l(k) - l\pi}{k' + k} \right) \right] \]

(1517)

The region of physical interest is that in which both \( k \) and \( k' \) are both positive. In the limit \( r \to \infty \), the first term dominates the above expression and so the normalization integral can be expressed as

\[ = \frac{\pi}{2} \delta( k' - k ) \]

(1518)

where we have used the representation of the delta function

\[ \lim_{N \to \infty} \frac{\sin N x}{x} \to \delta(x) \]

(1519)

This shows that the orthonormality condition of the continuum states must involve the Dirac delta function

\[ \int_0^\infty dr \, r^2 R^*_l,k'(r) \, R^l,k(r) = \frac{\pi}{2} \delta( k' - k ) \]

(1520)

The orthonormality condition of the spherical Bessel functions provides one concrete example of this relation. For the free particle, the radial wave function is identified with the spherical Bessel function by

\[ R_l(r) = k j_l(kr) \]

(1521)

since we require that, when \( r \to \infty \), the radial wave function has the same normalization as the asymptotic form given in eqn(1515). Therefore, one recovers the identity

\[ \int_0^\infty dr \, r^2 j_l(k'r) \, j_l(kr) = \frac{\pi}{2k' k^2} \delta( k' - k ) \]

(1522)

where \( k \) and \( k' \) are both restricted to have positive values.
Figure 83: The Dirac delta function \( \delta(x) \) can be regarded as the limit \( N \to \infty \) of the sequence of functions \( \frac{\sin N x}{\pi x} \).

4.6.4 The Spherical Square Well

The spherically symmetric potential represents a short ranged potential, in which \( q \phi(r) = -V_0 \) for \( r < a \) and \( q \phi(r) = 0 \) for \( r > a \). The states of angular momentum \( l \) have radial wave functions which satisfy

\[
-\frac{\hbar^2}{2m} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} R = (E + V_0) R \quad (1523)
\]

for \( r < a \) and

\[
-\frac{\hbar^2}{2m} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} R = E R \quad (1524)
\]

for \( r > a \). The condition for regularity at the origin leads us to select the solution

\[ R(r) = C_l j_l(k'r) \quad (1525) \]

for \( r < a \), where \( k' \) is given by

\[
\frac{\hbar^2}{2m} k'^2 = 2m (E + V_0) \quad (1526)
\]

If \( E > 0 \), the solutions outside the well are oscillatory and correspond to linear combinations of the spherical Bessel and spherical Neumann functions. These
solutions correspond to scattering states. On the other hand, the bound states have energies \( E < 0 \) which correspond to imaginary values of \( k \). The bound state radial wave functions ought to vanish as \( r \to \infty \).

**Scattering States**

Inside the well, the radial wave function with angular momentum \( l \) must be proportional to the spherical Bessel function with wave vector \( k' \)

\[
R_{l,E}(r) = C_l \ j_l(k'r) \quad (1527)
\]

for \( r < a \). As previously mentioned, the spherical Neumann function diverges at the origin and, therefore, is not an physically acceptable solution inside the well. Outside the well, \( r > a \), the scattering states can be written as the linear combination

\[
R_{l,E}(r) = A_l \ j_l(kr) + B_l \ \eta_l(kr) \quad (1528)
\]

The ratio of the coefficients \( A_l \) and \( B_l \) can be obtained from the continuity conditions at \( r = a \). These conditions are that the radial wave function is continuous at \( r = a \),

\[
\lim_{\epsilon \to 0} R_{l,E}(a + \epsilon) = \lim_{\epsilon \to 0} R_{l,E}(a - \epsilon) \quad (1529)
\]

and that the derivative is also continuous at \( r = a \)

\[
\lim_{\epsilon \to 0} \frac{\partial}{\partial r} R_{l,E}(r) \big|_{a+\epsilon} = \lim_{\epsilon \to 0} \frac{\partial}{\partial r} R_{l,E}(r) \big|_{a-\epsilon} \quad (1530)
\]

These equations can be divided, yielding

\[
\frac{k' \ j'_l(k'a)}{k \ j'_l(k'a)} = \frac{A_l \ j'_l(ka) + B_l \ \eta'_l(ka)}{A_l \ j_l(ka) + B_l \ \eta_l(ka)} \quad (1531)
\]

Thus, the ratio of \( B_l \) to \( A_l \) is determined as

\[
\frac{B_l}{A_l} = \frac{k' \ j'_l(k'a) \ j_l(ka) - k \ j'_l(ka) \ j_l(k'a)}{k' \ \eta'_l(k'a) \ j_l(ka) - k \ \eta'_l(ka) \ j_l(k'a)} \quad (1532)
\]

This ratio is usually written in terms of the tangent of the phase shift \( \delta_l(k) \). The phase shift (modulo \( 2 \pi \)) can be inferred from experiments in which a beam of particles of energy \( E \) falls incident on the potential. For low energies, the scattering is obviously dominated by the \( l = 0 \) phase shift, since classically the angular momentum is given by \( l = k r \). Hence, only the \( l = 0 \) contribution is expected to be important at low energies where \( k \to 0 \).

For the case \( l = 0 \), the matching procedure leads to

\[
\frac{B_0}{A_0} = \frac{k' \ \cos k'a \ \sin ka - k \ \cos ka \ \sin k'a}{k' \ \cos k'a \ \cos ka + k \ \sin ka \ \sin k'a} \quad (1533)
\]
The ratio of amplitudes can be expressed in terms of the $l = 0$ phase shift $\delta_0(k)$, via the definition

$$- \tan \delta_0(k) = \frac{B_0}{A_0} \quad (1534)$$

Hence, the phase shift is given by

$$\tan \delta_0(k) = \left( \frac{k}{k'} \right) \tan k' a - \tan k a \quad (1535)$$

or

$$\delta_0(k) = \tan^{-1} \left( \frac{k}{k'} \tan k' a \right) - k a \quad (1536)$$

where $\hbar^2 k'^2 = \hbar^2 k^2 + 2 m V_0$. The phase shift vanishes identically for $k' = k$ and, therefore, is a non-linear measure of the strength of the potential. The phase shift $\delta_0(k)$ (in units of $\pi$) is shown in fig(84) as a function of $k' a/\pi$ for fixed small values of the energy. The phase shifts are only slightly dependent on $k$ at low energies. It is seen that the phase shift rapidly increases by $\pi$ at various

---

Phase Shift for the attractive spherical potential well

![Phase Shift Plot](image)

Figure 84: The $l = 0$ phase shift $\delta_0(k)$ for low-energy particles incident on an attractive potential well, as a function of $k' a/\pi$.

values of $k' a$. These values are tabulated in Table(6). At these particular values of $k' a$, the potential is almost strong enough to produce another bound state with $l = 0$. This can be demonstrated by noting that these special values of $k' a$ correspond to $k' a = (n + \frac{1}{2}) \pi$, so the radial wave function inside the potential
Table 6: The values of \( \frac{k'a}{\pi} \) near which the \( l = 0 \) phase shift changes by \( \pi \) and resonant scattering occurs.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \frac{k'a}{\pi} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.48</td>
</tr>
<tr>
<td>2</td>
<td>1.50</td>
</tr>
<tr>
<td>3</td>
<td>2.51</td>
</tr>
<tr>
<td>4</td>
<td>3.50</td>
</tr>
<tr>
<td>5</td>
<td>4.51</td>
</tr>
<tr>
<td>6</td>
<td>5.51</td>
</tr>
</tbody>
</table>

well has a node at the origin and has zero slope at the edge of the well. The wave function with zero slope inside the well only matches to a wave function with zero slope outside the well. Outside the well, the eigenfunction is constant (since \( k = 0 \)) and corresponds to having a zero value of the decay constant \( \kappa \) and, therefore, represents a zero energy bound state. As seen in fig(85), the scattering cross-sections are large for low-energy particles incident on potentials where \( V_0 \) is close to these critical values. This type of scattering is known as

![Figure 85: The \( l = 0 \) scattering cross-section for low-energy particles incident on an attractive potential well, as a function of \( k'a \).](image-url)
resonant scattering.

In the limit $k \to 0$, the matching condition reduces to

$$\frac{B_0}{A_0} = k \left( 1 - \frac{\tan k' a}{k' a} \right)$$

(1537)

Hence, the ratio vanishes proportionally to $k$, as $k \to 0$. This means that the asymptotic, large $r$, radial wave function has the form of

$$\lim_{k \to 0} R_{0,k}(r) = A_0 \left( \frac{\sin kr}{kr} - \frac{B_0}{A_0} \frac{\cos kr}{kr} \right)$$

$$= A_0 \left( 1 - \frac{a_{sc}}{r} \right)$$

(1538)

where

$$a_{sc} = a \left( 1 - \frac{\tan k' a}{k' a} \right)$$

(1539)

is the scattering length.$^{20}$ In the limit of low energies, the differential scattering cross-section is given by

$$\frac{d\sigma}{d\Omega} = |a_{sc}|^2$$

(1540)

which is isotropic, that is, independent of the scattering angle $\theta$.

Example: $l = 0$ Scattering from a Repulsive Spherical Well Potential.

In this case, we consider the energy eigenstates with $l = 0$ of the spherically symmetric potential

$$V(r) = V_0 \quad \text{if} \quad r < a$$

$$V(r) = 0 \quad \text{if} \quad r > a$$

(1541)

We shall consider the case where $E < V_0$. By analytic continuation from the case where $V_0 > E$, the radial wave function on the inside of the well has the form

$$R_0(r) = C_0 \frac{\sinh \kappa r}{\kappa r}$$

(1542)

which is proportional to the $l = 0$ spherical Bessel function for imaginary argument. This function satisfies the radial equation, if the energy eigenvalue is related to the potential $V_0$ and $\kappa$ via

$$E = V_0 - \frac{\hbar^2 \kappa^2}{2 m}$$

(1543)

$^{20}$Note that if the magnitude of the potential is such that $k' a$ is close to an odd multiple of $\pi$, the scattering length can be anomalously large. When this occurs, low energy particles are resonantly scattered.
Outside the well, the radial wave function is given by a linear combination of the $l = 0$ spherical Bessel and Neumann functions

$$R_0(r) = A_0 \frac{\sin k r}{k r} - B_0 \frac{\cos k r}{k r}$$

(1544)

where $k$ is related to the energy eigenvalue by

$$E = \frac{\hbar^2 k^2}{2 m}$$

(1545)

The matching conditions for the radial wave function at $r = a$ lead to the equation

$$\frac{\tan( k a + \delta_0(k) )}{k a} = \tanh \kappa a$$

(1546)

The matching condition leads to the phase shift being given by

$$\delta_0(k) = \tan^{-1} \left( \frac{k}{\kappa} \tanh \kappa a \right) - k a$$

(1547)

In the limit of a hard sphere, $V_0 \to \infty$, so $\kappa a \to \infty$. In the hard sphere limit, the above expression for the phase shift simplifies to

$$\lim_{V_0 \to \infty} \delta_0(k) \to - k a$$

(1548)

The $k \to 0$ limit of the scattering amplitude is found as

$$a_{sc} = - \lim_{k \to 0} \frac{\tan \delta_0(k)}{k} = a$$

(1549)

Therefore, at low energies where the scattering is isotropic and independent of $k$, the total scattering cross-section of the hard sphere is found as

$$\sigma_T = \int d\Omega \left( \frac{d\sigma}{d\Omega} \right) = \int d\Omega \ a_{sc}^2 = 4 \pi a^2$$

(1550)

This derivation is only valid for small $k$. The total cross-section should be compared with geometrical cross-section, which is defined as the area of (the front half of) the target’s surface projected onto the plane of the beam. As seen in fig(86), the geometrical cross-section for the hard sphere is given by $\pi a^2$, the area of a disk of radius $a$. Therefore, as the total scattering cross-section of the hard sphere potential is $4 \pi a^2$, the total cross-section is four times greater than the geometrical cross-section.
Figure 86: The geometrical scattering cross-section for particles incident on a hard sphere.

**Bound States**

In order to determine the bound states it is necessary to examine the behavior of the radial wave function for imaginary wave vectors as \( r \to \infty \). It is useful to define certain combinations of the spherical Bessel and Neumann functions that prove to be useful. From the asymptotic variation of the Bessel and Neumann functions, one recognizes that the combinations

\[
\begin{align*}
    h_i^{(1)}(\rho) &= j_i(\rho) + i \eta_i(\rho) \\
    h_i^{(2)}(\rho) &= j_i(\rho) - i \eta_i(\rho)
\end{align*}
\]

(1551)

known as the spherical Hankel functions of the first and second kind, have simple exponential variations

\[
\begin{align*}
    h_i^{(1)}(\rho) &= \frac{1}{\rho} \exp \left[ + i \left( \rho - (l + 1) \frac{\pi}{2} \right) \right] \\
    h_i^{(2)}(\rho) &= \frac{1}{\rho} \exp \left[ - i \left( \rho - (l + 1) \frac{\pi}{2} \right) \right]
\end{align*}
\]

(1552)

For imaginary \( k \), such that \( \rho = + i \kappa r \), only the spherical Hankel functions of the first kind decay exponentially at \( r \to \infty \). Thus, when discussing bound
Table 7: The spherical Hankel Functions $h_l^{(m)}(z)$

<table>
<thead>
<tr>
<th></th>
<th>$h_l^{(1)}(z)$</th>
<th>$h_l^{(2)}(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l = 0$</td>
<td>$-\frac{i}{z} \exp[ + i z ]$</td>
<td>$+\frac{i}{z} \exp[ - i z ]$</td>
</tr>
<tr>
<td>$l = 1$</td>
<td>$-i \frac{(1-iz)}{z^2} \exp[ + i z ]$</td>
<td>$i \frac{(1+iz)}{z^2} \exp[ - i z ]$</td>
</tr>
<tr>
<td>$l = 2$</td>
<td>$-i \frac{(3-3iz-z^2)}{z^3} \exp[ + i z ]$</td>
<td>$i \frac{(3+3iz-z^2)}{z^3} \exp[ - i z ]$</td>
</tr>
<tr>
<td>$l = 3$</td>
<td>$-i \frac{(15-15iz-6z^2+iz^3)}{z^4} \exp[ + i z ]$</td>
<td>$i \frac{(15+15iz-6z^2-iz^3)}{z^4} \exp[ - i z ]$</td>
</tr>
</tbody>
</table>

states it is useful to express the radial wave function outside the well in terms of the spherical Hankel function of the first kind.

The wave functions in the interior and exterior regions should be matched at $r = a$. For the bound states, since $E < 0$, the radial wave functions exterior to the well have the form $h_l^{(1)}(i \kappa r)$ while the wave functions interior to the well have the form $j_l(k' r)$. Therefore, on equating the logarithmic derivatives, one finds the condition

$$\frac{k' j_l'(k' a)}{j_l(k' a)} = \frac{i \kappa h_l^{(1)}(i \kappa a)}{h_l^{(1)}(i \kappa a)}$$

(1553)

which, together with the relation

$$k'^2 - 2 \frac{m V_0}{\hbar^2} = - \kappa^2$$

(1554)

leads to discrete values of $\kappa$ and, hence, discrete energy eigenvalues $E_{\kappa,l}$.

This procedure for graphically determining the allowed values of $\kappa$ illustrated for the $l = 0$ bound states in fig(87). The dashed curves show the relationship between $\kappa$ and $k'$ of eqn(1554), for different values of $V_0$. The intersection of the solid lines and the dashed lines yield the allowed values of $\kappa$ for the $l = 0$ bound states. The number of intersections and the bound states increase as $V_0$ increases. The wave function for the lowest energy $l = 0$ bound state is shown in fig(88), for various values of $V_0$. 

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Figure 87: The graphical solution of the $l = 0$ version of the self consistency condition (eqn(1553)), for various values of $V_0$.

4.6.5 Exercise 87

The deuteron consists of a neutron which is bound in an $l = 0$ state to a proton by a short-ranged attractive potential. The neutron and proton in the deuteron are in a spin triplet state. Assume that the potential can be represented by a spherically symmetric “square” well of depth $V_0$ and radius $a$. The experimentally determined binding energy $E_0$ is 2.21 MeV. The scattering length $a^{1}_t$ for a neutron-proton system in a triplet spin state is inferred, from low-energy elastic scattering experiments\(^\text{21}\), to have a magnitude of 5.38 F. Using this data and the reduced mass, estimate the depth of the potential $V_0$ and the radius $a$. The estimated value of $a$ can be compared with the value of 2.1 F for the rms radius of the charge distribution deuteron and 0.8 F for the rms radius for the charge distribution of the proton, obtained by the diffraction of high-energy electrons\(^\text{22}\).

The neutron-proton interaction is highly spin-dependent. For example, the experimentally determined singlet neutron-proton scattering length is given by $a^{s}_sc = -23.7$ F.

The radial wave function for the $l=0$ bound state

![The radial wave function for the l=0 bound state](image)

Figure 88: The lowest energy $l = 0$ bound state wave function, for various values of $V_0$.

4.6.6 Solution 87

The triplet scattering length $a_{sc}^t = 5.38$ F, was measured in experiments involving the scattering of very low-energy particles. For the model potential, the scattering length is given by

$$a_{sc} = a \left(1 - \frac{\tan k''a}{k''a}\right)$$  (1555)

where the wave vector $k''$ is associated with a zero-energy particle within the well. Therefore,

$$\frac{\hbar^2 k'^{2}}{2 \mu} = V_0$$  (1556)

If the potential only has one bound state and the scattering is resonant, then the product $k'' a$ must be slightly greater than $\frac{\pi}{2}$.

The bound state energy $E_0$ is related to the imaginary wave vector $\kappa$ via

$$E_0 = -\frac{\hbar^2 \kappa^2}{2 \mu}$$  (1557)

where $\mu = \frac{m}{2}$ is the reduced mass of the neutron-proton system. The bound
state energy is determined from the condition

\[ k' \cot k'a = -\kappa \] (1558)

where

\[ V_0 = \frac{\hbar^2}{2\mu} \left( k'^2 + \kappa^2 \right) \] (1559)

or

\[ k''^2 = k'^2 + \kappa^2 \] (1560)

There are two parameters that need to be determined \( a \) and \( k'' \). We shall eliminate \( a \) in terms of \( k' \), via

\[ \kappa a = \frac{\kappa}{\sqrt{k''^2 - \kappa^2}} \tan^{-1} \left[ -\frac{\sqrt{k''^2 - \kappa^2}}{\kappa} \right] \] (1561)

where the inverse tangent has to be understood as giving an angle greater than \( \pi/2 \). The equation involves the dimensionless variable \( x = \frac{k''}{\kappa} \). The resulting value of \( a \) is to be substituted in the equation for the scattering length, yielding the equation

\[ \kappa a^{t}_{sc} = \frac{1}{\sqrt{x^2 - 1}} \tan^{-1} \left[-\sqrt{x^2 - 1}\right] - \frac{1}{x} \tan \left[ \frac{x \tan^{-1} \left[-\sqrt{x^2 - 1}\right]}{\sqrt{x^2 - 1}} \right] \] (1562)

This equation involves the dimensionless product \( \kappa a^{t}_{sc} \) which for triplet scattering has a value \( \kappa a^{t}_{sc} \sim 1.23 \). This leads to the value of \( x = 4.05 \). The depth of the potential is then given by

\[ V_0 = E_0 x^2 \] (1563)

which is estimated to be \( V_0^t = 36.25 \text{ MeV} \). The width of the well is given by \( a = 2.01 \text{ F} \).

Since the experimentally determined singlet neutron-proton scattering length is given by \( a^{s}_{sc} = -23.7 \text{ F} \), then using the value of \( a \) just calculated, one determines that the depth of the singlet potential is \( V_0^s = 23.7 \text{ MeV} \). The singlet potential is not deep enough to bind the neutron and proton. Similar results were obtained by using a more realistic form of the potential\(^{23}\).

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\(^{23}\)P.M. Morse, J.B. Fisk and L.I. Schiff, Phys. Rev. 50, 748 (1936).
4.6.7 Exercise 88

Find the energy eigenvalues of the $l = 0$ states of the spherically symmetric infinite square well potential,

$$V(r) = \begin{cases} \infty & \text{if } r > a \\ 0 & \text{if } r < a \end{cases}$$

(1564)

4.6.8 Exercise 89

Show that the spherical square well has no bound states unless

$$V_0 a^2 > \frac{\hbar^2 \pi^2}{8 m}$$

(1565)

4.6.9 Solution 89

The bound state solution outside the well has to have the form of a decaying exponential and, therefore, is given by a spherical Hankel function in which $k \rightarrow i \kappa$, and is given by a spherical Bessel function inside the well, with wave vector $k'$, where

$$\frac{\hbar^2 k^2}{2 m} - V_0 = -\frac{\hbar^2 \kappa^2}{2 m}$$

(1566)

On matching the exponentially decaying spherical Hankel functions with imaginary $k$ with the spherical Bessel functions of argument $k' r$ at $r = a$ one obtains a transcendental equation for the bound state. The largest value of $\kappa$ occurs, for fixed $V_0$, when $l = 0$ as this minimizes the effect of the rotational kinetic energy or centrifugal potential and, therefore, maximizes the effect of the attractive potential. For $l = 0$, the bound state condition simplifies to

$$k' \cot k' a = -\kappa$$

(1567)

On squaring this equation, one obtains

$$k'^2 \cot^2 k' a = +\kappa^2 = \frac{2 m V_0}{\hbar^2} - k'^2$$

(1568)
which contains some spurious solutions. The left hand side is greater or equal to zero, and only falls to zero for \( k' \) equal to every odd multiple of \( \frac{\pi}{2a} \). The right hand side is an inverse parabola, which becomes negative for \( k'^2 \) greater than \( \frac{2m V_0}{\hbar^2} \). The solutions of the squared equation are, therefore, restricted to the region of relatively small \( k' \) where the inverted parabola is positive. The solutions of the squared equation correspond to the solutions of the original equation only in the restricted range where \( \cot k' a \) is negative. Thus, the lowest energy bound states occur for \( \frac{\pi}{2a} < k' < \frac{\pi}{a} \). Hence, on increasing the strength of \( V_0 \) from zero, the lowest energy bound state first occurs when

\[
\frac{2m V_0}{\hbar^2} \geq \frac{\pi^2}{4a^2}
\]  

(1569)

4.6.10 Exercise 90

Show that if a square well just binds an energy level of angular momentum \( l \), the parameters satisfy the equation

\[
j_{l-1} \left( \sqrt{\frac{2m V_0 a^2}{\hbar^2}} \right) = 0
\]  

(1570)

which utilized the recurrence formulas for the Bessel functions.

4.6.11 Solution 90

Inside the well of radius \( a \), \( a > r \), the solution for the radial wave function, with angular momentum \( l \), is proportional to the spherical Bessel function

\[
R_l(r) = A_l \ j_l(kr)
\]  

(1571)

The wave vector \( k \) is related to the energy eigenvalue by

\[
E = \frac{\hbar^2 k^2}{2m} - V_0
\]  

(1572)

Since the spherical Neumann function \( \eta_l(kr) \) diverges at \( r = 0 \), it yields an unphysical probability density and, therefore, is discarded for \( r < a \).

Outside the well, \( r > a \), the solution is proportional to the spherical Hankel function

\[
R_l(r) = B_l \ h_l^{(1)}(i kr)
\]  

(1573)
where
\[ h^{(1)}_l(i\kappa r) = j_l(i\kappa r) + i \eta_l(i\kappa r) \]  
(1574)

Since \( E \leq 0 \), the momentum is imaginary and is given by
\[ E = -\frac{\hbar^2 \kappa^2}{2m} \]  
(1575)

The spherical Hankel function \( h^{(1)}_l(i\kappa r) \) represents the combination of the possible solutions which decays exponentially as \( r \to \infty \). The other combination \( h^{(2)}_l(i\kappa r) \) blows up as \( r \to \infty \) and so is not normalizable and, therefore, the unphysical solution is discarded.

The bound state wave functions must satisfy the continuity conditions at \( r = a \), which can be combined to yield
\[ \frac{k j'_l(ka)}{j_l(ka)} = \frac{i \kappa h^{(1)}_l(i\kappa a)}{h^{(1)}_l(i\kappa a)} \]  
(1576)

If the potential is so weak that it just binds the particle, then \( E \sim 0 \), and hence \( \kappa = 0 \). The spherical Hankel functions are dominated by the spherical Neumann functions as they diverge like \( (\kappa a)^{-(l+1)} \) in the limit \( \kappa \to 0 \). Hence, in the limit \( \kappa \to 0 \), the matching condition becomes
\[ \frac{k j'_l(ka)}{j_l(ka)} = -\frac{(l + 1)}{a} \]  
(1577)

and we have the condition
\[ k a j'_l(ka) + (l + 1) j_l(ka) = 0 \]  
(1578)

The recurrence relations for the spherical Bessel functions can be combined to yield
\[ (l + 1) j_l(ka) + ka j'_l(ka) = ka j_{l-1}(ka) \]  
(1579)

Hence, on using the above recurrence relation, we find that the condition that the spherical square potential well is just sufficiently strong that it starts have a bound state of angular momentum \( l \) is given by
\[ j_{l-1}(ka) = 0 \]  
(1580)
in which
\[ k^2 = \frac{2m V_0}{\hbar^2} \]  
(1581)
since \( E = 0 \). Thus, we have derived the required condition.

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4.6.12 Exercise 91

Find the bound states corresponding to angular momentum \( l = 0 \) for the attractive delta function spherical shell potential

\[
V(r) = -V_0 a \delta( |r| - a )
\]  

(1582)

Find the minimum value of \( V_0 \) for which a bound state occurs.

4.6.13 Solution 91

The energy eigenfunction function for a spherically symmetric Hamiltonian can be separated in terms of a radial function \( R(r) \) and an angular function \( Y^l_m(\theta, \varphi) \),

\[
\Phi(r) = R_{n,l}(r) \ Y^l_m(\theta, \varphi)
\]

(1583)

The solution for the radial function inside the potential shell is given by the analytic continuation of the spherical Bessel function, of angular momentum \( l \),

\[
R_{n,l}(r) = A_l \ j_l( i \ \kappa \ r ) \quad \text{for} \quad r < a
\]

(1584)

since the wave function must be normalizable at the origin. However, outside the shell it is given by a linear combination of the spherical Bessel and Neumann functions that decay as \( r \to \infty \) exponentially. This combination defines the spherical Hankel functions,

\[
R_{n,l}(r) = B_l \ j_l( i \ \kappa \ r ) + C_l \ \eta_l( i \ \kappa \ r ) \quad \text{for} \quad r > a
\]

(1585)

The wave function is continuous at \( r = a \). Thus,

\[
R_{n,l}(a + \epsilon) = R_{n,l}(a - \epsilon)
\]

(1586)

The delta function only depends on \( r \) and so the first derivative has a discontinuous slope at \( r = a \), given by integrating the radial equation

\[
\int_{a-\epsilon}^{a+\epsilon} dr \ r^2 \left( \frac{\hbar^2}{2 \ m} \ \frac{1}{r^2} \ \frac{\partial}{\partial r} r^2 \ \frac{\partial}{\partial r} + V_0 a \ \delta( r - a ) + E \right) R_{n,l}(r) = 0
\]

(1587)

Taking the limit \( \epsilon \to 0 \), one obtains

\[
R'_{n,l}(a + \epsilon) - R'_{n,l}(a - \epsilon) + \frac{2 \ m \ V_0 a}{\hbar^2} \ R(a) = 0
\]

(1588)

The energy eigenvalue is given by

\[
E = -\frac{\hbar^2 \ \kappa^2}{2 \ m}
\]

(1589)
For \( l = 0 \), one has

\[
R_{n,0}(r) = A_0 \frac{\sinh \kappa r}{r} \quad \text{for} \quad r < a
\]

\[
R_{n,0}(r) = B_0 \frac{\exp \left[ - \kappa r \right]}{r} \quad \text{for} \quad r > a
\]  

(1590)

On eliminating \( B \) and \( A \), we find the eigenvalue equation for \( \alpha \)

\[
\exp \left[ \kappa a \right] \kappa = \frac{2 m V_0 a}{\hbar^2} \sinh \kappa a
\]  

(1591)

The bound state just forms when the solution \( \kappa \to 0 \), where \( \sinh \kappa a \to \kappa a \). In this case we have

\[
V_0 = \frac{\hbar^2}{2 m a^2}
\]  

(1592)

### 4.6.14 Exercise 92

A particle is confined to move in the volume between two concentric spheres of radius \( R_0 \) and radius \( R_1 \), where \( R_1 > R_0 \). The potential is radially symmetric and has the form

\[
V(r) = 0 \quad \text{if} \quad R_1 > r > R_0
\]

\[
V(r) \to \infty \quad \text{elsewhere}
\]  

(1593)

(a) Find the values of the energy eigenvalues if the particle has angular momentum given by \( l = 0 \).

(b) Consider the limit \( R_1 \to R_0 \), which resembles a particle rigidly bound at radius \( R_1 \), but is free to rotate. Assume that the particle is in the ground state. The excitation energy of any energy state is defined as the difference between its energy eigenvalue and the energy of the ground state. In this limit, show that the excitation energies for fixed \( l \) are independent of the value of \( l \). Also, evaluate all of the remaining finite excitation energies.

### 4.6.15 Solution 92

The general solution for the energy eigenstates of angular momentum \( l \) is of the form

\[
\phi_l(r, \varphi) = \left( A_l j_l(kr) + B_l \eta_l(kr) \right) Y^l_m(\theta, \varphi)
\]  

(1594)

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for $R_1 > r > R_0$, and zero elsewhere. The wave function has to satisfy the boundary conditions

$$\left( A_l j_l(kR_1) + B_l \eta_l(kR_1) \right) = 0 \quad (1595)$$

at $r = R_1$ and

$$\left( A_l j_l(kR_0) + B_l \eta_l(kR_0) \right) = 0 \quad (1596)$$

at $r = R_0$. These equations can be used to eliminate the ratio of $A_l$ to $B_l$, yielding a transcendental equation for $k$

$$\frac{j_l(kR_0)}{\eta_l(kR_0)} = \frac{j_l(kR_1)}{\eta_l(kR_1)} \quad (1597)$$

For $l = 0$, this can be re-written as

$$\sin k (R_0 - R_1) = 0 \quad (1598)$$

which yields the allowed values of $k$ as

$$k_n = \frac{n \pi}{R_1 - R_0} \quad (1599)$$

and has the energy eigenvalue

$$E_{n,l=0} = \frac{\hbar^2 n^2 \pi^2}{2 m (R_1 - R_0)^2} \quad (1600)$$

In the limit $R_1 \to R_0$, the energy differences between the eigenstates of different $n$ (with fixed $l$) are independent of $l$ as the radial equation becomes

$$- \frac{\hbar^2}{2 m R_0^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R_l(r)}{\partial r} \right) R_l(r) = \left( E - \frac{\hbar^2 l (l + 1)}{2 m R_0^2} \right) R_l(r) \quad (1601)$$

Thus, the differences in the eigenvalues, for fixed $l$, are identical to the differences with $l = 0$, which we have shown tend to infinity. The only remaining finite excitation energies correspond to states of the same $n$ values but with different rotational energies. That is we have a rigid rotor, with excitation energies

$$E_{l' - l} = \frac{\hbar^2}{2 m R_0^2} \left( l' (l' + 1) - l (l + 1) \right) \quad (1602)$$

This corresponds to the excitation energies of a three-dimensional rigid rotor, with moment of inertia $I = m R_0^2$. The difference between successive excitation energies increase with increasing $l$ as $\frac{\hbar^2}{I} (l + 1)$. These differences in excitation energies are frequently observed in the optical absorption spectra of molecules.
4.6.16 Ladder operators for a free particle

The radial wave function \( R_l(r) \) for a free particle with angular momentum \( l \) satisfies the eigenvalue equation

\[
0 = - \left( \frac{\partial^2 R_l}{\partial \rho^2} \right) - \frac{2}{\rho} \left( \frac{\partial R_l}{\partial \rho} \right) + \left[ \frac{l(l+1)}{\rho^2} - 1 \right] R_l
\]

where the dimensionless variable \( \rho \) is defined by

\[
\rho = k r
\]

and \( k \) is related to the energy eigenvalue \( E \) via

\[
E = \frac{\hbar^2 k^2}{2 m}
\]

We shall introduce ladder operators that transform radial wave functions \( R_l(r) \) into radial wave functions with the same value of the energy but with different values of the angular momentum \(^{24}\). Since the ladder operators that are to be introduced keep the energy \( E \) unchanged, the raising and lowering operators can be expressed in terms of the variable \( \rho \) and the derivative with respect to \( \rho \).

The raising operator \( \hat{A}_l^+ \) is defined via

\[
\hat{A}_l^+ = - \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho + \frac{l}{\rho}
\]

The lowering operator \( \hat{A}_l^- \) is the Hermitian conjugate of the raising operator \( \hat{A}_l^+ \). In three dimensions, the lowering operator \( \hat{A}_l^- \) is calculated as

\[
\hat{A}_l^- = + \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho + \frac{l}{\rho}
\]

The products of the raising and lowering operators are given by

\[
\hat{A}_l^+ \hat{A}_l^- = - \frac{1}{\rho} \frac{\partial^2}{\partial \rho^2} \rho + \frac{l(l+1)}{\rho^2}
\]

or, when taken in the opposite order

\[
\hat{A}_l^- \hat{A}_l^+ = - \frac{1}{\rho} \frac{\partial^2}{\partial \rho^2} \rho + \frac{l(l-1)}{\rho^2}
\]

On comparing the above two forms, we find the relation

\[
\hat{A}_l^- \hat{A}_l^+ = \hat{A}_{l-1}^+ \hat{A}_{l-1}^-
\]

\(^{24}\)L. Infeld, Phys. Rev. 59, 737 (1941).
Thus, we have found two equivalent forms of the operator that appears in the radial equation with angular momentum \((l - 1)\).

When acting on \(R_l\), the lowering operator \(\hat{A}_l^-\) produces the radial wave function \(R_{l-1}\) which is an energy eigenstate with the same energy. This can be seen by first using eqn(1608) to write the radial equation in the form

\[
\left( \hat{A}_l^+ \hat{A}_l^- - 1 \right) R_l = 0 \quad (1611)
\]

and then acting on this with \(\hat{A}_l^-\). This yields the equation

\[
\hat{A}_l^- \left( \hat{A}_l^+ \hat{A}_l^- - 1 \right) R_l = 0 \quad (1612)
\]

which can be re-written as

\[
\left( \hat{A}_l^- \hat{A}_{l-1}^+ - 1 \right) \hat{A}_l^- R_l = 0 \quad (1613)
\]

Hence, on using eqn(1610), one finds

\[
\left( \hat{A}_{l-1}^+ \hat{A}_{l-1}^- - 1 \right) \hat{A}_l^- R_l = 0 \quad (1614)
\]
which indicates that $\hat{A}_l^- R_l$ is proportional to the radial wave function $R_{l-1}$ with angular momentum $(l-1)$ and the same energy $E$

$$R_{l-1} \propto \hat{A}_l^- R_l$$  \hspace{1cm} (1615)

Since the angular momentum is reduced by unity, the above relation justifies naming $\hat{A}_l^-$ as the lowering operator.

The raising operator $\hat{A}_l^+ + 1$ acting on $R_l$ produces a radial wave function $R_{l+1}$ where the angular momentum is raised by one unit. This can be shown by first substituting $l$ by $(l+1)$ in eqn(1610), to produce

$$\hat{A}_{l+1}^- \hat{A}_{l+1}^+ = \hat{A}_l^- \hat{A}_l^+$$  \hspace{1cm} (1616)

The radial equation for $R_l$ can be written as

$$\left( \hat{A}_{l+1}^- \hat{A}_{l+1}^+ - 1 \right) R_l = 0$$  \hspace{1cm} (1617)

If the raising operator $\hat{A}_{l+1}^+$ acts on the radial equation as expressed in eqn(1617), one has

$$0 = \hat{A}_{l+1}^+ \left( \hat{A}_{l+1}^- \hat{A}_{l+1}^+ - 1 \right) R_l$$

$$0 = \left( \hat{A}_{l+1}^+ \hat{A}_{l+1}^- - 1 \right) \hat{A}_{l+1}^+ R_l$$  \hspace{1cm} (1618)

The factor in the parentheses is identified as the radial equation operator with angular momentum $(l+1)$, therefore the product $\hat{A}_{l+1}^+ R_l$ must be the radial wave function with angular momentum $(l+1)$. Hence, we have

$$R_{l+1} \propto \hat{A}_{l+1}^+ R_l$$  \hspace{1cm} (1619)

so the raising operator $\hat{A}_{l+1}^+$ increases the angular momentum of the radial wave function $R_l$ by one unit, but keeps the energy unchanged.

The radial wave function with $l = 0$ can be determined from the radial equation, which we write in the form

$$\frac{\partial^2 \rho R_0}{\partial \rho^2} = -\rho R_0$$  \hspace{1cm} (1620)

The general solution is easily found and is given by

$$\rho \ R_0(r) = A_0 \ \sin \rho + B_0 \ \cos \rho$$  \hspace{1cm} (1621)

The physically acceptable solution has $B_0 = 0$ since the probability of finding the particle in the neighborhood of $\rho \to 0$ must be finite. Hence, the radial wave function with $l = 0$ is given by

$$R_0(r) = A_0 \left( \frac{\sin \rho}{\rho} \right)$$  \hspace{1cm} (1622)
which is proportional to the zero-th order spherical Bessel function \( j_0(\rho) \) which is given by

\[
j_0(\rho) = \left( \frac{\sin \rho}{\rho} \right) \quad (1623)
\]

The radial wave functions with \( l \neq 0 \) can be found by successive use of the raising operators. For example, the radial wave function with \( l = 1 \) is found from \( j_0(\rho) \) by

\[
R_1(r) \propto \left[ -\frac{1}{\rho} \frac{\partial}{\partial \rho} \rho + \frac{1}{\rho} \right] j_0(\rho) = -A_1 \frac{\rho}{\rho^2} \frac{\partial}{\partial \rho} \left( \sin \rho \right) + A_0 \frac{1}{\rho} \frac{\sin \rho}{\rho} = A_1 \left( \frac{\sin \rho - \rho \cos \rho}{\rho^2} \right) \quad (1624)
\]

The radial wave function \( R_1(r) \) is proportional to the spherical Bessel function \( j_1(\rho) \), which is given by

\[
j_1(\rho) = \left( \frac{\sin \rho - \rho \cos \rho}{\rho^2} \right) \quad (1625)
\]

It is seen that the spherical Bessel function of order one tends to zero like \( \rho \) when \( \rho \to 0 \). Repeated applications of the raising operators yield the un-normalized radial functions in the form

\[
R_l(r) = A_l j_l(\rho) \quad (1626)
\]

where the coefficient \( A_l \) is an arbitrary complex number. These solutions, like the spherical Bessel functions, are all well-behaved at the origin. Furthermore, the probability of finding the particle near the origin must decrease as \( l \) increases, due to the increase of the centrifugal barrier in the effective potential.

The spherical Neumann functions \( \eta_l(\rho) \) of order \( l \) are independent solutions of the radial equation with angular momentum \( l \). However, these solutions are singular at the origin, as can be seen by examining the spherical Neumann function of order zero

\[
\eta_0(\rho) = -\left( \frac{\cos \rho}{\rho} \right) \quad (1627)
\]

which diverges like \( \rho^{-1} \) when \( \rho \to 0 \). Other independent solutions of the radial equation can be obtained by successive actions of the raising operators. For example, the spherical Neumann function of order one is obtained from \( \eta_0(\rho) \) by

\[
\eta_1(\rho) = \left( -\frac{1}{\rho} \frac{\partial}{\partial \rho} \rho + \frac{1}{\rho} \right) \eta_0(\rho)
\]
\(-\left(-1 + \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho + \frac{1}{\rho}\right) \left(\cos \frac{\rho}{\rho}\right)\)

\(-\left(\cos \frac{\rho}{\rho} + \frac{\rho \sin \rho}{\rho^2}\right)\) (1628)

The function \(\eta_1(\rho)\) diverges like \(\rho^{-2}\) as \(\rho \to 0\). The general form of \(\eta_l(\rho)\) as \(\rho \to 0\) can be determined by induction. One can show that if

\[\lim_{\rho \to 0} \eta_l(\rho) \sim -\frac{1}{\rho^{l+1}}\] (1629)

then since

\[\eta_{l+1}(\rho) = \left(-1 + \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho + \frac{(l+1)}{\rho}\right) \eta_l(\rho)\] (1630)

one must have

\[\lim_{\rho \to 0} \eta_{l+1}(\rho) \sim -\left(-1 + \frac{1}{\rho} \frac{\partial}{\partial \rho} \frac{1}{\rho^l} + \frac{(l+1)}{\rho^{l+2}}\right)\]

\[= -\frac{1}{\rho^{l+2}}\] (1631)

Since the asymptotic form holds true for \(l = 0\), one has shown that

\[\lim_{\rho \to 0} \eta_l(\rho) \sim -\frac{1}{\rho^{l+1}}\] (1632)

is true for all values of \(l\). The asymptotic \(\rho \to 0\) behavior of the spherical Bessel functions is given by

\[\lim_{\rho \to 0} j_l(\rho) \sim \rho^l\] (1633)

The above two asymptotic forms of the independent solutions can be simply obtained from the radial equation, if one assumes that the leading terms of the solutions are of the form \(R \sim \rho^\alpha\) for some unknown values of \(\alpha\).

\subsection*{4.6.17 The Rayleigh Equation}

A plane wave can be expanded in a series of spherical waves, via the Rayleigh equation

\[\exp \left[ i \frac{k}{r} \cos \theta \right] = \sum_l i^l (2l + 1) j_l(\frac{kr}{\rho}) P_l(\cos \theta)\] (1634)

The expansion can be thought of in terms as the decomposition of a wave front (a plane of constant phase) of a beam in terms of its angular momentum components, as is indicated schematically in fig(90). The above expansion is to be expected since the eigenstates of the Laplacian with eigenvalue \(-k^2\), which are simultaneous eigenfunctions of the linear momentum must be related to
Classical decomposition of a beam into angular momentum eigenstates

$\ell = k \ r$

1 = 0
1 = 1
1 = 2
1 = 3
1 = 4

Cross section of the Beam

Figure 90: A semi-classical description of the decomposition of a plane wave in terms of states with angular momentum $\ell$. If a point on the wave front at a distance $r$ from the axis with $(l + \frac{1}{2}) \hbar > pr > (l - \frac{1}{2}) \hbar$ has angular momentum $l$.

the eigenstates of the Laplacian which are simultaneous eigenfunctions of the angular momentum. The Rayleigh expansion can be verified by differentiating the above relation with respect to $k \ r$ leading to

$$i \cos \theta \exp \left[ i \ k \ r \ \cos \theta \right] = \sum_l i^l \ (2 \ l + 1) \ j_l^l(kr) \ P_l(\cos \theta)$$

$$\cos \theta \sum_l i^{l+1} \ (2 \ l + 1) \ j_{l+1}(kr) \ P_l(\cos \theta) = \sum_l i^l \ (2 \ l + 1) \ j_l^l(kr) \ P_l(\cos \theta)$$

(1635)

The recurrence relation

$$(2 \ l + 1) \ z \ P_l(z) = (l + 1) \ P_{l+1}(z) + l \ P_{l-1}(z)$$

(1636)

can be used to write

$$\sum_l i^{l+1} \ j_{l+1}(kr) \left[ (l + 1) \ P_{l+1}(\cos \theta) + l \ P_{l-1}(\cos \theta) \right]$$

$$= \sum_l i^l \ (2 \ l + 1) \ j_l^l(kr) \ P_l(\cos \theta)$$

(1637)

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The recurrence relation for $j'_l(kr)$ given by

$$ (2l + 1) j'_l(kr) = l j_{l-1}(kr) - (l + 1) j_{l+1}(kr) \quad (1638) $$

can be used in eqn(1637) to obtain

$$ \sum_l i^{l+1} j_l(kr) \left[ (l + 1) P_{l+1}(\cos \theta) + l P_{l-1}(\cos \theta) \right] = \sum_l i^l \left[ l j_{l-1}(kr) - (l + 1) j_{l+1}(kr) \right] P_l(\cos \theta) \quad (1639) $$

which, on changing the index from $l + 1$ to $l$ in the first term and $l - 1$ to $l$ in the second term, yields the equality

$$ \sum_l i^{l+1} \left[ j_{l-1}(kr) l P_l(\cos \theta) - j_{l+1}(kr) (l + 1) P_l(\cos \theta) \right] = \sum_l i^l \left[ j_{l-1}(kr) - (l + 1) j_{l+1}(kr) \right] P_l(\cos \theta) \quad (1640) $$

This concludes the proof of the Rayleigh expansion.

An alternate proof can be found by using the orthogonality of the Legendre polynomials and forming the matrix elements with the plane wave expansion

$$ \exp \left[ i k r \cos \theta \right] = \sum_{l'} a_{l'} P_{l'}(\cos \theta) \quad (1641) $$

with unknown expansion coefficients $a_{l'}$. Then, on multiplying by $P_l(\cos \theta) \sin \theta$ and integrating w.r.t. $\theta$, and using the orthogonality condition, one finds

$$ \int_{-1}^{1} d\cos \theta P_l(\cos \theta) \exp \left[ i k r \cos \theta \right] = \sum_{l'} a_{l'} \frac{2 \delta_{l,l'}}{2l + 1} \quad (1642) $$

Thus, the expansion coefficients are evaluated as

$$ a_l = \frac{(2l + 1)}{2} \int_{-1}^{1} ds \exp \left[ i s k \right] P_l(s) $$

$$ = (2l + 1) i^l j_l(kr) \quad (1643) $$

where we have used the Rodriguez formula expression for the Legendre polynomial

$$ P_l(s) = \frac{1}{2^l l!} \frac{\partial^l}{\partial s^l} (s^2 - 1)^l \quad (1644) $$

and integrated by parts $l$ times and then used an integral representation of the spherical Bessel function

$$ j_l(z) = \frac{z^l}{2^{l+1} l!} \int_{-1}^{1} ds \exp \left[ i z s \right] (1 - s^2)^l \quad (1645) $$

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The above two expressions allowed us to express the integral involving the Legendre polynomial in terms of the spherical Bessel function. The Rayleigh expansion is often used in considerations of scattering.

4.6.18 The Isotropic Planar Harmonic Oscillator

The potential for the Isotropic Planar Harmonic Oscillator is given by

\[ V(r) = \frac{m \omega^2 r^2}{2} \]  

which only depends on the radial distance \( r \). In planar polar coordinates \( (r, \varphi) \), the energy eigenvalue equation for the isotropic two-dimensional Harmonic Oscillator is of the form

\[
\left[ -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} - \frac{\hbar^2}{2mr^2} \frac{\partial^2}{\partial \varphi^2} + \frac{m \omega^2 r^2}{2} - E \right] \Psi(r, \varphi) = 0
\]  

The Laplacian in the eigenvalue equation is expressed in the form appropriate for two-dimensional motion. In particular, it can be seen that this operator is Hermitean if one uses the two-dimensional measure of “volume”, \( dr \ r \ d\varphi \), in the definition of the inner product. The potential only depends on the radial distance \( r \), and so the two-dimensional angular momentum operator \( \hat{L}_z \) commutes with the Hamiltonian. Thus, the energy and angular momentum are conserved. Also, it is possible to find simultaneous eigenfunctions of \( \hat{H} \) and \( \hat{L}_z \).

The eigenvalue of \( \hat{L}_z \) is denoted by \( \hbar m_z \). On introducing the separable form for the eigenfunction

\[ \Psi(r, \varphi) = R(r) \frac{1}{\sqrt{2\pi}} \exp\left[ i m_z \varphi \right] \]  

the differential equation for the radial wave function becomes

\[
\left[ -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{\hbar^2}{2mr^2} \frac{m^2 z^2}{2} + \frac{m \omega^2 r^2}{2} - E \right] R(r) = 0
\]

On introducing the dimensionless variable, \( \rho \), defined by

\[ \rho = \frac{m \omega r^2}{\hbar} \]  

it is found that the derivative with respect to \( r \) is given in terms of the differential with respect to \( \rho \), via

\[
\frac{\partial}{\partial r} = \frac{\partial \rho}{\partial r} \frac{\partial}{\partial \rho} = 2 \rho^2 \sqrt{\frac{m \omega}{\hbar}} \frac{\partial}{\partial \rho}
\]  

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Thus, the radial differential equation takes the dimensionless form
\[
h \omega \left[ -2 \frac{\partial^2}{\partial \rho^2} - 2 \frac{\partial}{\partial \rho} + \frac{m_z^2}{2 \rho} + \frac{\rho}{2} - \frac{E}{\hbar \omega} \right] R(r) = 0 \quad (1652)
\]

Furthermore, the radial function is parameterized in the form
\[
R(r) = \rho^{|m_z|} \exp \left[ -\frac{\rho^2}{2} \right] L(\rho) \quad (1653)
\]

which has the physically acceptable asymptotic variation at the boundaries, \( \rho \to 0 \) and \( \rho \to \infty \). The term proportional to \( \rho^{|m_z|} \) indicates that we seek the solution which is normalizable at \( \rho = 0 \). The exponential factor indicates that we seek the solution which decays exponentially as \( \rho \to \infty \). The first order derivative of \( R(r) \) is evaluated as
\[
\frac{\partial R}{\partial \rho} = \rho^{|m_z|} \exp \left[ -\frac{\rho^2}{2} \right] \left( \frac{\partial L}{\partial \rho} + \frac{|m_z|}{2 \rho} L - \frac{1}{2} L \right) \quad (1654)
\]

and the second order derivative is given by a lengthier, but analogous, expression. The differential equation becomes
\[
-2 \rho \frac{\partial^2 L}{\partial \rho^2} + 2 (\rho - |m_z| - 1) \frac{\partial L}{\partial \rho} + \left( |m_z| + 1 - \frac{E}{\hbar \omega} \right) L = 0 \quad (1655)
\]

which is the differential equation for the associated Laguerre polynomials. The differential equation can be solved by the Fröbenius method, in which we expand the solution in powers of \( \rho \)
\[
L(\rho) = \sum_{n=0}^{\infty} a_n \rho^n \quad (1656)
\]

On substituting the series into the differential equation, and demanding that the coefficient of \( \rho^n \) should vanish, one finds the recurrence relation
\[
(n + 1) (n + |m_z| + 1) a_{n+1} = \left( n + \frac{1}{2} (|m_z| + 1 - \frac{E}{\hbar \omega}) \right) a_n \quad (1657)
\]

which relates \( a_{n+1} \) to \( a_n \). Thus, all the coefficients in the series are determined in terms of \( a_0 \). The value of \( a_0 \) is only determined from the normalization of the wave function. If the series did not truncate, then one can show that the solution would diverge exponentially as \( \rho \to \infty \), and would not be normalizable. Thus, in order to satisfy the boundary conditions the series must truncate. The series truncates at the \( n_r \)-th term, so \( a_{n_r+1} = a_{n_r+2} = a_{n_r+3} = \ldots = 0 \), if the energy eigenvalue is given by
\[
E = \hbar \omega \left( 2 n_r + |m_z| + 1 \right) \quad (1658)
\]

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In Cartesian coordinates, the energy eigenvalue equation separates into two ordinary differential equations, and each differential equation represents a one-dimensional Harmonic Oscillator. The energy eigenvalue corresponds to the sum of the energy eigenvalues for the two one-dimensional problems. Therefore, the energy is given by

\[ E = \hbar \omega \left( n_x + \frac{1}{2} + n_y + \frac{1}{2} \right) \]  

which contains a contribution of \( \hbar \omega \) from the energy of the zero-point motion.

### 4.6.19 The Spherical Harmonic Oscillator

The potential for the spherically symmetric Harmonic Oscillator is given by

\[ V(r) = \frac{m \omega^2}{2} r^2 \]  

As the potential is only a function of \( r \), the angular momentum operators \( \hat{L}_z \) and \( \hat{L}_z \) commute with the Hamiltonian. Thus, angular momentum is conserved, and one can find simultaneous eigenstates of the operators \( \hat{H}, \hat{L}_2 \) and \( \hat{L}_z \).

The energy eigenvalue equation for the Spherically Symmetric Harmonic Oscillator is separable in spherical polar coordinates. If the wave function is assumed to be of the form

\[ \Psi(r, \theta, \phi) = R_l(r) Y_l^m(\theta, \phi) \]

then, after using the properties of the spherical harmonics, it is found that the radial wave function \( R(r) \) satisfies an equation independent of the variables, \( \theta \) and \( \phi \). The radial equation for the spherically symmetric harmonic oscillator is given by

\[ -\frac{\hbar^2}{2 m r^2} \frac{d}{dr} \left( r^2 \frac{d R}{dr} \right) + \left[ \frac{\hbar^2}{2 m r^2} \frac{l(l+1)}{2} + \frac{m \omega^2}{2} r^2 \right] R = E R \]

The solution can be written in the form

\[ R_l(r) = r^l \exp \left( -\frac{m \omega}{2 \hbar} r^2 \right) f(r) \]

which minimizes the effect of the centrifugal potential barrier at the origin, and the exponential term takes care of the binding at asymptotic large values of \( r \). It should be noted that a second solution exists which, at large \( r \), varies asymptotically as

\[ R(r) \sim \exp \left( +\frac{m \omega}{2 \hbar} r^2 \right) \]
This solution has been discarded as it is not normalizable, and hence, unphysical. On changing variable to
$$\rho = \frac{m \omega r^2}{\hbar}$$
and on substituting the wave function into eqn(1662), one finds
$$\rho \frac{\partial^2 f}{\partial \rho^2} + \left( \frac{3}{2} + l - \rho \right) \frac{\partial f}{\partial \rho} + \frac{1}{2} \left( \frac{E}{\hbar \omega} - \left( \frac{3}{2} + l \right) \right) f = 0 \quad (1666)$$
which leads to $f(\sqrt{\frac{\hbar \rho}{m \omega}})$ being recognized as being proportional to an associated Laguerre polynomial in the variable $\rho$. The associated Laguerre polynomial $L_a(z)$ is a solution of the differential equation
$$z \frac{\partial^2}{\partial z^2} L(z) + ( c + 1 - z ) \frac{\partial}{\partial z} L(z) + a L(z) = 0 \quad (1667)$$
The solutions of this equation only satisfy the appropriate boundary conditions at $z \to \infty$ for specific values of $a$. This discrete set of $a$ values give rise to the discrete eigenvalues of the energy $E$ of the harmonic oscillator. This can be seen by substituting the Frobenius series for $L(z)$
$$L(z) = \sum_n a_n z^n \quad (1668)$$
into the radial equation and combining like powers of $z^n$. The form of $L(z)$ satisfies the differential equation if the coefficients of each power of $z$ vanish identically. This procedure results in the recursion relations for the coefficients $a_n$,
$$( n + 1 ) ( n + c + 1 ) a_{n+1} = ( n - a ) a_n \quad (1669)$$
If the series did not terminate, then the asymptotic large $n$ behavior would result in the sum of the series $L(\rho)$ having a positive exponential variation ($L(\rho) \sim \exp[ + \rho \rho]$) since $a_n \sim \frac{a_n}{n}$. If this hypothetical form of the exponential factor for the series sum was combined with the explicit exponential factor which we extracted from the radial wave function via the substitution
$$R(\rho) = \rho^{\frac{d}{2}} \exp \left[ - \frac{\rho}{2} \right] L(\rho) \quad (1670)$$
this would lead to a solution which has the second form of asymptotic variation ($R(\rho) \sim \exp[ + \frac{\rho}{2}]$) as $r \to \infty$. If this were the case, the radial wave function would not be square integrable and would not represent a bound state. Therefore, the series must terminate. For the series to terminate, one requires that $n = a$ for some $n$. For an integer value of $a$, say equal to $n_r$, the Laguerre polynomials truncate after the first $( n_r + 1 )$ terms, and all the higher order coefficients vanish, $a_{n_r+1} = a_{n_r+2} = \ldots = 0$. The series expansion always converges and the wave function satisfies appropriate boundary conditions at $r \to 0$ and at $r \to \infty$. For the isotropic three-dimensional harmonic oscillator,
enforcing the requirement that the boundary conditions are satisfied, i.e. the series truncates, yields the eigenvalues as

\[ E = \hbar \omega \left( \frac{3}{2} + l + 2 n_r \right) \]  

The factor of \( \frac{3}{2} \) is the sum of the three independent zero-point motions, and \( 2 n_r + l \) are the number of excited quanta. Since each state with given \( l \) has a degeneracy of \( 2l + 1 \), and states with \( N \) quanta have a degeneracy corresponding to the range of values of \( l \) from 0 to \( N \), the states with \( N \) quanta are highly degenerate. The degeneracy of a state with energy \( E = \hbar \omega \left( \frac{3}{2} + N \right) \) is equal to \( \frac{(N + 2)(N + 1)}{2} \).

Figure 91: The radial wavefunction \( R_{nl}(r) \) for the simple harmonic oscillator for \( l = 0 \) and \( n_r = 0, 1, 2 \). The radial quantum number \( n_r \) determines the number of nodes in the radial wave function.

4.6.20 Exercise 93
Show that the substitution of

\[ R(r) = \rho^\frac{1}{2} \exp \left[ -\frac{\rho}{2} \right] L(\rho) \]  

(1672)
Radial wave functions for the spherical harmonic oscillator

Figure 92: The radial wavefunction $R_{n,l}(r)$ for the simple harmonic oscillator for $n_r = 0$ and $l = 0, 1, 2$. For non-zero values of $l$, the centrifugal barrier prevents particles from reaching the origin.

where

$$\rho = \frac{m \omega}{\hbar} r^2$$

into the radial equation

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial R}{\partial r} + \frac{\hbar^2}{2} \frac{l(l+1)}{2m r^2} R + \frac{m \omega^2}{2} r^2 R = E R$$

leads to the differential equation for the associated Laguerre polynomials.

---

4.6.21 Solution 93

On defining the dimensionless variable $\rho$ through

$$\rho = \frac{m \omega}{\hbar} r^2$$

one finds that

$$\frac{\partial}{\partial r} = \frac{\partial \rho}{\partial r} \frac{\partial}{\partial \rho} = 2 \sqrt{\frac{m \omega}{\hbar}} \rho^\frac{1}{2} \frac{\partial}{\partial \rho}$$

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The radial differential equation becomes

\[
0 = \frac{-\hbar \omega}{2} \left[ 4 \rho \frac{\partial}{\partial \rho} \rho \left( \frac{\partial}{\partial \rho} - \frac{l (l + 1)}{\rho} \right) - \rho + \frac{2 E}{\hbar \omega} \right] R
\]

\[
= \frac{-\hbar \omega}{2} \left[ 4 \rho \frac{\partial^2}{\partial \rho^2} + 6 \frac{\partial}{\partial \rho} - \frac{l (l + 1)}{\rho} - \rho + \frac{2 E}{\hbar \omega} \right] R
\]

(1677)

The derivatives of

\[
R(r) = \rho^\frac{l}{2} \exp \left[ -\frac{\rho}{2} \right] L(\rho)
\]

are evaluated as

\[
\frac{\partial R}{\partial \rho} = \frac{l}{2} \rho^{\frac{l-1}{2}} \exp \left[ -\frac{\rho}{2} \right] L(\rho) - \frac{1}{4} \rho^{\frac{l}{2}} \exp \left[ -\frac{\rho}{2} \right] L(\rho) + \rho^{\frac{l}{2}} \exp \left[ -\frac{\rho}{2} \right] \frac{\partial}{\partial \rho} L(\rho)
\]

and

\[
\frac{\partial^2 R}{\partial \rho^2} = \frac{l}{2} \left( \frac{1}{2} - 1 \right) \rho^{\frac{l-1}{2}} \exp \left[ -\frac{\rho}{2} \right] L(\rho) - \frac{l}{4} \rho^{\frac{l}{2}} \exp \left[ -\frac{\rho}{2} \right] L(\rho) \frac{\partial}{\partial \rho} L(\rho)
\]

\[
= \frac{l}{2} \rho^{\frac{l-1}{2}} \exp \left[ -\frac{\rho}{2} \right] \frac{\partial}{\partial \rho} L(\rho) - \frac{1}{4} \rho^{\frac{l}{2}} \exp \left[ -\frac{\rho}{2} \right] \frac{\partial}{\partial \rho} L(\rho)
\]

\[
+ \frac{l}{2} \rho^{\frac{l-1}{2}} \exp \left[ -\frac{\rho}{2} \right] \frac{\partial}{\partial \rho} L(\rho) - \frac{1}{2} \rho^{\frac{l}{2}} \exp \left[ -\frac{\rho}{2} \right] \frac{\partial}{\partial \rho} L(\rho)
\]

(1679)

Hence, we have

\[
4 \rho \frac{\partial^2 R}{\partial \rho^2} = \rho^{\frac{l}{2}} \exp \left[ -\frac{\rho}{2} \right] \left[ 4 \rho \frac{\partial^2}{\partial \rho^2} + 4 (l - \rho) \frac{\partial}{\partial \rho} + \frac{l (l - 2)}{\rho} + \rho - 2 l \right] L(\rho)
\]

(1681)

\[
6 \frac{\partial R}{\partial \rho} = \rho^{\frac{l}{2}} \exp \left[ -\frac{\rho}{2} \right] \left[ 6 \frac{\partial}{\partial \rho} - \frac{l}{\rho} + 3 \frac{l}{\rho} \right] L(\rho)
\]

(1682)

which on substituting into the radial equation leads to

\[
- \frac{\hbar \omega}{2} \rho^{\frac{l}{2}} \exp \left[ -\frac{\rho}{2} \right] \left[ 4 \rho \frac{\partial^2}{\partial \rho^2} + (4 l + 6 - 4 \rho) \frac{\partial}{\partial \rho} + \frac{2 E}{\hbar \omega} - (2 l + 3) \right] L(\rho) = 0
\]

(1683)
On cancelling the common factor and dividing by 4, one obtains
\[
\begin{array}{c}
\left[ \rho \frac{\partial^2}{\partial \rho^2} + \left( l + \frac{3}{2} - \rho \right) \frac{\partial}{\partial \rho} + \frac{E}{2 \hbar \omega} - \frac{1}{4} \left( 2 l + 3 \right) \right] L(\rho) = 0
\end{array}
\tag{1684}
\]
which is the associated Laguerre equation, as was to be shown.

4.6.22 Exercise 94

Consider the set of energy eigenstates of the isotropic harmonic oscillator with 
\[ \frac{E}{\hbar \omega} = \frac{3}{2}, \frac{5}{2} \text{ and } \frac{7}{2} \]. Show that the eigenfunctions of the lowest energy eigenstates are degenerate and that the wave functions and degeneracy found in the spherical polar representation coincide with the representation in terms of three independent one-dimensional harmonic oscillators. Evaluate the degeneracy of the energy eigenvalue with \( N \) quanta present.

The symmetry group of the spherical harmonic oscillator.

The degeneracy of a spherical harmonic oscillator can be discussed in terms of operators which, when acting on one state, produce other states degenerate with it. These operators only have finite matrix elements between degenerate states and must commute with the Hamiltonian. The commutators of these operators must also commute with the Hamiltonian and, therefore, the operators should generate a Lie algebra. Since the angular momentum must commute with the Hamiltonian, the Lie algebra of the three-dimensional harmonic oscillator should be greater than, and include, the angular momentum Lie algebra.

The Hamiltonian of the three-dimensional harmonic oscillator can be written in terms of the creation and annihilation operators of the three one-dimensional harmonic oscillators via
\[
\hat{H} = \frac{\hbar \omega}{2} \sum_{i=1}^{3} \left( a_{i}^\dagger a_{i} + a_{i} a_{i}^\dagger \right)
\tag{1685}
\]
Using the expressions for the position and momentum operators in terms of the creation and annihilation operators
\[
\hat{x}_{i} = \left( \frac{\hbar}{2 m \omega} \right)^{\frac{1}{2}} \left[ a_{i}^\dagger + a_{i} \right]
\tag{1686}
\]
and
\[
\hat{p}_{i} = i \left( \frac{\hbar m \omega}{2} \right)^{\frac{1}{2}} \left[ a_{i}^\dagger - a_{i} \right]
\tag{1687}
\]
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one can show that the operators representing the components of the angular momentum are given by

\[ \hat{L}_i = -i \hbar \sum_{j,k} \epsilon^{i,j,k} a_j^\dagger a_k \]  

(1688)

where \( \epsilon^{i,j,k} \) is the anti-symmetric Levi-Civita symbol. The states which correspond to the same total number of quanta are degenerate. The Lie algebra of the two-dimensional \( x - y \) sub-space is generated by the diagonal operator

\[ \hat{\tau}_z = \frac{1}{2} \left( a_1^\dagger a_1 - a_2^\dagger a_2 \right) \]  

(1689)

and the ladder operators

\[ \hat{\tau}_+ = a_1^\dagger a_2 \]

\[ \hat{\tau}_- = a_2^\dagger a_1 \]  

(1690)

These bi-linear \( \hat{\tau} \) operators do not change the total number of quanta and transform an energy eigenstate into eigenstates that are degenerate with it. The set of \( \hat{\tau} \) operators are linearly independent and obey similar commutation relations to the angular momentum operators. Hence, the degeneracy of the two-dimensional harmonic oscillator is describable by a \( SU(2) \) symmetry group and is a Lie algebra of rank unity\(^{25}\). The symmetry group of the three-dimensional harmonic oscillator must contain the \( SU(2) \) group as a sub-group. For the three-dimensional harmonic oscillator, the Lie algebra is supplemented by the diagonal operator

\[ \hat{\lambda} = \frac{1}{2\sqrt{3}} \left( a_1^\dagger a_1 + a_2^\dagger a_2 - 2 a_3^\dagger a_3 \right) \]  

(1691)

and, therefore, is a Lie algebra of rank 2. The Lie algebra of the three-dimensional harmonic oscillator also involves the following set of ladder operators

\[ \hat{\beta}_+ = a_1^\dagger a_3 \]

\[ \hat{\beta}_- = a_3^\dagger a_1 \]

\[ \hat{\gamma}_+ = a_2^\dagger a_2 \]

\[ \hat{\gamma}_- = a_3^\dagger a_3 \]  

(1692)

Hence, the Lie algebra contains eight generators and corresponds to the \( SU(3) \) Lie group\(^{26}\).

\(^{25}\)The rank of a Lie algebra is given by the maximal number of (linearly independent) simultaneously commuting operators in the algebra, excluding the Casimir operators. The Casimir operators are non-linear combinations of the generators that commute with every generator of the Lie algebra. For semi-simple Lie groups of rank \( r \), there are \( r \) Casimir operators, and their eigenvalues uniquely characterize the multiplets of the group.

\(^{26}\)The special unitary group in \( N \) dimensions \( SU(N) \) contains \( N^2 - 1 \) generators. The \( SU(N) \) symmetry groups are discussed by S. Sternberg in *Group Theory and Physics*, Cambridge University Press, (1994).
The time-independent Schrödinger equation for the attractive Coulomb potential is

\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} - \frac{Ze^2}{r} \right] R_{E,l}(r) = E R_{E,l}(r)
\]  

(1693)

where \(Z\) is the atomic number.

Figure 93: The radially symmetric potential, \(V(r)\), for the hydrogen atom. The energy eigenvalues are denoted by horizontal lines.

We introduce a dimensionless parameter

\[
\rho = \sqrt{-\frac{2mE}{\hbar^2}} r
\]

(1694)

and a dimensionless constant \(\rho_0\) such that

\[
\frac{V(r)}{E} = \frac{\rho_0}{\rho}
\]

(1695)

so that

\[
\rho_0 = \sqrt{-\frac{2m}{E}} \frac{Ze^2}{\hbar}
\]

(1696)

Then, the radial wave function is expressed in the form

$$R_{E,l}(r) = \rho^l \exp[-\rho] f(\rho)$$  \hspace{1cm} (1697)

which explicitly displays the limiting behavior needed at the boundaries. The factor proportional to $\rho^l$ is introduced so that the wave function satisfies the Schrödinger equation near the origin, where the centrifugal barrier dominates the potential. The exponential term describes the localization of the bound particle to the region around the origin. It should be noted that there is a second independent solution for which $R$ would diverge at large $\rho$ as $\exp[+\rho]$ but this second solution is to be discarded as it is not normalizable. Substituting the expression (1697) in the Schrödinger equation yields

$$\frac{\partial^2 f}{\partial \rho^2} + 2 \left( \frac{l + 1}{\rho} - 1 \right) \frac{\partial f}{\partial \rho} - \left[ \frac{2 \left( l + 1 \right) - \rho_0}{\rho} \right] f = 0$$  \hspace{1cm} (1698)

### Mathematical details

In terms of the dimensionless variables, the equation for the radial wave function $R(r)$ takes the form

$$-\frac{\partial^2 R}{\partial \rho^2} - \frac{2}{\rho} \frac{\partial R}{\partial \rho} + \left( \frac{l(l+1)}{\rho^2} + 1 \right) R - \frac{\rho_0}{\rho} R = 0$$  \hspace{1cm} (1699)

We shall substitute the radial wave function in the form

$$R(r) = \rho^l \exp[-\rho] f(\rho)$$  \hspace{1cm} (1700)

into the above equation. The detailed form of $R$ was chosen to satisfy our boundary conditions. The first derivative of $R$ is calculated as

$$\frac{\partial R}{\partial \rho} = \rho^l \exp[-\rho] \left[ \frac{l}{\rho} - 1 + \frac{\partial}{\partial \rho} \right] f(\rho)$$  \hspace{1cm} (1701)

The second derivative of $R$ is calculated as

$$\frac{\partial^2 R}{\partial \rho^2} = \rho^l \exp[-\rho] \left[ \frac{l(l-1)}{\rho^2} - \frac{2l}{\rho} + 1 \right] f(\rho)$$

$$+ \rho^l \exp[-\rho] \left[ \frac{l}{\rho} - 1 \right] \frac{\partial f}{\partial \rho}$$

$$+ \rho^l \exp[-\rho] \frac{\partial^2 f}{\partial \rho^2}$$  \hspace{1cm} (1702)

On substituting these expressions in eqn(1699), one finds

$$\frac{\partial^2 f}{\partial \rho^2} + 2 \left( \frac{l + 1}{\rho} - 1 \right) \frac{\partial f}{\partial \rho} - \left[ \frac{2 \left( l + 1 \right) - \rho_0}{\rho} \right] f = 0$$  \hspace{1cm} (1703)
On multiplying by $\rho$, this equation reduces to the differential equation for the associated Laguerre polynomials. On multiplying by $\rho$, this equation reduces to the equation for the associated Laguerre polynomials $L(z)$ in the variable $z = 2 \rho$,

$$z \frac{\partial^2 L}{\partial z^2} + \left( 2 ( l + 1 ) - z \right) \frac{\partial L}{\partial z} + \left[ \frac{\rho_0}{2} - l - 1 \right] L = 0 \quad (1704)$$

The solution has to satisfy the boundary condition at the origin $\rho = 0$ and at $\rho \to \infty$. The solution for $f(\rho)$ can be obtained as a Fröbenius series

$$f(\rho) = \sum_{n=0} a_n \rho^n \quad (1705)$$

On introducing this power series ansatz for the solution into the differential equation (1698) and combining terms of similar order, one finds a polynomial equation. The coefficients of the terms of various powers of $\rho$ in the resulting polynomial must vanish identically. This procedure leads to a recursion relation which relates the coefficients $a_n$ with different $n$. The recursion relation is found as

$$a_{n+1} \left( n + 1 \right) \left( n + 2 l + 2 \right) = a_n \left( 2 \left( n + l + 1 \right) - \rho_0 \right) \quad (1706)$$

If the series did not terminate, then one can show that the sum of the infinite series would be of order $\exp[ + 2 \rho ]$ for large $\rho$. This would result in the appearance of the second solution with the unphysical asymptotic behavior at large $r$

$$\lim_{r \to \infty} R(r) \sim \rho^l \exp \left[ + \rho \right] \quad (1707)$$

but this would not satisfy our boundary conditions. Therefore, one insists that the series must truncate if it is to represent a bound state. The series truncates at an integer value of $n$, say $n_r$, if

$$\rho_0 = 2 \left( n_r + l + 1 \right) \quad (1708)$$

and represents a bound state with radial quantum number $n_r$. On using

$$\rho_0 = \sqrt{\frac{2 m}{-E}} \frac{Z e^2}{\hbar} \quad (1709)$$

one finds the non-relativistic formula for the energy eigenvalues

$$E = -\frac{Z^2 e^4 m}{2 \hbar^2 \left( n_r + l + 1 \right)^2} \quad (1710)$$

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Furthermore, on defining a characteristic length scale \( r_0 \) in terms of \( \rho_0 \) and eqn(1694), one has

\[
r_0 = \sqrt{\frac{\hbar^2}{-2mE} \rho_0}
\]  

(1711)

Therefore, one has

\[
r_0 = 2 \left( n_r + l + 1 \right)^2 \frac{\hbar^2}{Ze^2} 
\]  

(1712)

and one identifies the characteristic length scale with twice the Bohr radius. The principal quantum number \( n \) is usually defined as

\[
n = \frac{\rho_0}{2} = (n_r + l + 1)
\]

(1713)

where \( l \) is the quantum number corresponding to the orbital angular momentum and \( n_r \) is the radial quantum number.

The lowest energy state or ground state corresponds to \( l = 0 \) and \( n_r = 0 \). The states with higher values of \( E \) are degenerate since for these energies, different values of \( n_r \) and \( l \) can be combined to give the same value of \( \rho_0 \) or \( n \). The possible values of \( l \) for a fixed \( \rho_0 \) are given by \( l = 0, 1, 2, \ldots, \frac{\rho_0}{2} - 1 \).

Since each \( l \) value has a degeneracy of \( 2l + 1 \) due to the different \( m \) values, the total degeneracy is

\[
\sum_{l=0}^{\frac{\rho_0}{2}-1} (2l + 1) = \left( \frac{\rho_0}{2} \right)^2 = n^2
\]  

(1714)

Thus, the energy eigenfunctions corresponding to the bound state energy \( E_n \) are \( n^2 \)-fold degenerate, if we neglect spin.

Note that if we had deformed the Coulomb potential slightly, the degeneracy between the states with principal quantum number \( n \) but with different orbital angular momentum \( l \) would be lifted. This occurs in \( H \), if one considers the effect of the finite size of the nucleus.

The “accidental degeneracy” of the energy eigenvalues \( E_n \) of the hydrogen atom, corresponding to the states with principal quantum number \( n \) but with different angular momentum quantum numbers \( l \), involves the group \( SO(4) \). More specifically, it can be shown that the energy eigenstates of the hydrogen atom can be transformed into the eigenstates of a free rotor in a four-dimensional space\(^{28}\).

Figure 94: The radial wave functions for the hydrogen atom $R_{n,l}(r)$, for $l = 0 , 1 , 2$. The radial quantum number $n_r$ determines the number of nodes in the wave function.
Figure 95: The probability density $P(r) = r^2 |R_{n,l}(r)|^2$ for finding an electron at a distance $r$ from the nucleus, for $n = 1, 2, 3$ and different $l$ values.
Figure 96: The probability density $P(r) = r^2 \mid R_{n,l}(r) \mid^2$ for finding an electron at a distance $r$ from the nucleus, for $n = 2, 3$ and different $l$ values. The classical probability densities are also shown. The classical probability densities are calculated with a fixed energy $E$ and angular momentum $l$, but unknown initial position $r$. Only the classical particle with $l = 0$ reaches the origin, however, it has a vanishing probability density there as the speed tends to infinity as $r \to 0$. 
4.6.24 Exercise 95

Derive the recursion relation for the series expansion of the associated Laguerre polynomials that occur in the radial wave functions of electrons in the bound states of Hydrogen atoms and determine the condition that the series terminates after \( n \) terms.

4.6.25 Exercise 96

An atom of tritium is in its ground state when the nucleus suddenly decays into a helium nucleus along with the emission of a fast electron (and an anti-neutrino) which leaves the atom without perturbing the extra-nuclear electron. Find the probability that the remaining \( He^+ \) atom will be left in the state with \( n = 1, l = 0 \) and \( n = 2, l = 0 \). What is the selection rule for the \( l \) quantum number?

4.6.26 Solution 96

The electronic state immediately before the decay is identical to that of the \( n = 1, l = 0 \) state of \( H \), i.e. \( Z = 1 \). Then,

\[
\Psi_{Z=1,n=1,l=0}(r) = \frac{1}{\sqrt{\pi}} a_0^{-\frac{3}{2}} \exp \left[-\frac{r}{a_0}\right] \tag{1715}
\]

The probability that the electron falls into the energy levels of \( He^+ \) is given by the overlap with the respective \( Z = 2 \) wave functions

\[
\Psi_{Z=2,n=1,l=0}(r) = \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{\frac{3}{2}} \exp \left[-2\frac{r}{a_0}\right] \tag{1716}
\]

and

\[
\Psi_{Z=2,n=2,l=0}(r) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{\frac{3}{2}} \left(1 - \frac{r}{a_0}\right) \exp \left[-\frac{r}{a_0}\right] \tag{1717}
\]

The matrix elements between the \( Z = 1 \) and \( Z = 2 \) states are evaluated via scaling and repeated integration by parts as

\[
C_{n=1,l=0} = 4 \pi \int_0^\infty dr \ r^2 \ \Psi_{Z=1,n=1,l=0}^*(r) \Psi_{Z=2,n=1,l=0}(r) = 4 \pi \frac{8^{\frac{3}{2}}}{\pi a_0^3} \int_0^\infty dr \ r^2 \exp \left[-3\frac{r}{a_0}\right]
\]

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Thus, the probability of the electron falling into the ground state is equal to
\[ P(0) = \frac{2^9}{3^6} \quad (1719) \]

Similarly,
\[
C_{n=2,l=0} = 4 \pi \int_0^{\infty} \int_0^{\infty}dr \ r^2 \ \Psi_{Z=1,n=1,l=0}^* \Psi_{Z=2,n=2,l=0}(r)
\]
\[
= 4 \pi \frac{1}{a_0} \int_0^{\infty} dr \ r^2 \left( 1 - \frac{r}{a_0} \right) \exp \left[ -2 \frac{r}{a_0} \right]
\]
\[
= 4 \int_0^{\infty} dx \ x^2 \ (1 - x) \exp \left[ -2 \ x \right]
\]
\[
= \frac{1}{2}
\quad (1720)\]

Thus, the probability of the electron falling into the first excited state is equal to
\[ P(1) = \frac{1}{2^2} \quad (1721)\]

The selection rule is \( \Delta l = 0 \). This follows as the potential is spherically symmetric, and so angular momentum is conserved. Mathematically this is manifested by the angular part of the wave function being given by spherical harmonics, and also by the fact that the spherical harmonics with different \( l \) are orthogonal.

**4.6.27 Exercise 97**

A tritium atom decays via the nuclear reaction
\[ ^3H \rightarrow ^3He + e^- + \nu \quad (1722) \]

and a fast electron leaves the atom almost instantaneously. Calculate the expectation value of the energy for the remaining electron. The probability that the remaining energy is in the \( n \)-th bound state is denoted by \( P(n) \). It is found that
\[
\sum_{n=1}^{\infty} P(n) = 0.9755 \quad (1723)
\]

and
\[
\sum_{n=1}^{\infty} P(n) \frac{1}{n^2} = 0.76660 \quad (1724)
\]
What is the probability that the Helium ion is doubly ionized and what is the average energy of the second emitted electron?

4.6.28 Ladder Operators for the Hydrogen Atom

The radial equation for the energy eigenstates of Hydrogen atom can be written in a dimensionless form. This is achieved by introducing a length scale $b$ defined by

$$ b = \frac{\hbar^2}{Ze^2 m} \quad (1725) $$

and a dimensionless variable $\rho$ defined by

$$ \rho = \frac{r}{b} \quad (1726) $$

The energy eigenvalue can then be expressed in dimensionless form as

$$ \epsilon = E \left( \frac{2 m b^2}{\hbar^2} \right) = E \left( \frac{2 \hbar^2}{Z^2 e^4 m} \right) = \left( \frac{E}{R} \right) \quad (1727) $$

Thus, the dimensionless energy $\epsilon$ corresponds to the value of $E$ when expressed in units of Rydbergs. In dimensionless units, the radial equation takes the form

$$ \left( -\frac{\partial^2}{\partial \rho^2} + \frac{l (l + 1)}{\rho^2} - \frac{2}{\rho} \right) u_{n,l} = \epsilon u_{n,l} \quad (1728) $$

where

$$ u_{n,l}(\rho) = \rho R_{n,l}(\rho) \quad (1729) $$

is the reduced radial wave function. The bound state wave functions have negative eigenvalues, are normalizable, satisfy the boundary condition $\lim_{\rho \to 0} u_{n,l}(\rho) \to \rho^{l+1}$ at $\rho = 0$, and vanish asymptotically as

$$ \lim_{\rho \to \infty} u_{n,l}(\rho) \to \exp \left[ -\sqrt{-\epsilon} \rho \right] \quad (1730) $$

when $\rho \to \infty$. The radial equation can be solved for the bound states using appropriate raising and lowering operators.

The lowering operator $\hat{A}_l^-$ is defined as

$$ \hat{A}_l^- = \frac{\partial}{\partial \rho} + \frac{l + 1}{\rho} - \frac{1}{l + 1} \quad (1731) $$
and the raising operator $\hat{A}_l^+$ is defined as the Hermitean conjugate of the lowering operator

$$\hat{A}_l^+ = -\frac{\partial}{\partial \rho} + \frac{l + 1}{\rho} - \frac{1}{l + 1} \quad (1732)$$

It immediately follows that

$$\hat{A}_l^- \hat{A}_l^+ = \left( -\frac{\partial^2}{\partial \rho^2} + \frac{l(l + 1)}{\rho^2} - \frac{2}{\rho} + \frac{1}{(l + 1)^2} \right) \quad (1733)$$

so the radial Schrödinger equation can be written as

$$\left( \hat{A}_l^- \hat{A}_l^+ - \frac{1}{(l + 1)^2} \right) u_{n,l} = \epsilon u_{n,l} \quad (1734)$$

The product of the raising and lowering operators, taken in the reverse order, can be expressed as

$$\hat{A}_l^+ \hat{A}_l^- = \left( -\frac{\partial^2}{\partial \rho^2} + \frac{(l + 2)(l + 1)}{\rho^2} - \frac{2}{\rho} + \frac{1}{(l + 1)^2} \right) \quad (1735)$$

Hence, one has the relation

$$\hat{A}_l^+ \hat{A}_l^- - \frac{1}{(l + 1)^2} = \hat{A}_{l+1}^- \hat{A}_{l+1}^+ - \frac{1}{(l + 2)^2} \quad (1736)$$

On multiplying the radial Schrödinger equation (as expressed in the form of eqn(1734)) by the raising operator $\hat{A}_l^+$, one has

$$\hat{A}_l^+ \left( \hat{A}_l^- \hat{A}_l^+ - \frac{1}{(l + 1)^2} \right) u_{n,l} = \epsilon \hat{A}_l^+ u_{n,l}$$

$$\left( \hat{A}_l^+ \hat{A}_l^- - \frac{1}{(l + 1)^2} \right) \hat{A}_l^+ u_{n,l} = \epsilon \hat{A}_l^+ u_{n,l} \quad (1737)$$

On substitution of the relation expressed by eqn(1736) in the above equation, one finds

$$\left( \hat{A}_{l+1}^- \hat{A}_{l+1}^+ - \frac{1}{(l + 2)^2} \right) \hat{A}_l^+ u_{n,l} = \epsilon \hat{A}_l^+ u_{n,l} \quad (1738)$$

Hence, we see that $\hat{A}_l^+ u_{n,l}$ is an eigenstate of the radial Schrödinger equation with angular momentum $l' = l - 1$ and energy eigenvalue $\epsilon$. Thus, $\hat{A}_l^+$ is a raising operator for the radial wave function.

The eigenstates with angular momentum $l' = l - 1$ can be obtained with the aid of the lowering operator. This can be shown by considering the Schrödinger equation written in the form

$$\left( \hat{A}_{l-1}^- \hat{A}_{l-1}^+ - \frac{1}{l'^2} \right) u_{n,l} = \epsilon u_{n,l} \quad (1739)$$
On applying $\hat{A}_{l-1}$ to this equation, one finds

$$\hat{A}_{l-1} \left( \hat{A}_{l-1} - \frac{1}{l^2} \right) u_{n,l} = \epsilon \hat{A}_{l-1} u_{n,l}$$

$$\left( \hat{A}_{l-1} - \frac{1}{l^2} \right) \hat{A}_{l-1} u_{n,l} = \epsilon \hat{A}_{l-1} u_{n,l}$$

$$\left( \hat{A}_{l-2} - \frac{1}{(l-1)^2} \right) \hat{A}_{l-1} u_{n,l} = \epsilon \hat{A}_{l-1} u_{n,l}$$

(1740)

where we have used eqn(1739) in the second line. On comparison of eqn(1740) with eqn(1739), one finds that $\hat{A}_{l-1} u_{n,l}$ is an eigenstate with eigenvalue $\epsilon$ and angular momentum $l' = l - 1$.

The energy eigenvalue $\epsilon$ satisfies an inequality which can be found directly from the Radial Schrödinger equation

$$\hat{A}_{l}^- \hat{A}_{l}^+ u_{n,l} = \left( \frac{1}{(l+1)^2} + \epsilon \right) u_{n,l}$$

(1741)

by multiplying by $u_{n,l}^*$ and integrating over $\rho$:

$$\int_0^\infty d\rho \ u_{n,l}^* \hat{A}_{l}^- \hat{A}_{l}^+ u_{n,l} = \int_0^\infty d\rho \ u_{n,l}^* \left( \frac{1}{(l+1)^2} + \epsilon \right) u_{n,l}$$

(1742)

However, $u_{n,l}$ is normalized to unity and $\hat{A}_{l}^-$ is the Hermitian conjugate of $\hat{A}_{l}^+$, so

$$\int_0^\infty d\rho \ |\hat{A}_{l}^+ u_{n,l}|^2 = \left( \frac{1}{(l+1)^2} + \epsilon \right)$$

(1743)

Since the left-hand side is positive, one finds the inequality

$$\epsilon \geq - \frac{1}{(l+1)^2}$$

(1744)

The inequality

$$\epsilon \geq - \frac{1}{(l+1)^2}$$

(1745)

involving the (negative) bound state energy eigenvalue $\epsilon$ and the angular momentum indicates that the angular momentum raising process must terminate. If this terminates for some value of $l$, say $l_{\text{max}}$, then the termination condition is expressed as

$$\hat{A}_{l_{\text{max}}}^+ u_{n,l_{\text{max}}} = 0$$

(1746)

---

29Due to the factor of $\rho$ which appears in the definition of $u_{n,l}$ in terms of the radial function $R_{n,l}(\rho)$, the three-dimensional radial equation is reduced to an effective one-dimensional Schrödinger equation. The factor of $\rho$ in $u_{n,l}$ also reduces the appropriate measure for the radial integration is reduced from $\rho^2$ to unity, as expected for an effective one-dimensional geometry.
On using the termination condition in the eigenvalue equation

\[
\left( \hat{A}_{l_{\text{max}}}^- \hat{A}_{l_{\text{max}}}^+ - \frac{1}{(l_{\text{max}} + 1)^2} \right) u_{n,l_{\text{max}}} = \epsilon \ u_{n,l_{\text{max}}} \tag{1747}
\]

so that the first term in the parenthesis is zero, one finds

\[
\epsilon = - \frac{1}{(l_{\text{max}} + 1)^2}
\tag{1748}
\]

or

\[
\epsilon = - \frac{1}{n^2}
\tag{1749}
\]

where \( n = (l_{\text{max}} + 1) \) is the principal quantum number.

The radial functions \( u_{n,l} \) can be obtained by first solving the first order differential equation for \( u_{n,l_{\text{max}}} \) that expresses the termination and then, using the lowering operator successively to find all the eigenfunctions with lower \( l \) values.

The termination condition

\[
\hat{A}_{l_{\text{max}}}^+ u_{n,l_{\text{max}}} = 0 \tag{1750}
\]

is expressed as

\[
\frac{\partial u_{n,l_{\text{max}}}}{\partial \rho} = \left( \frac{n}{\rho} - \frac{1}{n} \right) u_{n,l_{\text{max}}} \tag{1751}
\]

This can be integrated to yield

\[
\ln u_{n,l_{\text{max}}} = A + n \ln \rho - \frac{\rho}{n} \tag{1752}
\]

where \( A \) is a constant of integration. On exponentiating, one finds the radial wave function has the form

\[
u_{n,l_{\text{max}}} = C \ \rho^n \ \exp \left[ -\frac{\rho}{n} \right] \tag{1753}
\]

where the constant \( C \) has to be determined from the normalization condition. The above form of \( u_{n,l}(\rho) \) yields a solution for the radial wave function which does satisfy the correct boundary conditions.

The radial wave function with angular momentum \( l = l_{\text{max}} - 1 \) is obtained from \( u_{n,l_{\text{max}}} \) by the action of the lowering operator

\[
u_{n,l_{\text{max}}-1} \propto \hat{A}_{l_{\text{max}}-1}^- u_{n,l_{\text{max}}} \tag{1754}
\]

or, more explicitly

\[
u_{n,l_{\text{max}}-1} \propto \left( \frac{\partial}{\partial \rho} + \frac{n-1}{\rho} - \frac{1}{(n-1)} \right) u_{n,l_{\text{max}}} \tag{1755}
\]

\[
\propto \left( 1 - \frac{\rho}{n(n-1)} \right) \rho^{n-1} \exp \left[ -\frac{\rho}{n} \right]
\]
Table 8: Radial wave functions $R_{n,l}(\rho)$ for the Coulomb potential, where $\rho = \frac{Zr}{a_0}$. The Radial wave functions are normalized so that $\int_0^\infty d\rho \rho^2 R_{n,l}(\rho)^2 = 1$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$R_{n,l}(\rho)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$2 \exp\left[-\rho\right]$</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>$rac{1}{\sqrt{2}} \left(1 - \frac{\rho}{2}\right) \exp\left[-\frac{\rho}{2}\right]$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\frac{1}{2\sqrt{2}} \rho \exp\left[-\frac{\rho}{2}\right]$</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>$\frac{2}{3\sqrt{2}} \left(1 - \frac{\rho}{3}\right) \rho \exp\left[-\frac{\rho}{3}\right]$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$\frac{2}{3\sqrt{2}} \rho^2 \exp\left[-\frac{\rho}{3}\right]$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\frac{2}{3\sqrt{2}} \left(1 - \frac{\rho}{3} + \frac{2}{3\sqrt{2}} \rho^2\right) \exp\left[-\frac{\rho}{3}\right]$</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>$\frac{2}{3\sqrt{2}} \left(1 - \frac{\rho}{6}\right) \rho \exp\left[-\frac{\rho}{6}\right]$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$\frac{2}{3\sqrt{2}} \rho^2 \exp\left[-\frac{\rho}{6}\right]$</td>
</tr>
</tbody>
</table>

Therefore, the radial functions corresponding to smaller values of $l$ can be obtained by sequentially operating with the appropriate $\hat{A}_{l-1}$.

4.6.29 Rydberg Wave Packets

The correspondence between the classical picture of the orbital motion of electrons in the hydrogen atom and the quantum mechanical picture can be seen by examining the time dependence of the peak in the probability density $|\Psi(r, \theta, \varphi; t)|^2$. For convenience, we shall consider motion in the plane $\theta = \frac{\pi}{2}$, and so shall set $m$ to the maximal value $m = l$. In this case, due to the $\theta$ dependence given by $\Theta_l^m(\theta) \propto \sin^l \theta$, the probability density is maximal at $\theta = \frac{\pi}{2}$. To obtain a time dependence of the probability, it is necessary to superimpose energy eigenstates to produce a wave packet. In particular, to obtain a probability density that shows a time-dependent variation in the $\varphi$ dependence, eigenstates corresponding to different energy eigenvalues must be superimposed. We shall superimpose the energy eigenstates with $l = n - 1$, which are given by

$$\Psi_{n,n-1,n-1}(r, \theta, \varphi) = N^{-1} \left(\frac{r}{a_0}\right)^{n-1} \exp\left[-\frac{r}{n a_0}\right] \sin^{n-1} \theta \exp\left[i(n-1)\varphi\right]$$

(1756)
where \( a_0 = \frac{\hbar^2}{m e^2} \) is the Bohr radius, and \( \aleph \) is the normalization. This set of energy eigenstates correspond to circular orbits, as the radial quantum number \( n_r = 0 \). For the circular orbits, the principal quantum number \( n \) is just given by \( l + 1 \). The energy eigenvalues are given by

\[
E_n = -\frac{m e^4}{2 \hbar^2 n^2}
\]

These states have radii defined by the maxima in

\[
r^2 \left| \Psi_{n,n-1,n-1}(r,\theta,\varphi) \right|^2
\]

which occur at \( r = n^2 a_0 \). The products of the uncertainties in the radial position and the radial momentum are given by

\[
(\Delta r)_{\text{rms}} (\Delta p_r)_{\text{rms}} = \frac{\hbar}{2} \left( 1 + \frac{1}{2n} + \ldots \right)
\]

and also for the angular coordinates

\[
(\Delta \theta)_{\text{rms}} (\Delta p_{\theta})_{\text{rms}} = \frac{\hbar}{2} \left( 1 + \frac{1}{4n} + \ldots \right)
\]

A particular wave packet is represented by the wave function

\[
\Psi(r,t) = \sum_n C_n \Psi_{n,n-1,n-1}(r,\theta,\varphi) \exp\left[ -\frac{i}{\hbar} t E_n \right]
\]

where the distribution of \( C_n \) produces a mean value of \( n \) denoted by \( \bar{n} \), and a width given by \( \Delta n_{\text{rms}} \).

The probability density shows that the wave packet describes periodic circular orbits, with period given by the Kepler period \( T_K \). This is seen in fig(98). This can be derived from the expansion of the exponential factor in the wave packet about \( \bar{n} \)

\[
\exp\left[ i (\bar{n} \varphi - \frac{t}{\hbar} E_{\bar{n}}) \right] \exp\left[ i (n - \bar{n}) \left( \varphi - \frac{t}{\hbar} \left( \frac{\partial E_n}{\partial n} \right)_{n=\bar{n}} \right) \right] \ldots
\]

The first factor being a common overall phase factor does not appear in the probability density. If the terms of order \( (n - \bar{n})^2 \) can be neglected, the sum over \( n \) of the second factor produces a finite Fourier series. The resulting approximation to the wave packet is \( 2\pi \) periodic in the variable

\[
\varphi - \frac{t}{\hbar} \left( \frac{\partial E_n}{\partial n} \right)_{n=\bar{n}}
\]
Figure 97: A comparison of the quantum mechanical probability densities of the circular orbit with $l = n - 1$ (blue) and the linear orbit $l = 0$ (red). For the circular orbit with $n = l + 1$, the zero-point radial motion becomes negligible for large values of $l$ and the radial wave function becomes highly peaked at the radius of the orbit. The classical probability densities are denoted by the broken lines.

Thus, the Kepler period is given by

\[
\frac{2 \pi}{T_K} = \frac{1}{\hbar} \left( \frac{\partial E_n}{\partial n} \right)_{n=\pi} = \frac{m e^4}{\hbar^3 \pi^3}
\]

or

\[
T_K = \frac{2 \pi h^3 \pi^3}{m e^4}
\]

\[
= \frac{2 \pi}{\frac{\hbar^2 \pi^2}{m e^2}}
\]

\[
= \frac{2 \pi a_0 \pi^2}{\bar{v}}
\]

which is the size of the circular orbit divided by the average speed $\bar{v}$. The
average speed is given in terms of the fine structure constant and the velocity of light $c$ via

$$
\bar{v} = \frac{e^2}{\hbar \pi} = \frac{c}{\pi} \frac{e^2}{\hbar c} \quad (1766)
$$

The terms of order $\left( n - \pi \right)^2$ have the effect of dephasing the oscillations. At first, the $\varphi$ dependence of the wave packets distort by spreading slowly in time. This increases the range of $\varphi$ in which the wave packets have an appreciable magnitude. The initial spreading is similar to the spreading of a wave packet for a free particle. However, at large times, the wave packet recurs or re-forms as is shown in fig(99). The time scale for this phenomenon is found by expanding the energy about the average value of $n$,

$$
E_n = E_\pi + \left( n - \pi \right) \frac{\partial E}{\partial n} \bigg|_{n=\pi} + \frac{1}{2} \left( n - \pi \right)^2 \frac{\partial^2 E}{\partial n^2} \bigg|_{n=\pi} \quad (1767)
$$

The recurrence time $T_R$ is defined via

$$
- \frac{1}{\hbar} \frac{\partial^2 E}{\partial n^2} \bigg|_{n=\pi} = \frac{2 \pi}{T_R} \quad (1768)
$$

which yields

$$
T_R = \frac{\pi}{3} T_K \quad (1769)
$$

The recurrence time causes the wave function to dephase and recur at time $t = T_R$ but with a phase shift of $\pi$. The phenomenon of recurrence is a quantum effect involving the non-linear dependence of the energy eigenvalues.$^{30}$

### 4.6.30 Laguerre Polynomials

Laguerre’s differential equation is

$$
z \frac{\partial^2 \phi_n}{\partial z^2} + \left( 1 - z \right) \frac{\partial \phi_n}{\partial z} + n \phi_n = 0 \quad (1770)
$$

The solution can be represented by a contour integral

$$
\phi_n(z) = \oint dt \frac{dt}{2 \pi i} \exp \left[ - \frac{z}{1 - t} \right] \left( \frac{1}{1 - t} \right)^{n+1} \quad (1771)
$$

where the contour runs around a circle centered on the origin, with radius less than unity. We shall show that this is a solution of the differential equation. First we shall evaluate the derivatives

$$
\frac{\partial \phi_n}{\partial z} = - \oint dt \frac{dt}{2 \pi i} \exp \left[ - \frac{z}{1 - t} \right] \left( \frac{1}{1 - t} \right)^{n+1} \quad (1772)
$$

Figure 98: The time dependence of the probability density for an electron in a circular orbit, at times of order $T_K$. The wave packet rotates with period $T_k$. [After C. R. Stroud Jr. (1993).]

and

$$\frac{\partial^2 \phi_n(z)}{\partial z^2} = + \oint \frac{dt}{2 \pi i} \exp \left[ - \frac{z t}{1 - t} \right] \frac{t^2}{(1 - t)^3} t^{n+1}$$

(1773)
Then, on substituting the derivatives into the differential equation, one obtains

\[ 0 = \oint \frac{dt}{2 \pi i} \exp \left[ - \frac{z t}{1 - t} \right] \left( \frac{1}{1 - t} \right)^2 t^{n+1} \left[ z t^2 - t \left( 1 - t \right) \left( 1 - z \right) + n \left( 1 - t \right)^2 \right] \]

(1774)

The right hand side is identified as the integral of a perfect differential

\[ 0 = - \oint \frac{dt}{2 \pi i} \frac{\partial}{\partial t} \left( \exp \left[ - \frac{z t}{1 - t} \right] \frac{1}{\left( 1 - t \right)^n} \right) \]

(1775)

On integrating the perfect differential around a closed contour without crossing a branch point, we find zero. Thus, we have verified that the expression given by the contour integral does satisfy Laguerre’s equation.

We shall denote the solution of Laguerre’s equation by

\[ L_n(z) = \oint \frac{dt}{2 \pi i} \exp \left[ - \frac{z t}{1 - t} \right] \left( \frac{1}{1 - t} \right)^{n+1} \]

(1776)

The generating function for the Laguerre polynomials, \( G(z,t) \), can be found directly from this representation. Let

\[ G(z,t) = \sum_{n=0}^{\infty} L_n(z) t^n \]

(1777)
then divide by $t^{n+1}$ and integrate around a closed contour containing the origin. This procedure yields

\begin{equation}
\oint dt \frac{G(z,t)}{2\pi i} t^{n+1} = \sum_m L_m(z) \oint dt \frac{t^m}{2\pi i} t^{n+1} = L_n(z)
\end{equation}

since Cauchy’s theorem implies only the term with $n = m$ is non-zero. On comparing the first line with the integral expression for $L_n(z)$, we identify

\begin{equation}
G(z,t) = \frac{\exp \left[ -\frac{z}{1-t} \right]}{(1-t)}
\end{equation}

Thus, we have the generating function series expansion

\begin{equation}
\frac{\exp \left[ -\frac{z}{1-t} \right]}{(1-t)} = \sum_{n=0}^{\infty} L_n(z) t^n
\end{equation}

for $t < 1$. 386
A Rodriguez formula for the solution can be found by performing the non-linear transformation

\[ \frac{t}{1-t} z = s - z \]  

(1781)

which can be solved for \( t \) as

\[ t = \frac{s - z}{s} \]  

(1782)

In this variable, the contour integral in eqn(1776) takes on the form

\[ L_n(z) = \exp \left[ z \right] \oint \frac{ds}{2 \pi i} \frac{s^n \exp \left[ -s \right]}{(s - z)^{n+1}} \]  

(1783)

where the new contour encloses the point \( s = z \) which corresponds to \( t = 0 \). By Cauchy's theorem, this integral can be seen to be the \( n \)-th order derivative of the numerator evaluated at the pole

\[ L_n(z) = \frac{\exp \left[ z \right]}{n!} \frac{\partial^n}{\partial z^n} \left( z^n \exp \left[ -z \right] \right) \]  

(1784)

for integral \( n \).

The Laguerre differential operator is not Hermitean, but if the solution is expressed as

\[ \Phi_n(z) = \exp \left[ -\frac{z}{2} \right] L_n(z) \]  

(1785)

then the corresponding operator is Hermitean, and the differential equation becomes

\[ z \frac{\partial^2 \Phi_n}{\partial z^2} + \frac{\partial \Phi_n}{\partial z} + \left( n + \frac{1}{2} - \frac{z}{2} \right) \Phi_n(z) = 0 \]  

(1786)

Therefore, the Laguerre polynomials satisfy the orthogonality condition

\[ \int_0^\infty dz \, \exp \left[ -z \right] L_m(z) L_n(z) = \delta_{m-n} \]  

(1787)

The Associated Laguerre polynomials are defined by

\[ L_n^k(z) = (-1)^k \frac{\partial^k}{\partial z^k} L_{n+k}(z) \]  

(1788)

For fixed \( k \), one can find a generating function for \( L_n^k(z) \) from the generating function for the Laguerre polynomials

\[ \frac{\exp \left[ -\frac{z t}{1-t} \right]}{(1-t)} = \sum_{n=-k}^\infty L_{n+k}(z) t^{n+k} \]  

(1789)

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by differentiating $k$ times, with respect to $z$, obtaining

$$\exp\left[-\frac{zt}{1-t}\right] t^k \frac{1}{(1-t)^{k+1}} = \sum_{n=-k}^{\infty} (-1)^k \frac{\partial^k}{\partial z^k} L_{n+k}(z) t^{n+k} \quad (1790)$$

Hence, since $L_{n+k}(z)$ is a polynomial with highest order term of $z^{n+k}$, the sum has its first non-zero term when $n = 0$ and

$$\exp\left[-\frac{zt}{1-t}\right] \frac{1}{(1-t)^{k+1}} = \sum_{n=0}^{\infty} L_n^k(z) t^n \quad (1791)$$

which is the generating function expansion for the associated Laguerre polynomials. The expansion also shows that the associated Laguerre polynomials reduce to the Laguerre polynomials when $k = 0$.

The associated Laguerre polynomials satisfy the differential equation

$$z \frac{\partial^2}{\partial z^2} L_n^k + \left( k + 1 - z \right) \frac{\partial}{\partial z} L_n^k + n L_n^k = 0 \quad (1792)$$

The associated Laguerre polynomials have the Rodriguez representation

$$L_n^k(z) = \frac{1}{n!} \exp\left[+z\right] z^{-k} \frac{\partial^n}{\partial z^n} \left( \exp\left[-z\right] z^{n+k} \right) \quad (1793)$$

The differential equation for the associated Laguerre polynomials can be written in the form of a Hermitean operator eigenvalue equation by using the substitution

$$\phi_n^k(z) = z^k \exp\left[-\frac{z}{2}\right] L_n^k(z) \quad (1794)$$

The functions $\phi_n^k(z)$ form a complete orthonormal set because they satisfy the differential equation

$$z \frac{\partial^2 \phi_n^k}{\partial z^2} + \frac{\partial \phi_n^k}{\partial z} - \left( z - \frac{2}{4} n + k + \frac{1}{2} + \frac{k^2}{4z} \right) \phi_n^k = 0 \quad (1795)$$

The normalization integral is

$$\int_0^\infty dz \, z^k \exp\left[-z\right] L_n^k(z) L_m^k(z) = \frac{(n + k)!}{n!} \delta_{n-m} \quad (1796)$$

The normalized hydrogen atom wave function is given by

$$\Psi_{n,m,l}(r,\theta,\varphi) = C_{l,n,m} \rho^l \exp\left[-\rho\right] L_{n-l-1}^{2l+1}(2\rho) Y_{m}^{l}(\theta,\varphi) \quad (1797)$$
Table 9: The Associated Laguerre Polynomials $L_n^k(z)$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$k = 0$</th>
<th>$k = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L_n^0(z)$</td>
<td>$L_n^1(z)$</td>
</tr>
<tr>
<td>$n = 0$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$n = 1$</td>
<td>$1 - z$</td>
<td>$2 - z$</td>
</tr>
<tr>
<td>$n = 2$</td>
<td>$\frac{1}{2}(2 - 4z + z^2)$</td>
<td>$\frac{1}{2}(6 - 6z + z^2)$</td>
</tr>
<tr>
<td>$n = 3$</td>
<td>$\frac{1}{6}(6 - 18z + 9z^2 - z^3)$</td>
<td>$\frac{1}{6}(24 - 36z + 12z^2 - z^3)$</td>
</tr>
<tr>
<td></td>
<td>$k = 2$</td>
<td>$k = 3$</td>
</tr>
<tr>
<td></td>
<td>$L_n^2(z)$</td>
<td>$L_n^3(z)$</td>
</tr>
<tr>
<td>$n = 0$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$n = 1$</td>
<td>$3 - z$</td>
<td>$4 - z$</td>
</tr>
<tr>
<td>$n = 2$</td>
<td>$\frac{1}{2}(12 - 8z + z^2)$</td>
<td>$\frac{1}{2}(20 - 10z + z^2)$</td>
</tr>
<tr>
<td>$n = 3$</td>
<td>$\frac{1}{6}(60 - 60z + 15z^2 - z^3)$</td>
<td>$\frac{1}{6}(120 - 90z + 18z^2 - z^3)$</td>
</tr>
</tbody>
</table>
where we have written
\[ \rho = \frac{Z r}{n a_0} \] (1798)

and \( a_0 \) is the Bohr radius. The normalization constant is given by
\[ |C_{l,n,m}|^2 = \left( \frac{2 Z}{n a_0} \right)^3 \frac{2^{2l} (n - l - 1)!}{2^n (n + l)!} \] (1799)

---

4.6.31 Exercise 98

Show that for the hydrogen atom, the average values of the moments of the radial distance of the electron from the proton satisfy the following relations,
\[ \frac{4}{\rho_0^3} \rho^s - (2s + 1) a_0 \rho^{s-1} + \frac{s}{4} \left( (2l + 1)^2 - s^2 \right) a_0^2 \rho^{s-2} = 0 \]
\[ s > - (2l + 1) \] (1800)

where \( a_0 \) is the Bohr radius.

Also show that
\[ \tau = a_0 \rho_0^2 \left[ 1 + \frac{1}{2} \left( 1 - 4 \frac{l(l + 1)}{\rho_0^2} \right) \right] \]
\[ \frac{1}{\rho^{s-1}} = \frac{4}{a_0 \rho_0^2} \] (1801)

---

4.6.32 Solution 98

We shall use the dimensionless variable \( \rho \) where
\[ \rho = \kappa r = \sqrt{\frac{-2 m E}{\hbar^2}} r \] (1802)

and write the Radial part of the wave function as \( R(\rho) = \frac{f(\rho)}{\rho} \). We also introduce a constant \( \rho_0 \) by
\[ -\frac{Z e^2}{E} \frac{1}{r} = \frac{\rho_0}{\rho} \] (1803)
Then, the radial part of the energy eigenvalue equation becomes
\[
\left[ \frac{\partial^2 f}{\partial \rho^2} + \left( - \frac{l(l+1)}{\rho^2} + \frac{\rho_0}{\rho} - 1 \right) f \right] = 0 \quad (1804)
\]
We shall multiply this equation by
\[
\rho^{s+1} \frac{\partial f}{\partial \rho} - C \rho^s f
\]
and integrate over \( \rho \). Then, as the average of the powers of \( \rho \) are given by
\[
\overline{\rho^s} = \int_0^\infty d\rho \rho^s f(\rho) \rho f(\rho)
\]
this will give us terms that are equal to the required expectation values.

The terms proportional to \( C \) are evaluated as
\[
C \left( \frac{l(l+1)}{\overline{\rho^{s-2}}} - \rho_0 \overline{\rho^{s-1}} + \overline{\rho^s} \right)
\]
\[
- C \int_0^\infty d\rho \rho^s f \frac{\partial^2 f}{\partial \rho^2}
\]
(1807)
The last term can be integrated by parts, and the boundary terms vanish for appropriately large \( l \). Then we obtain
\[
C \left( \frac{l(l+1)}{\overline{\rho^{s-2}}} - \rho_0 \overline{\rho^{s-1}} + \overline{\rho^s} \right)
\]
\[
+ C \int_0^\infty d\rho \rho^s f \left( \frac{\partial f}{\partial \rho} \right)^2 - C \frac{s(s-1)}{2} \overline{\rho^{s-2}}
\]
(1808)
The remaining terms are re-written as
\[
\int_0^\infty d\rho \rho^{s+1} \frac{\partial f}{\partial \rho} \left[ \frac{\partial^2 f}{\partial \rho^2} + \left( - \frac{l(l+1)}{\rho^2} + \frac{\rho_0}{\rho} - 1 \right) f \right]
\]
\[
= \frac{1}{2} \int_0^\infty d\rho \rho^{s+1} \left( - \frac{l(l+1)}{\rho^2} + \frac{\rho_0}{\rho} - 1 \right) \left( \frac{\partial f}{\partial \rho} \right)^2
\]
\[
+ \int_0^\infty d\rho \rho^{s+1} \left( \frac{\partial f}{\partial \rho} \right) \left( \frac{\partial^2 f}{\partial \rho^2} \right)
\]
(1809)
These terms are evaluated as
\[
\frac{1}{2} \left( l(l+1)(s-1) \overline{\rho^{s-2}} - s \rho_0 \overline{\rho^{s-1}} + (s+1) \overline{\rho^s} \right)
\]
\[
- \frac{(s+1)}{2} \int_0^\infty d\rho \rho^s \left( \frac{\partial f}{\partial \rho} \right)^2
\]
(1810)
The terms involving \( \left( \frac{\partial f}{\partial \rho} \right)^2 \) vanish if we choose the constant \( C \) as

\[
C = \frac{s + 1}{2}
\]  

(1811)

As the sum of the two terms are equal to zero, due to \( F \) satisfying the differential equation, one has the equation relating the expectation values of powers of \( \rho \)

\[
s \left( l ( l + 1 ) - \frac{1}{4} ( s^2 - 1 ) \right) \rho^{s-2} - \frac{2}{2} \frac{s + 1}{\rho_0} \rho^{s-1} + ( s + 1 ) \overline{\rho}^s = 0
\]

(1812)

On putting \( s = 0 \) and noting \( \rho^0 = 1 \) we have

\[
\overline{\rho}^{s-1} = \frac{2}{\rho_0}
\]  

(1813)

and then with \( s = 1 \) we have

\[
2 \overline{\rho} = \frac{3}{2} \rho_0 - \frac{1}{4} \left[ \left( 2 l + 1 \right)^2 - 1 \right] \overline{\rho}^{-1}
\]

\[
= \frac{3}{2} \rho_0 - \frac{1}{2} \left[ \left( 2 l + 1 \right)^2 - 1 \right] \rho_0^{-1}
\]  

(1814)

On converting back from dimensionless variables, we find the result given.

---

### 4.6.33 Exercise 99

Find the momentum space wave functions for the two lowest \( m = 0 \) energy eigenstates of the hydrogen atom, given by

\[
\Psi_{1,0,0}(\mathbf{r}) = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \exp \left[ - \frac{Z r}{a_0} \right]
\]  

(1815)

and

\[
\Psi_{2,1,0}(\mathbf{r}) = \sqrt{\frac{3}{4 \pi 4!}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( \frac{Z r}{a_0} \right) \exp \left[ - \frac{Z r}{2 a_0} \right] \cos \theta
\]  

(1816)
4.6.34 Solution 99

The momentum space wave function is given by the Fourier transform

\[ \Phi(p) = \left( \frac{1}{2 \pi \hbar} \right)^{\frac{3}{2}} \int d^3r \exp \left[ -i \frac{\vec{p} \cdot \vec{r}}{\hbar} \right] \Psi(r) \]  

(1817)

For the \((1,0,0)\) wave function, the angular integration can be easily performed leading to

\[ \Phi_{1,0,0}(p) = \left( \frac{Z \hbar}{2 \pi \hbar a_0} \right)^{\frac{3}{2}} 2 \sqrt{\pi} \hbar \]

\[ \times \int_0^\infty dr \ r^2 \left( \frac{\exp \left[ i \frac{\pi}{2} (1 - i \frac{Z \hbar}{p r}) \right] - \exp \left[ i \frac{\pi}{2} (1 + i \frac{Z \hbar}{p r}) \right]}{i p r} \right) \exp \left[ -\frac{Z r}{a_0} \right] \]

(1818)

The first factor in the integrand is recognized as being proportional to the \(l = 0\) spherical Bessel function. The integral is easily evaluated to yield

\[ \Phi_{1,0,0}(p) = \left( \frac{Z \hbar}{2 \pi a_0} \right)^{\frac{3}{2}} 2 \sqrt{\pi} \frac{i}{p} \left[ \left( \frac{1}{p + i \frac{Z \hbar}{a_0}} \right)^2 - \left( \frac{1}{p - i \frac{Z \hbar}{a_0}} \right)^2 \right] \]

\[ = \left( \frac{Z \hbar}{2 \pi a_0} \right)^{\frac{3}{2}} 8 \sqrt{\pi} \left[ \frac{Z \hbar}{a_0} \left( \frac{Z \hbar}{a_0}^2 \right) \right] \]

(1819)

The second momentum space wave function is found by using the Rayleigh expansion of the exponential plane wave. The Legendre polynomial is given in terms of the angle between the momentum and the position vector. The spherical harmonic addition theorem is used to expand the Legendre polynomials in terms of the products of the spherical harmonics, each separately involving the directions of the momentum and position. On integrating over the directions of the position vector and using orthonormality, one finds that the momentum space wave function depends upon the spherical harmonic with the same \((l,m)\) as the real space wave function, except that it depends on the direction of the momentum, \((\theta_p, \phi_p)\), with respect to the Cartesian axes. The coefficient of the spherical harmonic \(Y_{lm}(\theta_p, \phi_p)\) is given by an integration involving the product of the spherical Bessel function \(j_l(kr)\) and the radial dependence of the real space wave function. The result entails evaluating integrals of the form

\[ \int_0^\infty dz \ z^{(2+m)} \exp \left[ -\alpha z \right] j_l(z) \]

(1820)

which for \(l = 2\) simplifies to

\[ \int_0^\infty dz \ z^{(2+m)} \exp \left[ -\alpha z \right] \left( \frac{\sin z - z \cos z}{z^2} \right) \]
Table 10: The Gegenbauer Functions $C_\mu^\nu(x)$.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$\mu = 1$</th>
<th>$\mu = 2$</th>
<th>$\mu = 3$</th>
<th>$\mu = 4$</th>
<th>$\mu = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu = 0$</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu = 1$</td>
<td>$2x$</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu = 2$</td>
<td>$4x^2 - 1$</td>
<td>$4x$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu = 3$</td>
<td>$8x^3 - 4x$</td>
<td>$12x^2 - 2$</td>
<td>$6x$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu = 4$</td>
<td>$16x^4 - 12x^2 + 1$</td>
<td>$32x^3 - 12x$</td>
<td>$24x^2 - 3$</td>
<td>$8x$</td>
<td>1</td>
</tr>
<tr>
<td>$\nu = 5$</td>
<td>$32x^5 - 32x^2 + 6x$</td>
<td>$80x^4 - 48x^2 + 3$</td>
<td>$80x^3 - 24x$</td>
<td>$40x^2 - 4$</td>
<td>$10x$</td>
</tr>
</tbody>
</table>

$$
= (-1)^m \frac{\partial^n}{\partial \alpha^m} \int_0^\infty dz \exp \left[ -\alpha z \right] \left( \sin z - z \cos z \right)
= (-1)^m \frac{\partial^n}{\partial \alpha^m} \left[ \frac{2}{(1 + \alpha^2)^2} \right]
$$  \hspace{1cm} (1821)

The momentum space wave function of a general energy eigenstate of a Hydrogen-like atom has been calculated by Podolsky and Pauling\textsuperscript{31}. The momentum eigenfunctions $\Phi_{n,l,m}(p, \theta, \varphi)$ are found to be given by the general expression

$$
\Phi_{n,l,m}(p, \theta, \varphi) = Y_l^m(\theta, \varphi) \left( \frac{n a_0}{Z \pi \hbar} \right)^{\frac{3}{2}} \left[ - (-i)^l \pi 2^{l+4} l! \left( \frac{n(n-l-1)!}{(n+l)!} \right)^{\frac{1}{2}} \right]
\times \frac{\xi^l}{(\xi^2 + 1)^{l+2}} C_{n-l-1}^{l+1} \left( \frac{\xi^2 - 1}{\xi^2 + 1} \right)
$$  \hspace{1cm} (1822)

where

$$
\xi = \frac{n p a_0}{Z \hbar}
$$  \hspace{1cm} (1823)

and $C_\mu^\nu(x)$ are the Gegenbauer functions. Some of the Gegenbauer functions are given in Table(10), and the others can be generated from the recursion relation

$$
C_\mu^\nu(x) = \frac{2 \mu}{\nu} \left[ x C_\nu^{\mu+1}(x) - C_\nu^{\mu+1}(x) \right]
$$  \hspace{1cm} (1824)

The momentum space distribution of the electrons in Hydrogen was determined experimentally\textsuperscript{32}. The experiments involved the ionization of atomic hydrogen by a beam of high-energy electrons.

Figure 101: The spherically averaged momentum-space distribution function for the few lowest energy eigenstates of Hydrogen.

4.6.35 Exercise 100
Find the scalar potential and vector potential produced by an electron in a \( l = 1 \) state of a hydrogen atom by first calculating the charge and current densities and then by using Maxwell’s equations.

4.6.36 Solution 100
The hydrogen atom in a \( 2p \) orbital has a charge distribution

\[
\rho(r, t) = |\Psi(r, t)|^2 = \frac{e e_{0}^2}{64 \pi a_0^5} r^2 \exp \left[ -\frac{r}{a_0} \right] \sin^2 \theta
\]  

(1825)

where \( a_0 \) is the Bohr radius \( \frac{\hbar^2}{m e^2} \). In this case, the charge density is independent of time. The electrostatic potential \( \phi(r) \) is given by

\[
\phi(r) = \frac{1}{4 \pi} \int d^3r' \frac{\rho(r')}{|r - r'|}
\]  

(1826)
We shall first perform the angular integral. The denominator is expanded in terms of the Legendre Polynomials via the expansion
\[
\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r_>} \sum_l \left(\frac{r_<}{r_>}\right)^l P_l(\cos \gamma) \quad (1827)
\]
where \(\gamma\) is the angle between \(\mathbf{r}\) and \(\mathbf{r}'\). Then using the addition theorem one has
\[
\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r_>} \sum_l \left(\frac{r_<}{r_>}\right)^l \frac{4 \pi}{2l + 1} \sum_{m=-l}^{m=l} Y^*_m(\theta', \varphi') Y^l_m(\theta, \varphi) \quad (1828)
\]

The angular dependence of the numerator can be expressed in terms of the spherical harmonics
\[
\sin^2 \theta' = (1 - \cos^2 \theta') = 2 \sqrt{\frac{4 \pi}{5}} \frac{2}{3} Y^0_m(\theta', \varphi') - \sqrt{\frac{4 \pi}{5}} \frac{2}{3} Y^2_m(\theta', \varphi') \quad (1829)
\]

The angular integration can be performed using the orthogonality of the spherical harmonics. Hence,
\[
\phi(r) = \left(\frac{e}{64 \pi a_0^5}\right) \int_0^\infty dr' r'^4 \frac{1}{r_>} \exp \left[-\frac{r'}{a_0}\right] \times \sum_l \left(\frac{r_<}{r_>}\right)^l \frac{1}{2l + 1} Y^l_m(\theta, \varphi) \left(\frac{2}{3} \sqrt{\frac{4 \pi}{5}} \delta_{l,0} - \sqrt{\frac{4 \pi}{5}} \frac{2}{3} \delta_{l,2}\right) = \frac{2}{3} \left(\frac{e}{64 \pi a_0^5}\right) \left[I_0 - \frac{1}{5} I_2 \left(3 \cos^2 \theta - 1\right)\right] \quad (1830)
\]

where
\[
I_0 = \int_0^\infty dr' r'^4 \left(\frac{1}{r_>}\right) \exp \left[-\frac{r'}{a_0}\right] \quad (1831)
\]
and
\[
I_2 = \int_0^\infty dr' r'^4 \left(\frac{r'^2}{r_>}\right) \exp \left[-\frac{r'}{a_0}\right] \quad (1832)
\]

The radial integrations are broken into two parts, one for \(r > r'\) and the other for \(r < r'\). One finds
\[
I_0 = \frac{a_0^5}{r} \left[24 - \left(24 + 24 \left(\frac{r}{a_0}\right) + 12 \left(\frac{r}{a_0}\right)^2 + 4 \left(\frac{r}{a_0}\right)^3 + \left(\frac{r}{a_0}\right)^4\right) \exp \left[-\frac{r}{a_0}\right] + \left(6 \left(\frac{r}{a_0}\right) + 6 \left(\frac{r}{a_0}\right)^2 + 3 \left(\frac{r}{a_0}\right)^3 + \left(\frac{r}{a_0}\right)^4\right) \exp \left[-\frac{r}{a_0}\right]\right] \quad (1833)
\]
and

\[
I_2 = \frac{a_0^7}{r^3} \left[ 6! - 6! \left( \frac{r}{a_0} \right) + \frac{6!}{2} \left( \frac{r}{a_0} \right)^2 + \\
+ 5! \left( \frac{r}{a_0} \right)^3 + 30 \left( \frac{r}{a_0} \right)^4 + 6 \left( \frac{r}{a_0} \right)^5 + \left( \frac{r}{a_0} \right)^6 \right] \exp \left[ - \frac{r}{a_0} \right]
\]

(1834)

Hence, for \( r \gg a_0 \) where all the exponential terms are suppressed, one finds that the electrostatic potential reduces to

\[
\phi(r) = \frac{e}{4 \pi} \left( \frac{1}{r} - \frac{a_0^2}{r^3} \frac{3 \cos^2 \theta - 1}{2} \right)
\]

(1835)

which is interpreted as the sum of a charge monopole and a quadrupole term. The deviation of the electron wave function from spherical symmetry has set up a quadrupolar electric field. When \( r < a_0 \), the potential is reduced from that of the monopole of charge \( e \), since a Gaussian surface enclosing the origin only contains a fraction of the total electron charge.

To find the vector potential, first we find the current density \( j \). The current density is found from the expression

\[
j(r, t) = \frac{e \hbar}{2 m i} \left( \Psi^*(r, t) \nabla \Psi(r, t) - \Psi(r, t) \nabla \Psi^*(r, t) \right)
\]

(1836)

In spherical polar coordinates, the gradient is written as

\[
\nabla = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi}
\]

(1837)

Therefore, the current density of the \( p \) electron is evaluated as

\[
j(r, t) = \hat{e}_\varphi \left( \frac{e \hbar}{64 \pi m a_0^3} \right) \exp \left[ - \frac{r}{a_0} \right] r \sin \theta \]

(1838)

The current density is resolved into Cartesian components, via

\[
\hat{e}_{\varphi'} = \cos \varphi' \hat{e}_y - \sin \varphi' \hat{e}_x
\]

(1839)

and is then expressed in terms of spherical harmonics. The result is

\[
j(r, t) = i \left( \frac{e \hbar}{64 \pi m a_0^3} \right) \exp \left[ - \frac{r}{a_0} \right] r \times \\
\times \sqrt{\frac{8 \pi}{3}} \left[ Y_1^1(\theta, \varphi) \hat{e}_x - \frac{i}{2} \hat{e}_y - Y_0^1(\theta, \varphi) \hat{e}_x + \frac{i}{2} \hat{e}_y \right]
\]

(1840)
which is time independent. The vector potential is given by

\[ A(r) = \frac{1}{4\pi} \int d^3r' \frac{j(r')}{|r - r'|} \]  

(1841)

Then the Legendre polynomial generating function expansion and the spherical harmonic addition theorem are used to perform the angular integral over the variables \((\theta', \phi')\). The integrations utilize the orthonormality of the spherical harmonics. The end result of the integrations over the angles \((\theta', \phi')\) is

\[ A(r) = \left( \frac{e\hbar}{64\pi ma_0^5} \right) \int_0^\infty dr' r'^3 \left( \frac{r_c}{r'^2} \right) \exp \left[ -\frac{r'}{a_0} \right] \times \]

\[ \times \sqrt{\frac{8\pi}{3}} \frac{1}{3} \left[ Y_{11}^1(\theta, \phi) \hat{e}_x - i \hat{e}_y - Y_{-1}^1(\theta, \phi) \frac{\hat{e}_x + i \hat{e}_y}{2} \right] \]

\[ = \hat{e}_\varphi \frac{1}{3} \left( \frac{e\hbar}{64\pi ma_0^5} \right) \int_0^\infty dr' r'^3 \left( \frac{r_c}{r'^2} \right) \exp \left[ -\frac{r'}{a_0} \right] \sin \theta \]

(1842)

The vector potential has a directional dependence which is similar to the current density. The radial integration can be performed, leading to the vector potential being dominated by a dipole contribution at large distances.
4.7 A Charged Particle in a Magnetic Field

Consider a particle of mass $m$ and charge $q$ moving in a uniform magnetic field $\mathbf{B}$ oriented along the $z$ axis.

$$\mathbf{B} = \hat{e}_z B_z$$

(1843)

The vector potential $\mathbf{A}(\mathbf{r})$ can be found as a solution of

$$\mathbf{B} = \nabla \wedge \mathbf{A}(\mathbf{r})$$

(1844)

One solution is given by

$$\mathbf{A}(\mathbf{r}) = -y B_z \hat{e}_x$$

(1845)

which corresponds to a particular choice of the gauge. The Hamiltonian of the charged particle in the field can be written as

$$\hat{H} = \frac{1}{2m} \left( \hat{p}_x - \frac{q}{c} A_x(\mathbf{r}) \right)^2 + \frac{1}{2m} \left( \hat{p}_y^2 + \hat{p}_z^2 \right)$$

$$\quad = \frac{1}{2m} \left( \hat{p}_x + \frac{q}{c} y B_z \right)^2 + \frac{1}{2m} \left( \hat{p}_y^2 + \hat{p}_z^2 \right)$$

(1846)

We note that the $x$ and $z$ components of the momentum commute with the Hamiltonian, as $x$ and $z$ do not appear in $\hat{H}$. Thus,

$$[ \hat{H} , \hat{p}_x ] = 0$$

$$[ \hat{H} , \hat{p}_y ] = 0$$

(1847)

which means that they are constants of motion. As the energy eigenstates are also eigenstates of $\hat{p}_x$ and $\hat{p}_z$, we shall write the energy eigenfunction as

$$\phi_{n,p_x,p_z}(\mathbf{r}) = \frac{1}{2\pi\hbar} \exp \left[ i \frac{p_x x + p_z z}{\hbar} \right] \phi_n(y)$$

(1848)

The energy eigenvalue equation can then be written in terms of the unknown function $\phi_n(y)$, as

$$\left[ \frac{\hat{p}_y^2}{2m} + \frac{m}{2} \left( \frac{q B_z}{mc} \right)^2 \left( y + \frac{e p_x}{q B_z} \right)^2 \right] \phi_n(y) = \left( E - \frac{p_z^2}{2m} \right) \phi_n(y)$$

(1849)

This equation looks like the energy eigenvalue equation for the one-dimensional harmonic oscillator, in which we have shifted the origin of the $y$ coordinate through a distance $\frac{e p_x}{q B_z}$. The frequency of the oscillator corresponds to the Larmor precession frequency $\omega_L$, which is given by

$$\omega_L^2 = \left( \frac{q B_z}{mc} \right)^2$$

(1850)

Using our previously gained knowledge of the one-dimensional harmonic oscillator, we find that the energy eigenvalues are then given by

$$E_{n,p_x} = \hbar \omega_L \left( n + \frac{1}{2} \right) + \frac{p_x^2}{2m}$$

(1851)
We note that these energy levels (known as Landau levels) are degenerate, as the introduction of the $B$ field causes states with different values of the (quasi-continuous quantum numbers) $p_x$ and $p_y$ to collapse onto states where the value of the energy is determined by the integer $n$. The wave functions with the different values of $p_x$ have the “oscillations” in the $y$ coordinate centered around different points.

### 4.7.1 Exercise 101

Show that both $x_0$ and $y_0$ commute with the Hamiltonian, where

\[
\begin{align*}
\hat{x}_0 &= \hat{x} + \frac{c \hat{p}_y}{q B_z} \\
\hat{y}_0 &= -\frac{c \hat{p}_x}{q B_z}
\end{align*}
\]

(1852)

but $x_0$ and $y_0$ do not commute,

\[
[\hat{x}_0, \hat{y}_0] \neq 0
\]

(1853)

Show that in the classical limit, these variables correspond to the projection of the particle’s orbit on the $x$-$y$ plane. Hence, $x_0$ and $y_0$ cannot be simultaneously known for the quantum system.

### 4.7.2 Exercise 102

Consider a particle of mass $m$ and charge $e$ in perpendicular uniform electric and magnetic fields, $\vec{E}$ and $\vec{B}$. Find the eigenfunctions and eigenvalues. Find the average velocity in the $x$ direction for any eigenstate.

### 4.7.3 Solution 102

Let the vector potential be written in the gauge

\[
A(r) = B z \hat{e}_x
\]

(1854)

and the scalar potential is also a function of $z$

\[
\phi(z) = -| \vec{E} | z
\]

(1855)

---

The Hamiltonian is given by

\[ \hat{H} = \frac{1}{2m} \left[ \left( \hat{p}_x - \frac{e}{c} B z \right)^2 + \hat{p}_y^2 + \hat{p}_z^2 \right] - e | E | z \]  

(1856)

which only depends on \( z \). The momentum components \( \hat{p}_x \) and \( \hat{p}_y \) are good quantum numbers. The eigenfunctions can be written as

\[ \Phi_{k_x,k_y,n}(r) = \exp \left[ i \left( k_x x + k_y y \right) \right] \phi_n(z) \]  

(1857)

and \( \phi_n(z) \) satisfies

\[ \left( E - \frac{\hbar^2 k_y^2}{2m} \right) \phi_n(z) = \left( \frac{1}{2m} \left[ \left( \hbar k_x - \frac{e}{c} B z \right)^2 + \hat{p}_y^2 + \hat{p}_z^2 \right] - e | E | z \right) \phi_n(z) \]  

(1858)

This is recognized as the eigenvalue equation for a linear harmonic oscillator centered on \( z_0 \)

\[ z_0 = \hbar k_x \frac{c}{e B} + m c^2 \frac{| E |}{e B^2} \]  

(1859)

Thus, the energy eigenvalue is given by

\[ E = \hbar \omega_c \left( n + \frac{1}{2} \right) + \frac{\hbar^2 k_y^2}{2m} - m c^2 \frac{| E |^2}{2 B^2} - \hbar k_x c \frac{| E |}{B} \]  

(1860)

The group velocity is given by

\[ v_x = \frac{\partial E}{\partial p_x} = -c \frac{| E |}{B} \]  

(1861)

### 4.7.4 The Degeneracy of the Landau Levels

We shall consider a particle in a uniform magnetic field aligned along the \( z \) direction. The particle is confined to move within a large volume. Let the volume be bounded by surfaces, so that the accessible volume is described by

\[ L_x > x > 0 \]
\[ L_y > y > 0 \]
\[ L_z > z > 0 \]  

(1862)

and the wave function should be zero outside this volume. Instead of applying these boundary conditions, we shall impose Born-von Karman or periodic
boundary conditions.

The vector potential \( A(r) \) is defined to be the solution of

\[
\mathbf{B} = \nabla \wedge A(r)
\]  

(1863)

One solution is given by

\[
A(r) = -y B_z \hat{e}_x
\]  

(1864)

which corresponds to a particular choice of the gauge. The Hamiltonian of the charged particle in the field can be written as

\[
\hat{H} = \frac{1}{2m} \left( \hat{p}_x - \frac{q}{c} A_x(r) \right)^2 + \frac{1}{2m} \left( \hat{p}_y^2 + \hat{p}_z^2 \right)
\]

\[
= \frac{1}{2m} \left( \hat{p}_x + \frac{q}{c} y B_z \right)^2 + \frac{1}{2m} \left( \hat{p}_y^2 + \hat{p}_z^2 \right)
\]

(1865)

in the region where the confining potential is zero.

The wave function that satisfies the boundary conditions, can be written as

\[
\Psi(r) = \frac{1}{\sqrt{L_x L_z}} \exp \left[ i \frac{2 \pi n_x}{L_x} \right] \exp \left[ i \frac{2 \pi n_z}{L_z} \right] f(y)
\]  

(1866)

where \( n_x \) and \( n_z \) are integers, \( n_x = 0, \pm 1, \pm 2, \ldots \) etc. It is then found that the function \( f(y) \) satisfies the eigenvalue equation

\[
\left[ \frac{1}{2m} \left( \frac{2 \pi \hbar n_x}{L_x} + \frac{q}{c} y B_z \right)^2 - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \right] f(y) = \left( E - \frac{2 \pi^2 \hbar^2 n_x^2}{m L_x^2} \right) f(y)
\]

(1867)

or

\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{q^2 B_z^2}{2mc^2} \left( \frac{2 \pi \hbar c n_x}{q B_z L_x} + y \right)^2 \right] f(y) = \left( E - \frac{2 \pi^2 \hbar^2 n_x^2}{m L_x^2} \right) f(y)
\]

(1868)

which can be re-written in the form of a displaced harmonic oscillator equation, by writing

\[
\omega_c = \frac{q B_z}{mc}
\]  

(1869)

Then, the eigenvalue equation becomes

\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{m \omega_c^2}{2} \left( y + \frac{n_x L_y \Phi_0}{\Phi} \right)^2 \right] f(y) = \left( E - \frac{2 \pi^2 \hbar^2 n_x^2}{m L_x^2} \right) f(y)
\]

(1870)

where we have introduced the flux \( \Phi \), defined by

\[
\Phi = L_x L_y B_z
\]  

(1871)
and the fundamental flux quantum $\Phi_0$ defined by

$$ \Phi_0 = \frac{2\pi \hbar c}{q} \quad (1872) $$

Therefore, the eigenvalue $E$ is just given by

$$ E = \hbar \omega_c \left( n + \frac{1}{2} \right) \quad (1873) $$

and the eigenfunctions $f(y)$ are the harmonic oscillator wave functions, $\phi_n(y)$ shifted through $-n_x \frac{\Phi_0}{\Phi} L_y$. That is, the normalized wave function is given by

$$ f(y) = \phi_n \left( y + n_x L_y \frac{\Phi_0}{\Phi} \right) \quad (1874) $$

The degeneracy can be found, in the semi-classical approximation, by assuming that the deviation of the position of the harmonic oscillator from the equilibrium value $y_0 = -n_x L_y \frac{\Phi_0}{\Phi}$ is minimal. Under these circumstances, one has $0 < y_0 < L_y$. Hence, $n_x$ is restricted to be such that

$$ L_y > -n_x L_y \frac{\Phi_0}{\Phi} > 0 \quad (1875) $$

Hence, the degeneracy is the given by the maximum number of values that $n_x$ can take. The degeneracy $N$ is given by

$$ N = \left( \frac{\Phi}{\Phi_0} \right) \quad (1876) $$

which is controlled by the number of flux quanta, threading through the area $L_x L_y$.

---

**4.7.5 Exercise 103**

Find the energy eigenvalues and eigenfunctions of a particle of charge $q$ and mass $m$ moving in two dimensions, in the presence of a uniform magnetic field. Calculate the degeneracy of the lowest Landau level. Use the symmetric gauge where

$$ A = \frac{\Phi}{2\pi R_0^2} \hat{r} \hat{\varphi} \quad (1877) $$

and $\Phi$ is the total flux enclosed in the circular area $\pi R_0^2$. 

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The energy eigenvalue equation is

\[
- \frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi}{\partial r} \right) + \frac{1}{2m} \left( -i \frac{\hbar}{r} \frac{\partial}{\partial \varphi} - \frac{q}{c} \frac{\Phi}{2 \pi R_0^2} r \right)^2 \phi = E \phi
\]

The z component of the angular momentum \( \hat{L}_z \) commutes with the Hamiltonian, and so one can find simultaneous eigenfunctions which are of the form

\[
\phi(r, \varphi) = \frac{1}{\sqrt{2\pi}} \exp \left[ i \mu \varphi \right] R(r)
\]

Hence, the radial wave function \( R(r) \) is given by

\[
- \frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial R}{\partial r} \right) + \frac{1}{2m} \left( \frac{\hbar \mu}{r} - \frac{q}{c} \frac{\Phi}{2 \pi R_0^2} r \right)^2 R = ER
\]

The radial wave function must satisfy boundary conditions at \( r = 0 \) and \( r \to \infty \). The physically acceptable form of the solution is

\[
R(r) = \rho^{\frac{\varphi}{2}} \exp \left[ - \rho \right] f(\rho)
\]

where

\[
\rho = \frac{q \Phi}{c \ 4 \pi \hbar R_0^2} r^2
\]

and \( f(\rho) \) is a finite order polynomial. The derivatives w.r.t. \( r \) can be expressed as derivatives with respect to \( \rho \) via

\[
\frac{\partial}{\partial r} = \frac{\partial \rho}{\partial r} \frac{\partial}{\partial \rho} = \frac{q \Phi}{c \ 2 \pi \hbar R_0^2} r \frac{\partial}{\partial \rho}
\]

and

\[
\frac{\partial^2}{\partial r^2} = \left( \frac{q \Phi}{c \ 2 \pi \hbar R_0^2} \right) \frac{\partial}{\partial \rho} + \left( \frac{q \Phi}{c \ 2 \pi \hbar R_0^2} \right)^2 r^2 \frac{\partial^2}{\partial \rho^2}
\]

Thus, the eigenvalue equation becomes

\[
-\rho \frac{\partial^2 R}{\partial \rho^2} - \frac{\partial R}{\partial \rho} + \frac{1}{\rho} \left( \frac{\mu}{2} - \rho \right)^2 R = ER
\]

On substituting the form

\[
R(r) = \rho^{\frac{\varphi}{2}} \exp \left[ - \rho \right] f(\rho)
\]
into the differential equation, we find

\[
\left( \frac{\hbar \gamma \Phi}{mc^2 \pi R_0^2} \right) \left[ -\rho \frac{\partial^2}{\partial \rho^2} + (2 \rho - \mu - 1) \frac{\partial f}{\partial \rho} + \left( 1 - \frac{E mc^2 \pi R_0^2}{\hbar \gamma \Phi} \right) f \right] = 0
\]

(1887)

This differential equation can be solved by the Fröbenius method, by expanding the solution in the form

\[
f(\rho) = \sum_{n=0}^{n_r} a_n \rho^n
\]

(1888)

On substituting the series into the differential equation, one finds the recursion relation

\[
a_{n+1} (n + 1) (n + \mu + 1) = \left( 2n + 1 - \frac{E mc^2 \pi R_0^2}{\hbar \gamma \Phi} \right) a_n
\]

(1889)

The series for the polynomial \( f(\rho) \) truncates if the energy is given by

\[
E = \left( \frac{\hbar \gamma \Phi}{mc^2 \pi R_0^2} \right) (2n_r + 1)
\]

(1890)

where \( n_r \) is an integer. In this case the boundary conditions are satisfied, and \( f(\rho) \) is a polynomial of degree \( n_r \).

The lowest energy eigenstates corresponds to \( n_r = 0 \) and the eigenfunction can be written as

\[
\phi(r, \varphi) \propto r^\mu \exp \left[ i \mu \varphi \right] \exp \left[ -\frac{q \Phi}{c^4 \pi \hbar R_0^2} r^2 \right]
\]

\[
\propto (x + iy)^\mu \exp \left[ -\frac{q \Phi}{c^4 \pi \hbar R_0^2} \left( x^2 + y^2 \right) \right]
\]

\[
\propto (x + iy)^\mu \exp \left[ -\left( \frac{\Phi}{\Phi_0} \right) \left( \frac{x^2 + y^2}{2 R_0^2} \right) \right]
\]

(1891)

The probability density is peaked on a circle around the origin. The radius of the circle, \( r_m \), is given by

\[
r_m^2 = \mu \frac{c^2 \pi \hbar R_0^2}{q \Phi}
\]

\[
= \mu \left( \frac{\Phi_0}{\Phi} \right) R_0^2
\]

(1892)

All the states with different \( \mu \) are degenerate. The degeneracy is given by the maximum number of different allowed \( \mu \) values. For a disk of area \( \pi R_0^2 \) the allowed values of \( r_\mu \) satisfy \( r_\mu < R_0 \), thus, the degeneracy is given by

\[
\mu_{\text{max}} = \left( \frac{\Phi}{\Phi_0} \right)
\]

(1893)

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4.7.7 The Aharonov-Bohm Effect

The Aharonov-Bohm effect\textsuperscript{34} provides a conclusive demonstration that a charged quantum mechanical particle is sensitive to the vector potential, and not to the magnetic induction field $\vec{B}$. In the Aharonov-Bohm effect, a charged particle moves in a region of space where the magnetic field is zero. The magnetic field free region is multiply connected, as a magnetic field threads through regions where the particle is excluded from\textsuperscript{35}.

In order to provide a simple example of the Aharonov-Bohm effect, consider a charged particle which is confined to move on ring of radius $R$. A magnetic flux of strength $\Phi$ threads through the center of the ring and is contained within a cylinder of radius $a$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{aharonov-bohm-effect.png}
\caption{In the version of the Aharonov-Bohm effect being considered, the applied magnetic flux $\Phi$ is confined within a cylinder of radius $a$. The charged particle is confined to move on a ring of radius $R$ which encircles the cylinder.}
\end{figure}

The magnetic induction is in the $z$ direction, so $\vec{B} = \hat{e}_z B_z$. The magnetic flux through the center of the ring is given by
\[
\Phi = \int dx \, dy \, B_z
\]

\textsuperscript{34}Y. Aharonov and D. Bohm, Phys. Rev. 115, 485 (1959).
\[ = \int d^2 S \cdot B \]  
(1894)

in which the integral runs over the area inside the ring, where \( B \) is finite. Since the magnetic field is related to the vector potential via

\[ B = \nabla \wedge A \]  
(1895)

then the flux is given by

\[ \Phi = \int d^2 S \cdot \left( \nabla \wedge A \right) \]  
(1896)

On using Stoke’s theorem, one finds the total flux is given by

\[ \Phi = \oint dr \cdot A \]  
(1897)

where the integral is around the perimeter of a ring of radius \( r \) and \( r > a \). If the tangential component of the vector potential is denoted by \( A_\varphi \), then the loop integral is given by

\[ \Phi = 2 \pi r A_\varphi \]  
(1898)

Hence, on considering the symmetry of the problem, one finds the vector potential is given by

\[ A = \frac{\Phi}{2 \pi r} \hat{e}_\varphi \]  
(1899)

There is no magnetic field present at this radius, since the definition

\[ B = \nabla \wedge A \]  
(1900)

yields the \( z \)-component as

\[
B_z = ( \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\varphi \frac{1}{r} \frac{\partial}{\partial \varphi} ) \wedge \frac{\Phi}{2 \pi r} \hat{e}_\varphi \\
= \hat{e}_r \wedge \hat{e}_\varphi \left( \frac{\Phi}{2 \pi r} \right) + \hat{e}_\varphi \frac{1}{r} \wedge \hat{e}_\varphi \frac{\Phi}{2 \pi r} \\
= \hat{e}_r \wedge \hat{e}_\varphi \left( \frac{\Phi}{2 \pi r} \right) - \frac{1}{r} \hat{e}_\varphi \wedge \hat{e}_r \frac{\Phi}{2 \pi r} \\
= 0
\]  
(1901)

The magnetic induction is zero since the total flux \( \Phi \) contained within a loop is constant, if \( r \geq a \). The vector potential in the region where the magnetic field is finite \( 0 < r < a \) is given by

\[ A = \frac{r \Phi}{2 \pi a^2} \hat{e}_\varphi \]  
(1902)

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The energy eigenvalue equation for the particle confined on the ring of radius $R$ is

$$\frac{1}{2m} \left( -i \frac{\hbar}{R} \frac{\partial}{\partial \varphi} - \frac{q}{c} \frac{\Phi}{2 \pi R} \right)^2 \Psi(\varphi) = E \Psi(\varphi) \quad (1903)$$

This has normalized eigenfunctions given by

$$\Psi(\varphi) = \frac{1}{\sqrt{2 \pi R}} \exp \left[ i \mu \varphi \right] \quad (1904)$$

where the energy eigenvalue $E$ is determined by $\mu$ from

$$\frac{1}{2 m R^2} \left( \mu \hbar - \frac{q \Phi}{2 \pi c} \right)^2 = E \quad (1905)$$

Thus, the energy is given by

$$\frac{\hbar^2}{2 m R^2} \left( \mu - \frac{q \Phi}{2 \pi \hbar c} \right)^2 = E \quad (1906)$$

where $\frac{2 \pi \hbar}{q} = \Phi_0$ is the fundamental flux quantum. The modulus of the wave function must be single valued, therefore

$$\Psi(\varphi) = \Psi(\varphi + 2\pi) \quad (1907)$$

or

$$1 = \exp \left[ i \mu 2 \pi \right] \quad (1908)$$

Hence, $\mu$ must be an integer, $m = 0, \pm 1, \pm 2 \ldots$ etc. The energy is given by

$$E = \frac{\hbar^2}{2 m R^2} \left( m - \frac{\Phi}{\Phi_0} \right)^2 \quad (1909)$$

and the ground state energy and wave function is determined by the integer value of $m$ which minimizes $E$ and, therefore, depends on the ratio of $\left( \frac{\Phi}{\Phi_0} \right)$.

The ground state corresponds to the value of $m$ such that

$$\frac{m - 1}{2} < \left( \frac{\Phi}{\Phi_0} \right) < \frac{m + 1}{2} \quad (1910)$$

Thus, the energy depends on the vector potential but not on the magnetic field $B$ in the region where the particle moves. Furthermore, the ground state energy is a periodic function of $\Phi$ with periodicity $\Phi_0$, as the value $m$ changes discontinuously from $m$ to $m + 1$ as $\Phi$ increases by an amount $\Phi_0$.

The current $I$ produced by the charged particle flowing around the ring is defined classically as

$$I = c \frac{\partial E}{\partial \Phi} \quad (1911)$$
Figure 103: The energy eigenvalues $E_m$ in the Aharonov-Bohm effect, as a function of the applied magnetic flux $\Phi$ threading the ring.

The quantum mechanical current operator is defined as

$$\hat{I} = e \frac{\partial \hat{H}}{\partial \Phi} = \frac{q \hbar}{2 \pi m R^2} \left( i \frac{\partial}{\partial \varphi} + \frac{\Phi}{\Phi_0} \right) \quad (1912)$$

Thus, in the ground state the current has an expectation value $\overline{T}$, given by

$$\overline{T} = -\frac{q \hbar}{2 \pi m R^2} \left( m - \frac{\Phi}{\Phi_0} \right) \quad (1913)$$

The current jumps discontinuously as the flux through the loop is increased by $\Phi_0$.

Example

Find the energy eigenvalues and eigenfunctions of a particle of charge $q$ and mass $m$ moving in two dimensions, in the presence of a uniform magnetic field.
Figure 104: The dependence of the current $I$ in the ground state on the applied flux $\Phi$.

Use the circularly symmetric gauge where

$$A = \frac{\Phi}{2\pi r} \hat{e}_\phi$$

(1914)

where $\Phi$ is the magnetic flux penetrating a ring of radius $R_0 \ll r$.

---

**Solution**

The energy eigenvalue equation is

$$\left[ -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial\phi}{\partial r} \right) + \frac{1}{2m} \left( -i \frac{\hbar}{r} \frac{\partial}{\partial \varphi} - \frac{q}{c} \frac{\Phi}{2\pi r} \right)^2 \phi \right] = E \phi$$

(1915)

The $z$ component of the angular momentum $\hat{L}_z$ commutes with the Hamiltonian, and so one can find simultaneous eigenfunctions which are of the form

$$\phi(r, \varphi) = \frac{1}{\sqrt{2\pi}} \exp \left[ i \mu \varphi \right] R(r)$$

(1916)

Hence, the radial wave function $R(r)$ is given by

$$\left[ -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial R}{\partial r} \right) + \frac{1}{2m r^2} \left( \hbar \mu - \frac{q}{c} \frac{\Phi}{2\pi} \right)^2 \frac{1}{R} \right] = E \frac{1}{R}$$

(1917)
The radial wave function must satisfy boundary conditions at \( r = 0 \) and \( r \to \infty \). The acceptable form for the solution at \( r = R_0 \to 0 \) vanishes at the origin as

\[
R(r) = r^\alpha
\]  

(1918)

which minimizes the effect of the centrifugal potential. On introducing a dimensionless variable

\[
\rho = k r
\]

(1919)

where

\[
E = \frac{\hbar^2 k^2}{2 m}
\]

(1920)

and the elemental flux quantum \( \Phi_0 \), defined by

\[
\Phi_0 = \frac{c}{q}
\]

(1921)

one finds that the equation can be put in the dimensionless form

\[
\frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial R}{\partial \rho} \right) + \left[ 1 - \frac{1}{\rho^2} \left( \mu - \frac{\Phi}{\Phi_0} \right)^2 \right] R = 0
\]

(1922)

This is Bessel’s equation. The physically acceptable solution is finite in the limit as \( r \to 0 \) and, therefore, the required solution is proportional to the Bessel function of order \( \nu \) where

\[
\nu = \mu - \left( \frac{\Phi}{\Phi_0} \right)
\]

(1923)

The eigenfunction is given by

\[
\phi(r, \varphi) = \frac{1}{\sqrt{2\pi}} \exp \left[ i \mu \varphi \right] J_\nu(kr)
\]

(1924)

The Bessel function has the asymptotic variation

\[
J_\nu(\rho) \sim \rho^\nu
\]

(1925)

as \( \rho \to 0 \) and varies as

\[
J_\nu(\rho) \sim \sqrt{\frac{2}{\pi \rho}} \cos \left( \rho - \left( \nu + \frac{1}{2} \right) \frac{\pi}{2} \right)
\]

(1926)

when \( \rho \to \infty \). Note that, if the flux quantum threading the origin is changed so that \( \nu \) increases, the maxima of the probability density moves radially outward, however, there is no change in energy. The absence of any energy change is not surprising in view of the fact that \( B = 0 \) in the region where the particle is moving and so, the effect of the vector potential can be absorbed into the phase of the wave function by a Gauge transformation.
4.8 The Pauli Spin Matrices

The Pauli Matrices are three two by two matrices, which have commutation relations similar to the commutation relations of the three components of the angular momentum operators. The Pauli matrices are represented by

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{1927}
\]

\[
\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{1928}
\]

\[
\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{1929}
\]

These matrices are traceless, and have the properties that their square is equal to the unit matrix, \(\sigma_0\),

\[
\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \sigma_0 \tag{1930}
\]

where the unit matrix is given by

\[
\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{1931}
\]

The three Pauli matrices and the unit matrix are linearly independent, and form a basis for the two by two matrices. That is, any two by two matrix can be expressed as a linear combination of the identity and Pauli matrices. Furthermore, they also satisfy the commutation relations

\[
[\sigma_x, \sigma_y] = 2i \sigma_z \\
[\sigma_z, \sigma_x] = 2i \sigma_y \\
[\sigma_y, \sigma_z] = 2i \sigma_x \tag{1932}
\]

When the Pauli matrices are multiplied by a factor of \(\frac{\hbar}{2}\), these commutation relations become identical to the commutation relations of the components of angular momentum, for fixed \(l\). Thus, if one multiplies the Pauli matrices by \(\frac{\hbar}{2}\), one can identify these matrices as representing angular momentum operators where the total angular momentum corresponds to \(l = 1/2\). The spin angular momentum operators are defined in terms of the Pauli matrices via

\[
\hat{S}_i = \frac{\hbar}{2} \sigma_i \tag{1933}
\]

where the index \(i\) can take on the values \(x, y\) and \(z\).

The Pauli spin operators act on the space of two-component column vectors, \(\Psi\),

\[
\Psi = \begin{pmatrix} \Psi_+ \\ \Psi_- \end{pmatrix} \tag{1934}
\]
An arbitrary operator $\hat{A}$ given by

$$\hat{A} = \begin{pmatrix} A_{1,1} & A_{1,2} \\ A_{2,1} & A_{2,2} \end{pmatrix}$$  (1935)

transforms the state $\Psi$ according to the laws of matrix multiplication. That is, $\hat{A}$ acting on the state $\Psi$ produces another state given by

$$\hat{A} \Psi = \begin{pmatrix} A_{1,1} \Psi_+ + A_{1,2} \Psi_- \\ A_{2,1} \Psi_+ + A_{2,2} \Psi_- \end{pmatrix}$$  (1936)

A vector $\Psi^\dagger$ which is the dual of the column vector $\Psi$ is defined as the complex conjugate of the row vector

$$\Psi^\dagger = \begin{pmatrix} \Psi^*_+ & \Psi^*_- \end{pmatrix}$$  (1937)

An inner product can be defined for any two vectors on this space as the complex number formed from the components of the vectors

$$\Phi^\dagger \Psi = \begin{pmatrix} \Phi^*_+ & \Phi^*_- \end{pmatrix} \begin{pmatrix} \Psi_+ \\ \Psi_- \end{pmatrix} = \begin{pmatrix} \Phi^*_+ \Psi_+ + \Phi^*_- \Psi_- \end{pmatrix}$$  (1938)

which, again, uses the laws of matrix multiplication. Physical states $\Psi$ are to be normalized such that

$$\Psi^\dagger \Psi = 1$$  (1939)

which results in the normalization condition

$$\left( |\Psi_+|^2 + |\Psi_-|^2 \right) = 1$$  (1940)

The existence of the inner product allows one to define the adjoint or Hermitian conjugate of the operator $\hat{A}$ as the operator $\hat{A}^\dagger$ which has the effect

$$\Phi^\dagger \hat{A} \Psi = \begin{pmatrix} \Phi^*_+ & \Phi^*_- \end{pmatrix} \begin{pmatrix} A_{1,1} & A_{1,2} \\ A_{2,1} & A_{2,2} \end{pmatrix} \begin{pmatrix} \Psi_+ \\ \Psi_- \end{pmatrix} = \begin{pmatrix} \Phi^*_+ \Psi_+ + \Phi^*_- \Psi_- \end{pmatrix}$$  (1941)

$$= \left( \Psi^\dagger \hat{A}^\dagger \Phi \right)^*$$

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Hence, the Hermitean conjugate of $\hat{A}$ is given by the transpose of the complex conjugate of $\hat{A}$

$$\hat{A}^\dagger = \left( \begin{array}{cc} A_{1,1}^* & A_{1,2}^* \\ A_{2,1}^* & A_{2,2}^* \end{array} \right)$$ (1942)

A Hermitean matrix is a matrix for which $\hat{A} = \hat{A}^\dagger$.

The Pauli spin operators are Hermitean, and hence can represent physical quantities such as the components of the angular momentum. The vector spin angular momentum is defined as

$$\vec{S} = \hbar \sigma = \hat{e}_x \hbar \sigma_x + \hat{e}_y \hbar \sigma_y + \hat{e}_z \hbar \sigma_z$$ (1943)

and the magnitude is given by

$$\vec{S}^2 = \vec{S}_x^2 + \vec{S}_y^2 + \vec{S}_z^2$$

$$= \frac{\hbar^2}{4} \sigma_x^2 + \frac{\hbar^2}{4} \sigma_y^2 + \frac{\hbar^2}{4} \sigma_z^2$$

$$= \frac{3}{4} \hbar^2 \sigma_0$$ (1944)

The unit matrix $\sigma_0$ is the identity operator as, when it acts on an arbitrary state, $\Psi$, it has the effect

$$\sigma_0 \Psi = \Psi$$ (1945)

and so the eigenvalues of the unit matrix are unity. As the eigenvalues of the magnitude of the spin angular momentum are $s \ ( s + 1 ) \ \hbar^2$, this means that $s = \frac{1}{2}$. The Pauli spin operators only act on the space formed by $s = \frac{1}{2}$. This space is two-dimensional as the eigenvalues of $\vec{S}^2$ have a degeneracy of $(2s + 1) = 2$. Thus, there are two independent basis states which can be chosen as the two column vectors that are the eigenvectors of $\sigma_z$

$$\sigma_z \chi_\pm = \pm \chi_\pm$$ (1946)

The eigenvector corresponding to the up-spin state with spin eigenvalue of $+ \frac{\hbar}{2}$ is

$$\chi^+ = \left( \begin{array}{c} 1 \\ 0 \end{array} \right)$$ (1947)

while the eigenvector corresponding to the down-spin state, with spin eigenvalue $- \frac{\hbar}{2}$ is represented by

$$\chi^- = \left( \begin{array}{c} 0 \\ 1 \end{array} \right)$$ (1948)
It should be noted that any pair of Pauli matrices, with different indices $i$ and $j$, anti-commute. That is

$$\sigma_i \sigma_j + \sigma_j \sigma_i = 2 \sigma_0 \delta_{i,j} \tag{1949}$$

The raising and lowering operators are defined as

$$\sigma_{\pm} = \sigma_z \pm i \sigma_y \tag{1950}$$

which yields the representations

$$\sigma_+ = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \tag{1951}$$

and

$$\sigma_- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} \tag{1952}$$

4.8.1 Exercise 104

Prove that the above two column vectors of eqn(1947) and eqn(1948) are eigenstates of the $z$ component of the spin operator $S_z = \frac{\hbar}{2} \sigma_z$, and find the effect of the raising and lowering operators on these states.

4.8.2 Solution 104

The column vector $\chi_+$ is an eigenvalue of $\sigma_z$, since it satisfies the eigenvalue equation

$$\sigma_z \chi_+ = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \chi_+ \tag{1953}$$

with eigenvalue 1. Also, the column vector $\chi_-$ is an eigenvalue of $\sigma_z$, since it satisfies the eigenvalue equation

$$\sigma_z \chi_- = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

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$$= \begin{pmatrix} 0 \\ -1 \end{pmatrix}$$
$$= - \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$
$$= - \chi_- \quad (1954)$$

with eigenvalue $-1$. Hence, $\chi_\pm$ are eigenstates of $\hat{S}_z$ with eigenvalues of $\pm \frac{h}{2}$.

The effect of the raising operator, $\hat{S}_+ = \hat{S}_x + i \hat{S}_y$ on the eigenstates of $\hat{S}_z$ with eigenvalue $-\frac{h}{2}$ is found from the effect of $\sigma_+$

$$\hat{S}_+ = \frac{\hbar}{2} \sigma_+ = \frac{\hbar}{2} \left( \sigma_x + i \sigma_y \right) \quad (1955)$$

acting on the eigenstates. This leads to

$$\sigma_+ \chi_- = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$
$$= \begin{pmatrix} 2 \\ 0 \end{pmatrix}$$
$$= 2 \chi_+ \quad (1956)$$

This shows that the raising operator increases the eigenvalue from $-\frac{h}{2}$ to $+\frac{h}{2}$. When the raising operator acts on the state $\chi_+$ it has the effect

$$\sigma_+ \chi_+ = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$= \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$
$$= 0 \quad (1957)$$

The raising operator annihilates the state with the maximal eigenvalue of $\hat{S}_z$, since by definition it cannot raise it any further.

The effect of the lowering operator, $\sigma_- = \sigma_x - i \sigma_y$ on the eigenstates of $\hat{S}_z$ are given by

$$\sigma_- \chi_+ = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$= 2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (1958)$$
which lowers the eigenvalue. However, since the state $\chi_-$ has the lowest eigenvalue of $\sigma_z$ one finds

$$
\sigma_- \chi_- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} = 0
$$

Thus, the lowering operator produces zero when it acts on the state with the lowest eigenvalue.

These equations can be summarized as

$$
\hat{S}_+ \chi_- = \hbar \chi_+ \\
\hat{S}_+ \chi_+ = 0 \\
\hat{S}_- \chi_+ = \hbar \chi_- \\
\hat{S}_- \chi_- = 0
$$

4.8.3 Exercise 105

Show that any two by two matrix can be expressed as a linear combination of the Pauli matrices and the unit matrix. Also show that any two-component column vector $\Psi$ can be represented as the linear superposition of the two eigenstates of $\sigma_z$, where

$$
\Psi = \begin{pmatrix} \Psi_+ \\
\Psi_- \end{pmatrix}
$$

4.8.4 Solution 105

Consider an arbitrary two by two matrix

$$
\begin{pmatrix} A & B \\
C & D \end{pmatrix}
$$
This can be expressed as the sum of four two by two matrices each with just one non-zero element

\[
\begin{pmatrix}
A & B \\
C & D
\end{pmatrix} = A \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + B \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\
+ C \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} + D \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}
\]

(1963)

The four by four matrices with components on the diagonal can be expressed in terms of the sum of the unit matrix \( \sigma_0 \) and \( \sigma_z \) via

\[
\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \frac{1}{2} \left[ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right]
\]

(1964)

while the matrix

\[
\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2} \left[ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right]
\]

(1965)

can be expressed as the difference.

The off-diagonal matrices can be expressed in terms of \( \sigma_x \) and \( \sigma_y \) via

\[
\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} = \frac{1}{2} \left[ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + i \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \right]
\]

(1966)

while the matrix

\[
\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = \frac{1}{2} \left[ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - i \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \right]
\]

(1967)

can be expressed as the difference.

Hence, we have the result that the arbitrary two by two matrix can be expressed as

\[
\begin{pmatrix}
A & B \\
C & D
\end{pmatrix} = \frac{1}{2} (A + D) \sigma_0 + \frac{1}{2} (A - D) \sigma_z + \frac{1}{2} (B + C) \sigma_x + \frac{i}{2} (B - C) \sigma_y
\]

(1968)

This proves that the Pauli matrices and the identity span the linear space formed by two by two matrices.

The states \( \chi_+ \) and \( \chi_- \) are eigenstates of \( \sigma_z \). Since \( \sigma_z \) is a Hermitian operator, the eigenstates form a complete set. Thus, \( \chi_+ \) and \( \chi_- \) spans the space of the
column vectors as an arbitrary vector can be expressed as
\[
\Psi = \begin{pmatrix} \Psi_+ \\ \Psi_- \end{pmatrix}
\]
\[
= \begin{pmatrix} \Psi_+ \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ \Psi_- \end{pmatrix}
\]
\[
= \Psi_+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \Psi_- \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\]
\[
= \Psi_+ \chi_+ + \Psi_- \chi_-
\]
(1969)
as was expected.

### 4.8.5 Exercise 106

Prove the identity
\[
\left( \mathbf{\sigma} \cdot \mathbf{a} \right) \left( \mathbf{\sigma} \cdot \mathbf{b} \right) = \mathbf{\sigma}_0 \left( a \cdot b \right) + i \mathbf{\sigma} \cdot \left( a \wedge b \right)
\]
(1970)
in which the spin vector is written in terms of the Pauli matrices as
\[
\mathbf{\sigma} = \hat{e}_x \sigma_x + \hat{e}_y \sigma_y + \hat{e}_z \sigma_z
\]
(1971)

### 4.8.6 Solution 106

First we note that the Pauli matrices satisfy the commutation relations
\[
[ \sigma_i, \sigma_j ] = 2i \sum_k \epsilon_{i,j,k} \sigma_k
\]
(1972)
where \( \epsilon_{i,j,k} \) is the anti-symmetric Levi-Civita symbol.

Also we note that the Pauli matrices satisfy
\[
\sigma_i \sigma_j = -\sigma_j \sigma_i
\]
(1973)
if \( i \neq j \), whereas if \( i = j \) then
\[
\sigma_i \sigma_i = \sigma_0
\]
(1974)
where $\sigma_0$ is the unit matrix. These relations can be combined in the anti-commutation relation
\[
\{ \sigma_i, \sigma_j \} = 2 \delta_{ij} \sigma_0
\] (1975)
in which the anti-commutator of two operators $\hat{A}$ and $\hat{B}$ is defined as $\{ \hat{A}, \hat{B} \}$, where
\[
\{ \hat{A}, \hat{B} \} = \hat{A} \hat{B} + \hat{B} \hat{A}
\] (1976)
Hence, on adding the commutation and anti-commutation relations, one has the identity
\[
\sigma_i \sigma_j = \delta_{i,j} \sigma_0 + i \sum_k \epsilon_{i,j,k} \sigma_k
\] (1977)
The identity to be proved follows immediately by expressing the scalar product in terms of the sum of Cartesian components
\[
\left( \sigma \cdot a \right) \left( \sigma \cdot b \right) = \sum_i \sigma_i a_i \sum_j \sigma_j b_j
\]
\[
= \sum_{i,j} \sigma_i \sigma_j a_i b_j
\]
\[
= \sum_{i,j} \left( \delta_{i,j} \sigma_0 + i \sum_k \epsilon_{i,j,k} \sigma_k \right) a_i b_j
\]
\[
= \sum_{i,j} \delta_{i,j} \sigma_0 a_i b_j + i \sum_k \sigma_k \sum_{i,j} \epsilon_{i,j,k} a_i b_j
\]
\[
= \sigma_0 \left( a \cdot b \right) + i \sum_k \sigma_k \left( a \wedge b \right)_k
\]
\[
= \sigma_0 \left( a \cdot b \right) + i \sigma \cdot \left( a \wedge b \right)
\] (1978)
This completes the proof.

4.8.7 Exercise 107
Find all the eigenfunctions and eigenvalues for the Pauli matrix $\sigma_x$, and show that they form a complete orthonormal set.

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The matrix $\sigma_x$ is given by

$$
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (1979)
$$

and the eigenfunctions satisfy the eigenvalue equation

$$
\sigma_x \chi^x = \lambda \chi^x \quad (1980)
$$

The eigenfunctions are represented by column vectors of the form

$$
\chi^x = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (1981)
$$

which are normalized when

$$
|\alpha|^2 + |\beta|^2 = 1 \quad (1982)
$$

The eigenvalue equations are expressed as the coupled algebraic equations for the components of $\Psi$ as

$$
\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \lambda \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (1983)
$$

or

$$
\begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0 \quad (1984)
$$

This equation only has a solution if the inverse matrix does not exist. Since the inverse matrix is inversely proportional to the determinant, the determinant must vanish for there to be a non-trivial solution for the components. Therefore, the eigenvalue $\lambda$ is given by the solution of

$$
\begin{vmatrix} -\lambda & 1 \\ 1 & -\lambda \end{vmatrix} = 0 \quad (1985)
$$

or

$$
\lambda^2 = 1 \quad (1986)
$$

which is consistent with the relation

$$
\sigma_x^2 = \sigma_0 \quad (1987)
$$

The eigenvalues of $\sigma_x$ are given by

$$
\lambda = \pm 1 \quad (1988)
$$
The eigenfunction $\chi_{x+1}^\dagger$ corresponding to $\lambda = 1$ is found from
\[
\begin{pmatrix}
0 & 1 \\
1 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta \\
\end{pmatrix} =
\begin{pmatrix}
\alpha \\
\beta \\
\end{pmatrix}
\tag{1989}
\]
which yields $\alpha = \beta$. Thus, the normalized eigenfunction is given by
\[
\chi_{x+1} = \frac{1}{\sqrt{2}} \begin{pmatrix}
1 \\
1 \\
\end{pmatrix}
\tag{1990}
\]
up to an arbitrary phase.

The eigenfunction corresponding to $\lambda = -1$ is found from
\[
\begin{pmatrix}
0 & 1 \\
1 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta \\
\end{pmatrix} = -\begin{pmatrix}
\alpha \\
\beta \\
\end{pmatrix}
\tag{1991}
\]
which yields $\alpha = -\beta$. Thus, the normalized eigenfunction is given by
\[
\chi_{x-1} = \frac{1}{\sqrt{2}} \begin{pmatrix}
1 \\
-1 \\
\end{pmatrix}
\tag{1992}
\]
up to an arbitrary phase.

The eigenstates of $\sigma_x$ are orthogonal as
\[
\chi_{x+1}^\dagger \chi_{x-1} = \frac{1}{2} \begin{pmatrix}
1 & 1 \\
\end{pmatrix} \begin{pmatrix}
1 \\
-1 \\
\end{pmatrix}
= \frac{1}{2} \begin{pmatrix}
1 & -1 \\
\end{pmatrix}
= 0
\tag{1993}
\]
Furthermore, since the space of column vectors is two-dimensional, the set of eigenfunctions are complete. That is, any arbitrary vector
\[
\Psi = \begin{pmatrix}
\alpha \\
\beta \\
\end{pmatrix}
\tag{1994}
\]
can be expressed as
\[
\begin{pmatrix}
\alpha \\
\beta \\
\end{pmatrix} = \frac{(\alpha + \beta)}{\sqrt{2}} \frac{1}{\sqrt{2}} \begin{pmatrix}
1 \\
1 \\
\end{pmatrix} + \frac{(\alpha - \beta)}{\sqrt{2}} \frac{1}{\sqrt{2}} \begin{pmatrix}
1 \\
-1 \\
\end{pmatrix}
\tag{1995}
\]
where the expansion coefficients were determined from the inner products with
the eigenstates
\[
\chi_{x+1}^+ \Psi = \left( \frac{\alpha + \beta}{\sqrt{2}} \right) \quad (1996)
\]
and
\[
\chi_{x-1}^- \Psi = \left( \frac{\alpha - \beta}{\sqrt{2}} \right) \quad (1997)
\]
Thus, we have shown that an arbitrary state can be expanded in terms of the
eigenstates of \( \sigma_x \) as
\[
\Psi = \frac{\alpha + \beta}{\sqrt{2}} \chi_{x+1}^+ + \frac{\alpha - \beta}{\sqrt{2}} \chi_{x-1}^- \quad (1998)
\]

Thus, the Pauli matrices form a representation of half-integer angular mo-
momentum, called spin. The spin quantum numbers are intrinsic to the particle
and, therefore, the operators cannot be represented in terms of the position and
momentum of the particle. The spin of a particle first became manifest in the
anomalous Zeeman effect, in which there is a coupling between the spin state
and an external magnetic field.

4.8.9 Exercise 108
Find the eigenvalues and eigenvectors of the component of the spin along the
unit vector \( \hat{\eta} \), where
\[
\hat{\eta} = \sin \theta \cos \varphi \, \hat{e}_x + \sin \theta \sin \varphi \, \hat{e}_y + \cos \theta \, \hat{e}_z \quad (1999)
\]
Work in the basis in which \( \hat{\sigma}_z \) is diagonal.

Hence, find the unitary matrix \( U_{\hat{\sigma}_z}(\theta) \) which produces a rotation of the spin
states through an angle \( \theta \), about the axis
\[
\hat{e} = -\sin \varphi \, \hat{e}_x + \cos \varphi \, \hat{e}_y \quad (2000)
\]
perpendicular to the plane of \( \hat{e}_z \) and \( \hat{\eta} \).

Hint: In addition to producing the transformation of the spin state “aligned”
parallel to the axis \( z \) to the spin state “aligned” with \( \hat{\eta} \), it is also required that
the rotation does not change the “direction” of spin states aligned parallel to
the rotation axis. This is indicated schematically in figs(105) and (106) for a
Rotation of a set of Spin States

Figure 105: A spin state with eigenvalue of \( \hat{S}_z \) equal to \(+\hbar\) is to be transformed to a spin state which an eigenstate of \( \hat{S}_\eta \), with eigenvalue of \(+\hbar\).

\[ S_\eta = 0 \]
\[ S_\eta = 1 \]
\[ S_\eta = -1 \]

4.8.10 Solution 108

We seek the eigenvalues and eigenfunctions of the operator

\[ \eta \cdot \sigma = \sin \theta \cos \varphi \hat{\sigma}_x + \sin \theta \sin \varphi \hat{\sigma}_y + \cos \theta \hat{\sigma}_z \]  

which has the matrix representation

\[ \eta \cdot \sigma = \hbar \begin{pmatrix} \cos \theta & \sin \theta \exp[-i \varphi] \\ \sin \theta \exp[i \varphi] & -\cos \theta \end{pmatrix} \]  

in the basis where \( \hat{\sigma}_z \) is diagonal. The eigenvalues \( \mu \) \( \hbar \) are determined from the secular equation

\[ 0 = \begin{vmatrix} \cos \theta - \mu & \sin \theta \exp[-i \varphi] \\
\sin \theta \exp[i \varphi] & -\cos \theta - \mu \end{vmatrix} \]
Rotation of a set of Spin States

\[ S_\varepsilon = 0 \]
\[ S_\varepsilon = 1 \]
\[ S_\varepsilon = -1 \]

\[ \gamma \]
\[ \eta \]
\[ \phi \]
\[ \epsilon \]
\[ S \]

Figure 106: It is also required that a spin rotation around the axis \( \hat{e} \) does not change the eigenstates of \( \hat{S}_\varepsilon \).

and, thus, are found to be \( \mu = \pm \hbar \). The eigenfunction \( \chi_\mu^\eta \) corresponding to the eigenvalue \( \mu \), is expressed in terms of its components through

\[ \chi_\mu^\eta = \begin{pmatrix} \alpha_\mu^\eta \\ \beta_\mu^\eta \end{pmatrix} \]

(2004)

The components for \( \mu = +1 \) are found from the eigenvalue equation

\[ \begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} ( \cos \theta - 1 ) & \sin \theta \exp[ -i \varphi ] \\ \sin \theta \exp[ +i \varphi ] & - ( \cos \theta + 1 ) \end{pmatrix} \begin{pmatrix} \alpha_+^\eta \\ \beta_+^\eta \end{pmatrix} \]

(2005)

Thus, the normalized eigenfunction of the operator in eqn(2001) corresponding to the \( \mu = 1 \) eigenvalue is found as

\[ \chi^\eta_+ = \begin{pmatrix} \cos \theta/2 \\ \sin \theta/2 \exp[ +i \varphi ] \end{pmatrix} \]

(2006)

Likewise, one finds the eigenfunction corresponding to \( \mu = -1 \) is given by

\[ \chi^\eta_- = \begin{pmatrix} - \sin \theta/2 \exp[ -i \varphi ] \\ \cos \theta/2 \end{pmatrix} \]

(2007)
The rotation is about an axis in the plane perpendicular to the unit vectors \( \hat{e}_z \) and \( \hat{e}_\eta \). The matrix \( U_{\hat{e}}(\theta) \) is determined from its action on the two eigenstates of \( \hat{\sigma}_z \)

\[
\chi^\eta_\mu = U_{\hat{e}}(\theta) \chi^\mu_\mu
\]

Thus, we have

\[
\begin{pmatrix}
\alpha^\eta_\mu \\
\beta^\eta_\mu
\end{pmatrix} = \begin{pmatrix}
\cos \frac{\theta}{2} & -\sin \frac{\theta}{2} \\
\sin \frac{\theta}{2} \exp[i \varphi] & \cos \frac{\theta}{2}
\end{pmatrix}
\begin{pmatrix}
\alpha^\mu_\mu \\
\beta^\mu_\mu
\end{pmatrix}
\]

On recognizing that the component of the spin operator along the rotation axis is given by

\[
\begin{pmatrix}
\hat{e} \cdot \hat{\sigma}_z
\end{pmatrix} = \begin{pmatrix}
0 \\
+i \exp[i \varphi] \\
-i \exp[-i \varphi]
\end{pmatrix}
\]

and that the square is the unit matrix

\[
\begin{pmatrix}
\hat{e} \cdot \hat{\sigma}_z
\end{pmatrix}^2 = \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix} = \sigma_0
\]

we find that the spin rotation operator may be written in the form

\[
U_{\hat{e}}(\theta) = \cos \frac{\theta}{2} \hat{\sigma}_0 - i \sin \frac{\theta}{2} \begin{pmatrix}
\hat{e} \cdot \hat{\sigma}_z
\end{pmatrix}
\]

Hence, the spin rotation operator is given by

\[
U_{\hat{e}}(\theta) = \exp\left[-i \frac{\theta}{2} \hat{e} \cdot \hat{\sigma}_z\right]
\]

\[
= \exp\left[-i \frac{\theta}{\hbar} \hat{e} \cdot \hat{\mathcal{S}}\right]
\]

where the spin is defined as

\[
\hat{\mathcal{S}} = \frac{\hbar}{2} \hat{\sigma}
\]

4.8.11 The Pauli Equation

The existence of spin was first inferred by Uhlenbeck and Goudsmit as a result of experiments where atoms were placed in a strong magnetic field and

\[\text{G.E. Uhlenbeck and S.A. Goudsmit, Naturwissenschaften, 13, 953 (1925) and Nature, 117, 264 (1926).}\]
the absorption lines were measured. In the ordinary Zeeman effect, the orbital angular momentum of a charged electron produces a magnetic moment which couples to the field and, therefore, raises the degeneracy of the electronic levels. This results in a splitting of the absorption lines, when the field is applied. The number of lines that are seen is equal to the degeneracy of the atomic levels in the absence of the field which are labeled by \( n \) and \( l \). In general, the degeneracy is expected to be given by \( 2l + 1 \) corresponding to the different \( m \) values. However, due to the presence of spin, there are more lines seen than predicted by the spin-less version of the Schrödinger equation. Even the \( \ell = 0 \) state is split into two levels corresponding to a degeneracy of 2. On introducing a spin operator \( S \) representing spin angular momentum and equating the degeneracy \( 2S + 1 = 2 \), one finds that the spin must be half-integer \( S = \frac{1}{2} \).

The Pauli equation\(^{37}\) assumes that the wave function for a spin half particle has two components

\[
\Psi(r) = \begin{pmatrix} \Psi_{+}(r) \\ \Psi_{-}(r) \end{pmatrix}
\]

and expresses the kinetic energy operator of the free particle in terms of the product of a Laplacian and the unit two by two matrix,

\[
\hat{T} = \frac{\hat{p}^2}{2m}
\]

which can be re-written as

\[
\hat{T} = \frac{(\hat{p} \cdot \sigma)(\hat{p} \cdot \sigma)}{2m}
\]

by using the identity

\[
\left(\sigma \cdot a\right)\left(\sigma \cdot b\right) = \sigma_0 \left( a \cdot b \right) + i \sigma \cdot (a \wedge b)
\]

with \( a = b = \hat{p} \). Thus, the time-dependent Schrödinger equation for the two-component (column vector) wave function \( \Psi(r) \) representing a free particle can be written in the form of the field-free Pauli equation

\[
i\hbar \frac{\partial}{\partial t} \Psi(r,t) = \left[ -\frac{\hbar^2}{2m} \left( \sigma \cdot \nabla \right)^2 \right] \Psi(r,t)
\]

The corresponding equation for a charged particle in an electromagnetic field is obtained by using the minimum coupling assumption \( p_{\mu} \rightarrow p_{\mu} - \frac{q}{c} A_{\mu} \). The resulting equation is found as

\[
i\hbar \frac{\partial}{\partial t} \Psi(r,t) = \left[ \frac{1}{2m} \left( \sigma \cdot \left( -i\hbar \nabla - \frac{q}{c} A(r,t) \right) \right)^2 + \sigma_0 q \phi(r,t) \right] \Psi(r,t)
\]

which, on using the identity, becomes
\[
\frac{i\hbar}{\partial t} \Psi(r,t) = \left[ \frac{1}{2m} \sigma_0 \left( -i\hbar \nabla - \frac{q}{c} A(r,t) \right)^2 \right.
\]
\[
- \frac{\hbar q}{2mc} \sigma \cdot \left( \nabla \wedge A(r,t) + A(r,t) \wedge \nabla \right)
\]
\[
+ \sigma_0 q \phi(r,t) \right] \Psi(r,t) \tag{2021}
\]
Furthermore, since
\[
\nabla \wedge A \Psi(r) = \Psi(r) \left( \nabla \wedge A \right) - A \wedge \nabla \Psi(r) \tag{2022}
\]
and \( B = \nabla \wedge A \), one finds
\[
\frac{i\hbar}{\partial t} \Psi(r,t) = \left[ \frac{1}{2m} \sigma_0 \left( -i\hbar \nabla - \frac{q}{c} A(r,t) \right)^2 \right.
\]
\[
- \frac{\hbar q}{2mc} \sigma \cdot B(r,t) + \sigma_0 q \phi(r,t) \right] \Psi(r,t) \tag{2023}
\]
Since the spin angular momentum \( S \) is given by \( \frac{\hbar}{2} \sigma \), one finds that the spin couples to the magnetic field giving rise to the anomalous Zeeman effect, but the relation between spin angular momentum and magnetic moment \( M \) is
\[
M = 2 \left( \frac{q}{2mc} \right) S \tag{2024}
\]
which is different from the relation between the orbital angular momentum \( L \) and the magnetic moment found in the ordinary Zeeman effect
\[
M = \left( \frac{q}{2mc} \right) L \tag{2025}
\]
The extra factor of 2 found for the spin half particle is known as the gyromagnetic ratio, \( g \), and the magnitude of the factor \( \frac{q}{2mc} \) is known as the Bohr magneton \( \mu_B \).

### 4.8.12 Spin Dynamics

We shall consider the dynamics of a particle with spin \( S = \frac{\hbar}{2} \) that is localized at some point in space, when a time-independent magnetic field \( B \) is applied to the system. The direction of the field may be taken to define the direction of the \( z \) axis of our Cartesian coordinate system. We shall only be concerned with the dynamics of the spin and, therefore, suppress any mention of the coordinate dependence of the wave function.
The wave function is then represented as a linear superposition of spin-up and spin-down states

$$
\Psi(t) = \begin{pmatrix} \Psi_+ (t) \\ \Psi_- (t) \end{pmatrix}
$$

(2026)

where $\Psi_{\pm}(t)$ are the time-dependent expansion coefficients. The Pauli equation is then given by the matrix equation

$$
i \hbar \frac{\partial}{\partial t} \Psi(t) = - \mu_B B_z \sigma_z \Psi(t)
$$

(2027)

where the Hamiltonian only consists of the Zeeman term. Since the energy eigenstates correspond to eigenstates of the $z$ component of the spin, $S_z = \hbar \sigma_z$, one may decompose the time-dependent wave function into energy eigenstates

$$
\Psi(t) = \Psi_+ (t) \chi_+ + \Psi_- (t) \chi_-
$$

(2028)

On substituting this into the time-dependent Schrödinger equation, one finds that

$$
i \hbar \frac{\partial}{\partial t} \Psi_\pm(t) = \mp \mu_B B \Psi_\pm(t)
$$

(2029)

which have the solutions

$$
\Psi_\pm(t) = \exp\left[ \pm \frac{\mu_B B t}{\hbar} \right] \Psi_\pm(0)
$$

(2030)

Hence, we have found the time dependence of our arbitrary initial spin wave function $\Psi(0)$ as

$$
\Psi(t) = \exp\left[ + \frac{\mu_B B t}{\hbar} \right] \Psi_+ (0) \chi_+ + \exp\left[ - \frac{\mu_B B t}{\hbar} \right] \Psi_- (0) \chi_-
$$

(2031)

If the initial state was known at $t = 0$ to be an eigenstate of, say $S_x$ with the eigenvalue $+\hbar/2$, then one has

$$
\Psi(0) = \frac{1}{\sqrt{2}} \left( \chi_+ + \chi_- \right)
$$

(2032)

or

$$
\Psi(0) = \frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ 1 \end{array} \right)
$$

(2033)

Thus, we have found that the time dependence of the wave function at later times, $t$, is given by

$$
\Psi(t) = \frac{1}{\sqrt{2}} \left( \exp\left[ + \frac{\mu_B B t}{\hbar} \right] \chi_+ + \exp\left[ - \frac{\mu_B B t}{\hbar} \right] \chi_- \right)
$$

(2034)
From this one can see that the probability of finding the particle in an eigenstate of $S_x$ with eigenvalue $+\frac{\hbar}{2}$ is going to oscillate with time, as is the probability that the particle is in the $S_x$ eigenstate with eigenvalue $-\frac{\hbar}{2}$. This oscillation corresponds to the classical precession of a spin around the $z$ axis, with a frequency given by $\omega = \frac{2 \mu_B B}{\hbar}$, known as the Larmor precession frequency.

![Figure 107: A classical magnetic moment $M$ in an applied magnetic field $B$ experiences a torque $\tau = M \times B$ and, hence, precesses around the direction of the field.](image)

4.8.13 Exercise 109

Evaluate the time dependence of the probability that a spin $\frac{1}{2}$ in a magnetic field $B$ aligned along the $z$-axis is found in the eigenstates of $S_y$, if the initial state is an eigenstate of $S_x$ with eigenvalue $+\frac{\hbar}{2}$.

4.8.14 Solution 109

The initial state is an eigenstate of $\hat{S}_x$ with eigenvalue $+\frac{\hbar}{2}$. The initial state can be represented as

$$\Psi(0) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

(2035)
which evolves with time as

$$\Psi(t) = \exp \left[ -i \frac{t}{\hbar} \hat{H} \right] \Psi(0) \quad (2036)$$

where the Hamiltonian is given by

$$\hat{H} = -\mu_B B \sigma_z \quad (2037)$$

The time-dependent state is given by

$$\Psi(t) = \frac{1}{\sqrt{2}} \exp \left[ i t \frac{\mu_B B}{\hbar} \right] \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{1}{\sqrt{2}} \exp \left[ -i t \frac{\mu_B B}{\hbar} \right] \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (2038)$$

The matrix $\sigma_y$ has eigenvalues of $\pm 1$ and the eigenvalues are given by

$$\chi_{\pm 1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \quad (2039)$$

respectively. The state $\Psi(t)$ is expanded in terms of the eigenstates $\chi_{\pm}^y$ as

$$\Psi(t) = \sum_{\pm} C_{\pm}(t) \chi_{\pm}^y \quad (2040)$$

where

$$C_{\pm}(t) = \frac{1}{2} \left( \exp \left[ i t \frac{\mu_B B}{\hbar} \right] \mp i \exp \left[ -i t \frac{\mu_B B}{\hbar} \right] \right) \quad (2041)$$

Thus, we have the time-dependent probability given by

$$P_{\pm}^y(t) = \frac{1}{2} \left( 1 \mp \sin \frac{2 \mu_B B t}{\hbar} \right) \quad (2042)$$

---

**4.8.15 Exercise 110**

A spin half nucleus is placed in a static magnetic field $B_0$ aligned along the $z$ axis and a smaller rotating magnetic field $B_1$ in the $x$ - $y$ plane. The frequency of the a.c. field is $\omega$. If the nucleus is initially pointing in the $+z$ direction at $t = 0$, what is the probability that it will be aligned with the $+z$ axis at later times?
Experiments were suggested and performed by I.I. Rabi and co-workers\textsuperscript{38} which were based on calculations of the above type.

4.8.16 Solution 110

The spin vector can be written as

\[ \Psi(t) = \begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix} \] (2043)

and the Schrödinger equation is

\[ i \hbar \frac{\partial}{\partial t} \Psi(t) = -\mu_N \left( B_0 \sigma_z + B_1 \sigma_x \cos \omega t - B_1 \sigma_y \sin \omega t \right) \Psi(t) \] (2044)

or

\[ i \frac{\partial}{\partial t} \Psi(t) = - \left( \frac{\mu_N B_0}{\hbar} \exp[-i\omega t] - \frac{\mu_N B_1}{\hbar} \exp[i\omega t] \right) \Psi(t) \] (2045)

We should note that the sense of the rotation of \( B_1 \) about the \( z \)-axis is such that the axis of rotation is anti-parallel to \( B_0 \). We are also implicitly assuming that \( \mu_N \) is positive. The equations for the components of the spinors are

\[ i \frac{\partial}{\partial t} \alpha(t) = - \left( \frac{\mu_N B_0}{\hbar} \right) \alpha(t) - \left( \frac{\mu_N B_1}{\hbar} \right) \exp[i\omega t] \beta(t) \] (2046)

and

\[ i \frac{\partial}{\partial t} \beta(t) = + \left( \frac{\mu_N B_0}{\hbar} \right) \beta(t) - \left( \frac{\mu_N B_1}{\hbar} \right) \exp[-i\omega t] \alpha(t) \] (2047)

On solving the first equation for \( \beta \) and substituting this into the second, one obtains a second order differential equation for \( \alpha \)

\[ \frac{\partial^2}{\partial t^2} \alpha(t) - i \omega \frac{\partial}{\partial t} \alpha(t) + \left( \left( \frac{\mu_N}{\hbar} \right)^2 \left( B_0^2 + B_1^2 \right) - \omega \frac{\mu_N B_0}{\hbar} \right) \alpha(t) = 0 \] (2048)

This is solved by assuming that $\alpha(t)$ has the form

$$\alpha(t) = \alpha(0) \exp\left[i \lambda t\right]$$

(2049)

The characteristic equation is a quadratic equation in $\lambda$ which can be solved, yielding

$$\lambda_{\pm} = + \frac{\omega}{2} \pm \sqrt{\left(\frac{\mu N B_0}{\hbar} - \frac{\omega}{2}\right)^2 + \left(\frac{g \mu N B_1}{\hbar}\right)^2}$$

(2050)

The general solution can be written as

$$\alpha(t) = a_+ \exp\left[i \lambda_+ t\right] + a_- \exp\left[i \lambda_- t\right]$$

(2051)

The components of $\beta$ can be written as

$$\beta(t) = \left( b_+ \exp\left[i \lambda_+ t\right] + b_- \exp\left[i \lambda_- t\right] \right) \exp\left[ - i \omega t \right]$$

(2052)

However, $b_+$ and $b_-$ are given in terms of the $a$'s via the original differential equations. Thus, $b_+$ is linear in $a_+$ and $b_-$ is linear in $a_-

$$\frac{b_+}{a_+} = \frac{(\frac{b_0}{2} - \mu N B_0) \mp \sqrt{\left(\frac{b_0}{2} - \mu N B_0\right)^2 + \left(\frac{\mu N B_1}{\hbar}\right)^2}}{\mu N B_1}$$

(2053)

To satisfy the initial conditions one must have $\alpha(0) = a_+ + a_- = 1$ and $\beta(0) = b_+ + b_- = 0$. These conditions allow one to solve for $\alpha(t)$. The probability of finding the spin-up eigenvalue is given by $|\alpha(t)|^2$ and

$$|\alpha(t)|^2 = 1 - \left[\frac{\left(\frac{\mu N B_1}{\hbar}\right)^2}{\left(\frac{\mu N B_0}{\hbar} - \frac{\omega}{2}\right)^2 + \left(\frac{\mu N B_1}{\hbar}\right)^2}\right] \times \left[\frac{\left(\frac{\mu N B_1}{\hbar}\right)^2}{\left(\frac{\mu N B_0}{\hbar} - \frac{\omega}{2}\right)^2 + \left(\frac{\mu N B_1}{\hbar}\right)^2}\right] \times \sin^2 \sqrt{\left(\frac{\mu N B_0}{\hbar} - \frac{\omega}{2}\right)^2 + \left(\frac{\mu N B_1}{\hbar}\right)^2} t$$

(2054)

As the spin one half wave function is normalized and has an overall phase factor, the spin state only depends on two variables. Therefore, the spin one half wave function can always be interpreted in terms of a classical state in which the spin has a definite direction. When the frequency $\omega$ is away from the resonance frequency

$$\omega = 2 \left(\frac{\mu N B_0}{\hbar}\right)$$

(2055)
the spin precesses around the z-axis with frequency $\omega$ and the z component also makes small amplitude oscillations. That is, the spin motion is confined within a small ring parallel the equator of the unit sphere. However, for frequencies near the resonance frequency, the z component of the spin performs large amplitude oscillations and almost flips to the other pole with frequency $2 \left( \frac{\mu_N}{\hbar} B_1 \right)$.

4.8.17 The Berry Phase

In the presence of a magnetic field, an isolated spin will find an equilibrium state which is the ground state. In the ground state the spin is aligned parallel to the field. If the direction of the field is subsequently changed, sufficiently slowly, one expects that the direction of the spin will continue to align with the magnetic field at every instant of time. That is, one does not expect the slowly time varying field to cause the spin to make a transition to states of higher energy. This expectation is borne out by detailed calculations on systems of various spin magnitudes. However, although the spin state does follow the field direction, the spin wave function does acquire an additional phase. If the field is returned to the original direction, the additional phase factor is determined by the topology of the spin’s motion. The motion of the spin can be visualized by projecting the spin direction onto the unit sphere. The direction of the spin can be specified by specifying the polar coordinates $(\theta(t), \phi(t))$. As the field is changed, the spins direction will map out a path on the unit sphere. The additional phase, or Berry phase $\delta$, acquired by the spin is determined by the solid angle $\Omega$ enclosed by the spin’s orbit. The Berry phase is determined by the solid angle and the magnitude of the spin, in units of $\hbar$. The path of the spin is parameterized as $\theta(\phi)$. Since the infinitesimal solid angle $d\Omega$ is given by

$$ d\Omega = d\phi \, d\theta \, \sin \theta $$

on integrating from the pole $\theta = 0$ to $\theta(\phi)$, the solid angle enclosed by the infinitesimal wedge is

$$ d\Omega = d\phi \, (1 - \cos \theta(\phi)) $$

(2057)

Then, the solid angle enclosed by the complete orbit is given by

$$ \Omega = \oint d\phi \, (1 - \cos \theta(\phi)) $$

(2058)

where the integral over $\phi$ runs over $2\pi$.

The Berry phase can be illustrated by considering a spin one half in a magnetic field of constant magnitude, $B$, oriented along the direction $(\theta, \varphi)$. In this case, the Zeeman Hamiltonian is given by

$$\hat{H}_Z = -\mu_B (B \cdot \sigma)$$

which, on using the Pauli-spin matrices, can be expressed as

$$\hat{H}_Z = -\mu_B B \left( \cos \theta \sigma_z + \sin \theta (\sin \varphi \sigma_y + \cos \varphi \sigma_x) \right)$$

For fixed $(\theta, \varphi)$, the time-independent Hamiltonian $\hat{H}_Z$ has an eigenstate with eigenfunction given by

$$\chi_+ = \left( \sin \frac{\theta}{2} \exp[i \varphi] \right)$$

corresponding to the eigenvalue

$$E_0 = -\mu_B B$$
Thus, in this eigenstate the spin is aligned parallel to the applied field. For a static field one has the time-dependent wave function given by

\[ \chi^+ = \begin{pmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} \end{pmatrix} \exp \left[ i \phi \right] \exp \left[ + i \frac{\mu_B B}{\hbar} t \right] \]  

(2063)

where the time dependence is given purely by the exponential phase factor.

If the direction of the field \((\theta(t), \phi(t))\) is changed very slowly, one expects the spin will adiabatically follow the field direction. That is, if the field is rotated sufficiently slowly, one does not expect the spin to make a transition to the state with energy \(E = + \mu_B B\) where the spin is aligned anti-parallel to the field. However, the wave function may acquire a phase which is different from the time and energy dependent phase factor expected for a static field. This extra phase is the Berry phase \(\delta\), which can be calculated from the Schrödinger equation

\[ i \hbar \frac{\partial}{\partial t} \begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix} = -\mu_B B \begin{pmatrix} \cos \theta(t) & \sin \theta(t) \exp[-i \phi(t)] \\ \sin \theta(t) \exp[i \phi(t)] & -\cos \theta(t) \end{pmatrix} \begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix} \]  

(2064)

We shall assume that the wave function takes the adiabatic form

\[ \begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix} = \begin{pmatrix} \cos \frac{\theta(t)}{2} \\ \sin \frac{\theta(t)}{2} \exp[i \phi(t)] \end{pmatrix} \exp \left[ + i \left( \frac{\mu_B B}{\hbar} t - \delta(t) \right) \right] \]  

(2065)

which instantaneously follows the direction of the field, but is also modified by the inclusion of the Berry phase \(\delta(t)\). On substituting this ansatz into the Schrödinger equation, one finds that the non-adiabatic terms satisfy

\[ -\frac{\partial \delta}{\partial t} \begin{pmatrix} \cos \frac{\theta(t)}{2} \\ \sin \frac{\theta(t)}{2} \exp[i \phi(t)] \end{pmatrix} + \frac{\partial \phi}{\partial t} \begin{pmatrix} \cos \frac{\theta(t)}{2} \\ \sin \frac{\theta(t)}{2} \exp[i \phi(t)] \end{pmatrix} = \begin{pmatrix} 0 \\ -\sin \frac{\theta(t)}{2} \exp[i \phi(t)] \end{pmatrix} \]  

\[ = \frac{i}{2} \frac{\partial \theta}{\partial t} \begin{pmatrix} \cos \frac{\theta(t)}{2} \\ \sin \frac{\theta(t)}{2} \exp[i \phi(t)] \end{pmatrix} \]  

(2066)

The above equation is then projected onto the adiabatic state by multiplying it by the row matrix

\[ \begin{pmatrix} \cos \frac{\theta(t)}{2} \\ \sin \frac{\theta(t)}{2} \exp[-i \phi(t)] \end{pmatrix} \]  

(2067)

One finds that the derivative of \(\theta\) w.r.t. \(t\) cancels and that the equation simplifies to

\[ -\frac{\partial \delta}{\partial t} + \frac{\partial \phi}{\partial t} \sin^2 \frac{\theta}{2} = 0 \]  

(2068)
Hence, the Berry phase is given by integrating w.r.t. to $t$,

\[
\delta(t) = \int_0^t dt' \frac{\partial \varphi}{\partial t'} \sin^2 \frac{\theta(t')}{2}
\]

\[
= \int d\varphi \sin^2 \frac{\theta(\varphi)}{2}
\]

\[
= \frac{1}{2} \int d\varphi \left( 1 - \cos \theta(\varphi) \right)
\]

(2069)

On completing one orbit in spin space, the extra phase is given by

\[
\delta = \frac{1}{2} \Omega
\]

(2070)

as was claimed.
4.9 Transformations and Invariance

The assumption underlying the application of quantum mechanics to physical systems is that the basic structure and predictions of experimental results on quantum mechanical systems are independent of the inertial coordinate system used. If we consider space-time which is governed by Galilean invariance, time being absolute and space being isotropic and governed by the laws of Euclidean geometry, we have non-relativistic quantum mechanics. Transformations between different coordinate systems (passive transformations) leave the physical system unaltered and merely provide relations between reference systems of different observers. Alternately, two different physical systems may be related to each other by a transformation of the physical position of the physical system and measuring devices. Under an active transformation such as a physical rotation of one system, the two systems may be brought into coincidence.

Equivalent quantum mechanical systems can be transformed into each other, via a unitary transformation associated with a unitary operator $\hat{U}$. The unitary operator is defined as an operator that has a Hermitean conjugate which is identical to the inverse operator

$$\hat{U}^\dagger = \hat{U}^{-1}$$

This has a consequence that the eigenvalues of a unitary operator are complex numbers of magnitude unity, and the eigenfunctions form an orthonormal set. This can be seen by considering the matrix elements of $\hat{U}^{-1} \hat{U}$ between two different eigenfunctions $\phi_{\lambda_1}$ and $\phi_{\lambda_2}$

$$\int d^3r \phi^*_{{\lambda_2}}(r) \hat{U}^{-1} \hat{U} \phi_{\lambda_1}(r) = \lambda^*_2 \lambda_1 \int d^3r \phi^*_{\lambda_2}(r) \phi_{\lambda_1}(r)$$

$$= \int d^3r \phi^*_{\lambda_2}(r) \phi_{\lambda_1}(r)$$

since $\hat{U}$ is unitary. Thus, we have

$$\left( \lambda^*_2 \lambda_1 - 1 \right) \int d^3r \phi^*_{\lambda_2}(r) \phi_{\lambda_1}(r) = 0$$

Hence, the eigenvalues have modulus unity as

$$\lambda^*_1 \lambda_1 = 1$$

and eigenfunctions corresponding to different eigenvalues are orthogonal.

Physically equivalent states are related via unitary transformations. Under a unitary transformation the states are transformed according to

$$\Psi(r) \rightarrow \Psi'(r) = \hat{U} \Psi(r)$$
which preserves the normalization of $\Psi'$ as
\[
\int d^3r \, \Psi^*(r) \, \Psi'(r) = \int d^3r \, \Psi^*(r) \, \hat{U} \, \hat{U}^\dagger \, \Psi(r) \\
= \int d^3r \, \Psi^*(r) \, \Psi(r) \\
= 1
\] (2076)

The operators are transformed according to
\[
\hat{A} \rightarrow \hat{A}' = \hat{U} \, \hat{A} \, \hat{U}^\dagger
\] (2077)
as the expectation values of the transformed operators sandwiched between the transformed states leads to the same expectation values as the untransformed operators in the untransformed states
\[
\int d^3r \, \Psi^*(r) \, \hat{A}' \, \Psi'(r) = \int d^3r \, \Psi^*(r) \, \hat{A} \, \Psi(r)
\] (2078)

4.9.1 Time Translational Invariance

The time translational operator $\hat{U}(t,t_0)$ is a unitary operator which is defined by its action on a wave function
\[
\hat{U}(t,t_0) \, \Psi(r,t_0) = \Psi(r,t)
\] (2079)
Since the wave function $\Psi(r,t)$ has the same normalization as $\Psi(r,t_0)$, the time evolution operator is a unitary operator as it is norm conserving.

The time translational operator can be expressed in terms of the time derivative, since
\[
\exp \left[ ( t - t_0 ) \, \frac{\partial}{\partial t_0} \right] \, \Psi(r,t_0) = \Psi(r,t)
\] (2080)
Thus, we find that the operator
\[
\frac{\partial}{\partial t_0}
\] (2081)
is the infinitesimal generator of time translations and the time translational operator can be expressed as
\[
\hat{U}(t,t_0) = \exp \left[ ( t - t_0 ) \, \frac{\partial}{\partial t_0} \right]
\] (2082)
The time dependence of the Schrödinger equation is governed by the Hamiltonian $\hat{H}$, and if this is time independent then
\[
i \, \hbar \, \frac{\partial}{\partial t} \equiv \hat{H}
\] (2083)
which gives the explicit term for the time translational operator

\[ \hat{U}(t, t_0) = \exp \left[ -i \frac{(t - t_0)}{\hbar} \hat{H} \right] \] (2084)

The time translational operator only depends on the time difference \( t - t_0 \).

The time translation operators can be compounded, thereby forming a group operation

\[ \hat{U}(t_2 - t_1) \hat{U}(t_1 - t_0) = \hat{U}(t_2 - t_0) \] (2085)

since \( \hat{U} \) only depends on the time differences \( t_2 - t_1 \). The identity operator is

\[ \hat{U}(0) = 1 \] (2086)

The inverse of \( \hat{U}(t) \) is

\[ \hat{U}^{-1}(t) = \hat{U}(-t) \] (2087)

such that

\[ \hat{U}(t) \hat{U}(-t) = \hat{U}(0) \] (2088)

If a physical quantity is represented by a time-independent operator \( \hat{A} \) in the Schrödinger picture, and its expectation values are given by

\[ \int d^3 \mathbf{r} \Psi^*(\mathbf{r}, t) \hat{A} \Psi(\mathbf{r}, t) = \int d^3 \mathbf{r} \Psi^*(\mathbf{r}, t_0) \hat{U}^\dagger(t, t_0) \hat{A} \hat{U}(t, t_0) \Psi(\mathbf{r}, t_0) \] (2089)

this is independent of time if

\[ \hat{U}^\dagger(t, t_0) \hat{A} \hat{U}(t, t_0) = \hat{A} \] (2090)

which is satisfied if the operator \( \hat{A} \) commutes with the Hamiltonian \( \hat{H} \),

\[ [\hat{H}, \hat{A}] = 0 \] (2091)

In particular, since time is homogeneous, and hence the Hamiltonian of a closed system is independent of time, the energy is conserved as \( \hat{H} \) commutes with itself.

### 4.9.2 Translational Invariance

A translation of a system by a distance \( \mathbf{a} \) changes the wave function of the system

\[ \Psi(\mathbf{r}) \rightarrow \Psi'(\mathbf{r}) = \hat{S}(\mathbf{a}) \Psi(\mathbf{r}) \] (2092)
The unitary operator that represents a displacement of a system from \( \mathbf{r} \) to \( \mathbf{r} + \mathbf{a} \) is given by

\[
\hat{S}(\mathbf{a}) = \exp \left[ - \mathbf{a} \cdot \mathbf{\nabla} \right]
\]  

(2093)

so

\[
\Psi'(\mathbf{r}) = \hat{S}(\mathbf{a}) \Psi(\mathbf{r})
\]

\[
= \exp \left[ - \mathbf{a} \cdot \mathbf{\nabla} \right] \Psi(\mathbf{r})
\]

\[
= \Psi(\mathbf{r} - \mathbf{a})
\]  

(2094)

Thus, the wave function \( \Psi' \) evaluated at \( \mathbf{r} + \mathbf{a} \) has the same value as \( \Psi \) evaluated at \( \mathbf{r} \). The translational operators \( \hat{S}(\mathbf{a}) \) can be combined to yield other operators of the same type

\[
\hat{S}(\mathbf{a}) \hat{S}(\mathbf{b}) = \hat{S}(\mathbf{a} + \mathbf{b})
\]  

(2095)

The translation operators form a representation of a group. The group is Abelian and it is a continuous group.

**Translation through distance \( \mathbf{a} \)**

![Figure 109: The translation of an arbitrary state \( \Psi(\mathbf{r}) \) through a distance \( \mathbf{a} \).](image)

For an infinitesimally small displacement \( \xi \), one has

\[
\hat{S}(\xi) = \begin{pmatrix} 1 - i \xi \cdot \mathbf{\nabla} \end{pmatrix} + O(\xi^2)
\]

\[
= \begin{pmatrix} 1 - i \frac{\xi}{\hbar} \cdot \mathbf{\hat{p}} \end{pmatrix} + O(\xi^2)
\]  

(2096)
\[ -i \nabla \] is the generator of infinitesimal transformations. The generator of infinitesimal transformations corresponds to the momentum operator.

If a system is invariant under displacements then the expectation values of physical operators in these states should be the same for \( \Psi \) as \( \Psi' \). In particular, the Hamiltonian is invariant under the transformation

\[ \hat{S}(\xi)^\dagger \hat{H} \hat{S}(\xi) = \hat{H} \]  \hfill (2097)

From the infinitesimal translation, we find that \( \hat{p} \) and \( \hat{H} \) must commute

\[ [\hat{p}, \hat{H}] = 0 \]  \hfill (2098)

Hence, we find \( \hat{p} \) is a constant of motion. Thus, for translationally invariant systems the momentum is conserved.

If we translate the state of the system and the measuring devices then, as space is homogeneous, this is equivalent to a passive transformation in which the system remains unchanged but is represented in a different coordinate system. The measuring devices in this new coordinate system are represented by the operators \( \hat{C}' \) which are given in terms of the operators of the old coordinate system via

\[ \hat{C}' = \hat{S}(a) \hat{C} \hat{S}^\dagger(a) \]  \hfill (2099)

The momentum and coordinate operators are transformed accordingly as

\[ \hat{p}' = \hat{S}(a) \hat{p} \hat{S}^\dagger(a) \]
\[ = \exp \left[ -a \cdot \nabla \right] \hat{p} \exp \left[ +a \cdot \nabla \right] \]
\[ = \hat{p} \]

and

\[ r' = \hat{S}(a) r \hat{S}^\dagger(a) \]
\[ = \exp \left[ -a \cdot \nabla \right] r \exp \left[ +a \cdot \nabla \right] \]
\[ = r - a \]  \hfill (2100)

For an active transformation, in which only the system is translated and the measuring systems are kept in place, the corresponding operators are those of the original system.

When the homogeneity of space is disturbed, for example by the application of a magnetic field, the translation operators take a different form. For a uniform magnetic field and no electrostatic potential, the system should be uniform and
so the translation operator should commute with the Hamiltonian. In this case, the correct generator of the translation is given by the pseudo-momentum

\[ \hat{K} = \hat{p} - \frac{q}{c} A + \frac{q}{c} B \wedge r \]  

(2101)

where the sum of the first two terms is recognized as the canonical momentum. The translation through a distance \( a \) is given by

\[ \hat{S}(a) = \exp \left[ -i \frac{a}{\hbar} \hat{K} \right] \]  

(2102)

The components of the pseudo-momenta do not commute, as

\[ [ \hat{K}_i , \hat{K}_j ] = -i \hbar \frac{q}{c} \epsilon_{i,j,k} B_k \]  

(2103)

and so the translation operators also do not commute

\[ \hat{S}(a) \hat{S}(b) = \hat{S}(b) \hat{S}(a) \exp \left[ +i \frac{q}{\hbar c} B \cdot (a \wedge b) \right] \]  

(2104)

The non-commutivity of the translational operators is a manifestation of the presence of an Aharonov - Bohm phase.

### 4.9.3 Periodic Translational Invariance

Consider a potential \( V(x) \) which is periodic in translations through any integer multiple of a discrete repeat distance \( a \). That is,

\[ V(x + na) = V(x) \]  

(2105)

This potential is periodic in \( x \) with period \( a \). We seek eigenvalues of the energy eigenvalue equation

\[ \hat{H} \phi(x) = E \phi(x) \]

\[ \left[ \frac{\hat{p}^2}{2m} + V(x) \right] \phi(x) = E \phi(x) \]  

(2106)

The unitary operator \( \hat{S}(na) \) defined by

\[ \hat{S}(na) = \exp \left[ -i \frac{n a}{\hbar} \hat{p} \right] \]  

(2107)

produces a translation of the wave function by a distance \( n a \).

\[ \phi(x - na) = \hat{S}(na) \phi(x) \]

\[ = \exp \left[ -i \frac{n a}{\hbar} \hat{p} \right] \phi(x) \]  

(2108)

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since the operator generates a Taylor-MacLaurin expansion in the displacement \( n \, a \). Furthermore, a displacement of \((n + m) \, a\) can be generated by successive displacements of \( n \, a \) and \( m \, a \). The unitary transformation corresponding to the combined displacement can be expressed as

\[
\hat{S}((n + m)\, a) = \hat{S}(n\, a) \hat{S}(m\, a) = \hat{S}(m\, a) \hat{S}(n\, a) \quad (2109)
\]

Thus, the unitary operators corresponding to translations through any integer multiple of the basic periodicity \( a \) commute.

Since under the displacement the potential transforms as

\[
V(x - na) = \hat{S}(na) \, V(x) \, \hat{S}^\dagger(na) \quad (2110)
\]

and as the potential is periodic

\[
V(x - na) = V(x) \quad (2111)
\]

one finds that

\[
\hat{S}(na) \, V(x) \, \hat{S}^\dagger(na) = V(x) \quad (2112)
\]

and so \( \hat{S}(na) \) commutes with the Hamiltonian, as

\[
\hat{H} = \hat{S}(na) \, \hat{H} \, \hat{S}^\dagger(na) \quad (2113)
\]

or, on post multiplying by \( \hat{S}(na) \), one has

\[
\hat{H} \, \hat{S}(na) = \hat{S}(na) \, \hat{H} \quad (2114)
\]

Thus, the set of operators \( \hat{H} \), and \( \hat{S}(na) \), form a set of mutually commuting operators and can be diagonalized.

We seek a simultaneous solution of the set of eigenvalue equations

\[
\begin{align*}
\hat{H} \, \phi(x) &= E \, \phi(x) \\
\hat{S}(na) \, \phi(x) &= \lambda_n \, \phi(x)
\end{align*} \quad (2115)
\]

for all \( n \). The eigenvalues of a unitary operator must have modulus of unity, so one has

\[
|\lambda_n|^2 = 1 \quad (2116)
\]

Since, the discrete translation operator satisfies the equation

\[
\hat{S}((n + m)a) = \hat{S}(na) \, \hat{S}(ma) \quad (2117)
\]

the eigenvalues must be related by the multiplicative relation

\[
\lambda_{n+m} = \lambda_n \, \lambda_m \quad (2118)
\]
Hence, the eigenvalues may be written as

$$\lambda_n = \exp\left[ i n \varphi \right] \quad (2119)$$

where $\varphi$ is a real phase. This is a one-dimensional version of Bloch’s theorem, which states that eigenfunctions of a Hamiltonian with a periodic potential, with periodicity $a$, can be chosen such that

$$\phi(x - na) = \exp\left[ i n \varphi \right] \phi(x) \quad (2120)$$

Therefore, by demanding that $\phi(x)$ is an eigenfunction of $\hat{S}(na)$ we have ensured that the solution is finite at $x \to \pm \infty$.

---

**Example**

As an example, consider a periodic potential composed of repulsive delta functions of strength $V_0 a$,

$$V(x) = \sum_{n=\pm \infty}^{n=\pm \infty} V_0 a \delta(x - na) \quad (2121)$$

Classically, a particle of energy $E > 0$ would be free to move in the regions between the repulsive delta functions. Quantum mechanically, we expect the particle to be able to tunnel through the narrow potential barrier.

---

**Solution**

The differential equation can be solved in the region between the barriers, say, in the region $n a < x < (n + 1) a$ the eigenfunction has the form

$$\phi(x) = A_n \exp\left[ i k x \right] + B_n \exp\left[ - i k x \right] \quad (2122)$$

corresponding to a linear superposition of a forward and backward travelling waves. The wave vector $k$ is related to the energy through

$$E = \frac{\hbar^2 k^2}{2 m} \quad (2123)$$

The wave function in the region $(n + 1) a < x < (n + 2) a$ also has the same form

$$\phi(x) = A_{n+1} \exp\left[ i k x \right] + B_{n+1} \exp\left[ - i k x \right] \quad (2124)$$
Figure 110: A periodic array of repulsive delta function potentials.

The pairs of coefficients \((A_n, B_n)\) and \((A_{n+1}, B_{n+1})\) on each side of the delta function barrier at \(x = (n + 1)a\) are related by demanding that the forms also satisfy the eigenvalue equation at the boundary. Continuity of the wave function at \(x = (n + 1)a\) yields the equation

\[
(A_{n+1} - A_n) \exp \left[ i k (n + 1) a \right] + (B_{n+1} - B_n) \exp \left[ -i k (n + 1) a \right] = 0
\]

(2125)

The discontinuity in the derivative at the boundary is related to the strength of the delta function barrier through

\[
(A_{n+1} - A_n) \exp \left[ i k (n + 1) a \right] - (B_{n+1} - B_n) \exp \left[ -i k (n + 1) a \right] = \left( \frac{2 m V_0 a}{i k \hbar^2} \right) \left( A_n \exp \left[ i k (n + 1) a \right] + B_n \exp \left[ -i k (n + 1) a \right] \right)
\]

(2126)

This pair of equations can be solved to yield \((A_{n+1}, B_{n+1})\) in terms of \((A_n, B_n)\). Thus, on adding the pair of equations one has

\[
2 (A_{n+1} - A_n) \exp \left[ i k (n + 1) a \right] = \left( \frac{2 m V_0 a}{i k \hbar^2} \right) \left( A_n \exp \left[ i k (n + 1) a \right] + B_n \exp \left[ -i k (n + 1) a \right] \right)
\]
while on subtracting them one obtains

\[ 2 \left( B_{n+1} - B_n \right) \exp \left[ -i k (n + 1) a \right] = - \left( \frac{2 m V_0 a}{i k h^2} \right) \left( A_n \exp \left[ i k (n + 1) a \right] + B_n \exp \left[ -i k (n + 1) a \right] \right) \]

The pair of equations may be re-written as

\[
A_{n+1} = \left( 1 + \frac{m V_0 a}{i k h^2} \right) A_n + \left( \frac{m V_0 a}{i k h^2} \right) \exp \left[ -2 i k (n + 1) a \right] B_n
\]

and

\[
B_{n+1} = \left( 1 - \frac{m V_0 a}{i k h^2} \right) B_n - \left( \frac{m V_0 a}{i k h^2} \right) \exp \left[ +2 i k (n + 1) a \right] A_n
\]

These two equations are not sufficient to determine a solution uniquely (up to an undetermined phase factor) since the ratio of the coefficients \( A_n \) and \( B_n \) are unknown. However, Bloch’s theorem gives the additional relation

\[ \phi(x - a) = \exp \left[ i \varphi \right] \phi(x) \]

which uniquely specifies the simultaneous eigenfunctions.

On using Bloch’s theorem, one finds

\[
\phi(x - a) = \exp \left[ i \varphi \right] \phi(x) = \exp \left[ i \varphi \right] \left( A_{n+1} \exp \left[ i k x \right] + B_{n+1} \exp \left[ -i k x \right] \right) = A_n \exp \left[ i k (x - a) \right] + B_n \exp \left[ -i k (x - a) \right]
\]

which, on equating the coefficients of the independent exponential functions, yields

\[ A_{n+1} = \exp \left[ -i (\varphi + k a) \right] A_n \]

and

\[ B_{n+1} = \exp \left[ -i (\varphi - k a) \right] B_n \]
This insures that the wave functions do not diverge in the limits \( x \to \pm \infty \). On using these relations to eliminate \( B_{n+1} \) and \( A_{n+1} \), one finds the two equations

\[
\left( \frac{m V_0 a}{i k h^2} \right) \left( \frac{B_n}{A_n} \right) \exp \left[ -2 i k (n + 1) a \right] = \exp \left[ -i (k a + \varphi) \right] - \left( 1 + \frac{m V_0 a}{i k h^2} \right) \tag{2135}
\]

\[
\left( \frac{m V_0 a}{i k h^2} \right) \left( \frac{A_n}{B_n} \right) \exp \left[ +2 i k (n + 1) a \right] = \left( 1 - \frac{m V_0 a}{i k h^2} \right) - \exp \left[ +i (k a - \varphi) \right] \tag{2136}
\]

The above two equations can be combined to eliminate the ratio of \( A_n / B_n \), which leads to the equation

\[
\left[ \exp \left[ -i (k a + \varphi) \right] - \left( 1 + \frac{m V_0 a}{i k h^2} \right) \right] \left[ \left( 1 - \frac{m V_0 a}{i k h^2} \right) - \exp \left[ +i (k a - \varphi) \right] \right] = \left( \frac{m V_0 a}{i k h^2} \right)^2 \tag{2137}
\]

On re-arranging this equation, one finds

\[
\exp \left[ -i 2 \varphi \right] - 2 \exp \left[ -i \varphi \right] \left( \cos k a + \sin k a \frac{m V_0 a}{k h^2} \right) + 1 = 0 \tag{2138}
\]

Multiplying this equation by \( \exp \left[ +i \varphi \right] \) leads to

\[
\cos \varphi = \left( \cos k a + \sin k a \frac{m V_0 a}{k h^2} \right) = 1 \tag{2139}
\]

This equation only has real solutions for \( \varphi \), when the right hand side has a magnitude less than unity. In these ranges of \( k \), the above equation can be solved to yield \( k \) as a function of \( \varphi \). We note that \( \varphi \) is only defined up to multiples of \( 2 \pi \). We shall examine the equation graphically, the right-hand side is plotted as a function of \( k a \) in fig(111). As a function of \( k \), the function

\[ F(k) = \left( \cos k a + \sin k a \frac{m V_0 a}{k h^2} \right) \tag{2140} \]

has a maximum at \( k = 0 \) with the value

\[ F(0) = 1 + \frac{m V_0 a^2}{h^2} \tag{2141} \]
and behaves as $\cos ka$ in the asymptotic large $k$ limit. The allowed values of $k$ are those for which $\cos \varphi$ exists and, therefore, the function $F(k)$ has a magnitude less than unity. Hence, not all values of $k$ will give rise to a solution. In particular, the values of $k$ for which $|F(k)| > 1$ do not yield a solution. The range of forbidden $k$ values (at large $k$) are near $ka = \mu \pi$, for integer $\mu$.

![Graphical Determination of Allowed Ranges of $k$](image)

Figure 111: The graphical determination of the allowed ranges of $k$.

Since, $E$ and $k$ are related via

$$E = \frac{\hbar^2 k^2}{2m}$$  \hspace{1cm} (2142)

and not all $k$ values are allowed, we find that the spectrum of energy eigenvalues have “gaps” centered near the energies

$$E = \frac{\hbar^2 \mu^2 \pi^2}{2 m a^2}$$  \hspace{1cm} (2143)

The allowed energies form bands, which are separated by band gaps. As $k \to \infty$ the band gaps become very narrow. Since the discontinuities become negligible at high energies, the band energies closely follow the parabolic dispersion relation. Since $k$ is not a good quantum number and due to the gaps in the $E(k)$ relation, the energies are not plotted as $E(k)$. However, $\varphi$ is a good quantum number as it determines the eigenvalue of the $S(a)$, thus the bands are usually plotted as $E(\varphi)$, against $\varphi$. Typical energy bands are shown in fig(112). It is
seen that there are energy gaps between the bands at the origin $\varphi = 0$ and at the boundary $\varphi = \pi$. The sizes of the gaps diminish and the widths of the bands increase as one successively inspects higher energy intervals.

![Dispersion Relation](image)

Figure 112: The band dispersion relation $E(\varphi)$ plotted as a function of the Bloch eigenvalue $\varphi$.

### 4.9.4 Exercise 111

Calculate the energy eigenvalues associated with a potential constructed from a periodic array of attractive delta function potentials

$$V(x) = - \sum_{n=-\infty}^{n=\infty} V_0 a \delta(x - n a)$$  \hspace{1cm} (2144)

Explicitly, consider the eigenfunctions corresponding to $E > 0$ and $E < 0$.  

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4.9.5 Solution 111

The solution for the states with energy \( E > 0 \) and wave vector \( k \) can be expressed as

\[
\phi(x) = A_n \exp\left[i \, k \, x\right] + B_n \exp\left[-i \, k \, x\right]
\] (2145)

in the intervals between the delta functions. The relation between the coefficients \( A_n \) and \( B_n \) in successive intervals can be expressed in terms of the Bloch label \( \varphi \). The Bloch label is given by the solution of the equation

\[
\cos \varphi = \left( \cos k \, a - \sin k \, a \, \frac{m \, V_0 \, a}{k \, \hbar^2} \right) \leq 1
\] (2146)

Not all values of \( k \) yield solutions for \( \varphi \), and as the energy eigenvalues are given by

\[
E = \frac{\hbar^2 \, k^2}{2 \, m}
\] (2147)

one finds band gaps, for \( E > 0 \).

![Graphical determination of the allowed ranges of k.](image)

Figure 113: The graphical determination of the allowed ranges of \( k \).

In addition to the \( E > 0 \) solutions, one has solutions which can be written as

\[
\phi(x) = A_n \exp\left[ + \kappa \, x\right] + B_n \exp\left[- \kappa \, x\right]
\] (2148)
in each interval. These solutions correspond to negative energy eigenvalues

\[ E = -\frac{\hbar^2 \kappa^2}{2m} \]  \hspace{1cm} (2149)

The eigenvalue of the translation operator can be expressed in terms of \( \varphi \) where

\[ \cos \varphi = \left( \cosh \kappa a - \sinh \kappa a \frac{m V_0 a}{\kappa \hbar^2} \right) \leq 1 \]  \hspace{1cm} (2150)

This only produces solutions for one finite range of \( \kappa \) values. Hence, we find a single band with negative energies. The dispersion relation is shown in fig(115).

![Graphical determination of the allowed ranges of \( \kappa \).](image)

**Figure 114:** The graphical determination of the allowed ranges of \( \kappa \).

### 4.9.6 Rotational Invariance

A rotation of a system (through an angle \( \theta \) about an arbitrary oriented axis represented by the unit vector \( \hat{e} \)) can be expressed in terms of a unitary operation

\[ \hat{U}_e(\theta) = \exp \left[ -i \frac{\theta}{\hbar} \left( \hat{e} \cdot \hat{J} \right) \right] \]  \hspace{1cm} (2151)

where \( \hat{J} \) is the total angular momentum operator

\[ \hat{J} = \hat{L} + \hat{S} \]  \hspace{1cm} (2152)
composed of the sum of the orbital angular momentum and the spin angular momentum operators.

That $\hat{U}_e(\theta)$ affects a rotation can be seen by its effect on the wave function of a spinless particle $\Psi(r)$. Consider a rotation about the $z$ axis through an infinitesimal angle $\delta\varphi = \frac{\varphi_0}{N}$ then

$$
\Psi'(r) = \hat{U}_z(\delta\varphi) \Psi(r) \\
= \exp \left[ -i \frac{\delta\varphi}{\hbar} \hat{L}_z \right] \Psi( z \hat{e}_z + \hat{e}_y y + \hat{e}_x x ) \\
= \left( 1 - \delta\varphi \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) + O(\delta\varphi^2) \right) \Psi(r) \\
= \Psi(r) + \delta\varphi \left( x \hat{e}_y - y \hat{e}_x \right) \cdot \nabla \Psi(r) + O(\delta\varphi^2)
$$

(2153)

and to lowest order in $\delta\varphi$, we recognize this as a Taylor expansion of

$$
\Psi(r + \delta\varphi x \hat{e}_y - \delta\varphi y \hat{e}_x)
$$

(2154)

When the position vector is represented as

$$
x = r \sin \theta \cos \varphi
$$
Figure 116: The unitary operator $\hat{U}_z(\theta)$ produces a rotation of the scalar wave function through an angle of $\theta$ around the $z$-axis. The rotation operator $\hat{R}$ acts on the coordinates and transforms the point $r$ to the point $r'$, i.e. $r' = \hat{R} r$. Under the rotation, the wave function $\Psi(r)$ is transformed to $\Psi'(r')$, such that the value of $\Psi$ at the point $r'$ is the same as the value of $\Psi$ at the point $r$. Therefore, $\Psi'(r') = \Psi(r)$ so, $\Psi'(\hat{R} r) = \Psi(\hat{R}^{-1} r)$. The unitary operator which transforms the wave function is then determined by $\Psi'(r) = \hat{U}_z(\theta) \Psi(r) = \Psi(\hat{R}^{-1} r)$.

$$
\begin{align*}
  y &= r \sin \theta \sin \varphi \\
  z &= r \cos \theta
\end{align*}
$$

we find that the transformed wave function is

$$
\begin{align*}
  \Psi'(r) &= \hat{U}_z(\delta \varphi) \Psi(r) \\
  &= \Psi( z \hat{e}_z + r \sin \theta (\sin \varphi - \cos \varphi \delta \varphi) \hat{e}_y + r \sin \theta (\cos \varphi + \sin \varphi \delta \varphi) \hat{e}_x ) \\
  &= \Psi( z \hat{e}_z + r \sin \theta \sin(\varphi - \delta \varphi) \hat{e}_y + r \sin \theta \cos(\varphi - \delta \varphi) \hat{e}_x )
\end{align*}
$$

which has suffered an infinitesimal rotation of $\delta \varphi$ about the $z$ axis. Thus, we find that the angular momentum operator is the generator for infinitesimal rotations.

A finite rotation through $\varphi_0$ can be built up from $N$ successive infinitesimal transformations through $\delta \varphi = \varphi_0/N$ by taking the limit $N \to \infty$ via

$$
\begin{align*}
  \hat{U}_z(\varphi_0) &= \lim_{N \to \infty} \hat{U}_z^N(\delta \varphi) \\
  &= \lim_{N \to \infty} \left( 1 - i \frac{\varphi_0}{N \hbar} \hat{L}_z \right)^N
\end{align*}
$$
\[ \exp \left[ -i \frac{\varphi_0}{\hbar} \hat{L}_z \right] \] (2157)

This could have been immediately recognized had we used the representation of both the operator \( \hat{L}_z \) and the wave function in spherical polar coordinates

\[
\Psi'(r, \theta, \varphi) = \hat{U}_z(\varphi_0) \Psi(r, \theta, \varphi) \\
= \exp \left[ -i \frac{\varphi_0}{\hbar} \hat{L}_z \right] \Psi(r, \theta, \varphi) \\
= \exp \left[ - \varphi_0 \frac{\partial}{\partial \varphi} \right] \Psi(r, \theta, \varphi) \\
= \Psi(r, \theta, \varphi - \varphi_0) \tag{2158}
\]

Rotation of a vector through \( \varphi \)

Figure 117: The rotation of an arbitrary vector \( \mathbf{r} \) about an angle \( \varphi \) about the axis \( \hat{e} \).

An alternate derivation of the effect of a finite rotation through an angle \( \varphi_0 \) about an arbitrary unit vector \( \hat{e} \) can be expressed in terms of its effect on the position vector. By composition, one can build up the effect of a rotation on an arbitrary wave function. Under a finite rotation, an arbitrary vector \( \mathbf{r} \) has simple transformational properties as it behaves like a state with angular
momenum \( l = 1 \). After the rotation, the vector is given by

\[
\begin{align*}
\mathbf{r}' &= (\mathbf{r} \cdot \hat{e}) \hat{e} - \sin \varphi_0 \hat{e} \wedge \mathbf{r} + \cos \varphi_0 \hat{e} \wedge \left( \mathbf{r} \wedge \hat{e} \right) \\
&= (\mathbf{r} \cdot \hat{e}) \hat{e} - \sin \varphi_0 \hat{e} \wedge \mathbf{r} + \cos \varphi_0 \left( \mathbf{r} - (\hat{e} \cdot \mathbf{r}) \hat{e} \right) \\
&= \mathbf{r} - \sin \varphi_0 \hat{e} \wedge \mathbf{r} + (\cos \varphi_0 - 1) \left( \mathbf{r} - (\hat{e} \cdot \mathbf{r}) \hat{e} \right)
\end{align*}
\]  

(2159)

We shall use the identity

\[
\hat{e} \wedge \mathbf{r} = \left( \hat{e} \wedge (\mathbf{r} \wedge \nabla) \right) \mathbf{r}
\]  

(2160)

and a second identity

\[
\hat{e} \wedge \left( \mathbf{r} \wedge \hat{e} \right) = -\left( \hat{e} \cdot (\mathbf{r} \wedge \nabla) \right)^2 \mathbf{r}
\]  

(2161)

Using these two identities, the rotated vector can be expressed as

\[
\begin{align*}
\mathbf{r}' &= \mathbf{r} - \sin \varphi_0 \left( \hat{e} \cdot (\mathbf{r} \wedge \nabla) \right) \mathbf{r} + (1 - \cos \varphi_0) \left( \hat{e} \cdot (\mathbf{r} \wedge \nabla) \right)^2 \mathbf{r} \\
&= \left[ 1 - \sin \varphi_0 \left( \hat{e} \cdot (\mathbf{r} \wedge \nabla) \right) + (1 - \cos \varphi_0) \left( \hat{e} \cdot (\mathbf{r} \wedge \nabla) \right)^2 \right] \mathbf{r} \\
&= \left[ 1 - i \sin \varphi_0 \left( \hat{e} \cdot \left( \frac{\hat{L}}{\hbar} \right) \right) - (1 - \cos \varphi_0) \left( \frac{\hat{e} \cdot \hat{L}}{\hbar} \right)^2 \right] \mathbf{r} \\
&= \left[ 1 + \sum_{n=0}^{\infty} \frac{(-i \varphi_0)^{2n+1}}{(2n+1)!} \left( \frac{\hat{e} \cdot \hat{L}}{\hbar} \right) + \sum_{n=1}^{\infty} \frac{(-i \varphi_0)^{(2n)}}{(2n)!} \left( \frac{\hat{e} \cdot \hat{L}}{\hbar} \right)^2 \right] \mathbf{r}
\end{align*}
\]  

(2162)

where we have introduced the angular momentum operator. Since the component \((\hat{e} \cdot \mathbf{r})\) of \(\mathbf{r}\) is an eigenstate of \((\hat{e} \cdot \hat{L})\) with eigenvalue 0, and since the perpendicular components are eigenstates of \((\hat{e} \cdot \hat{L})^2\) with eigenvalues \(+\hbar^2\), we have

\[
\left( \frac{\hat{e} \cdot \hat{L}}{\hbar} \right)^3 \mathbf{r} = \left( \frac{\hat{e} \cdot \hat{L}}{\hbar} \right) \mathbf{r}
\]  

(2163)

\(^{40}\text{This can be seen by introducing a basis consisting of three orthogonal unit vectors}
\]

\[
\hat{e}_\phi = \frac{1}{\sin \theta} \hat{e} \wedge \hat{r}
\]

\[
\hat{e}_\theta = \frac{1}{\sin \theta} \hat{e} \wedge (\hat{e} \wedge \hat{r})
\]

where \(\cos \theta = (\hat{e} \cdot \hat{r})\). In this basis, the vector \(\mathbf{r}\) has components \((\cos \theta, 0, -\sin \theta)\). The rotation through \(\varphi_0\) can then be performed in this coordinate system.
This identity can be used to insert extra factors of
\[
\left( \frac{\hat{e} \cdot \hat{L}}{\hbar} \right)^{2n}
\] (2164)
into the general terms of both the even and odd series so that the powers of \( \hat{L} \) match the powers of \( \varphi_0 \). The even and odd terms can be combined to form one series which exponentiates

\[
l' = \left[ \sum_{n=0}^{\infty} \frac{(-i \varphi_0)^n}{n!} \left( \frac{\hat{e} \cdot \hat{L}}{\hbar} \right)^n \right] l
\]
\[
= \exp \left[ -i \frac{\varphi_0}{\hbar} \hat{e} \cdot \hat{L} \right] l
\] (2165)
giving the desired result.

Rotations \( R \) can be combined to give other rotations. The rotations form a group. If a rotation is denoted by its axis \( \hat{e} \) and the angle of rotation \( \theta \), the rotation \( R_{\hat{e}}(\theta) \) can be represented on a unit sphere. The rotation axes can be labeled by their points of intersection with the unit sphere. The combination of two rotations \( R_{\hat{e}_1}(\theta_1) \) and \( R_{\hat{e}_2}(\theta_2) \) can be found from Euler’s construction shown in figs (118) and (119), and is neatly expressed algebraically in terms of multiplication of quaternions. Euler’s construction shows that rotations do not commute if the rotations do not share the same axis, and so groups of rotations can be non-Abelian.

We note that if the Hamiltonian of a system is invariant under rotations, then the angular momentum operator commutes with the Hamiltonian. If this is the case, then angular momentum is conserved.

For a particle with spin, the rotation operator consists of a product of two factors. The first factor acts on the spatial components and is identical to the rotation operator for the spinless particle. The second factor acts (locally) on the components of the spinor.

For a spin one half particle, the part of the unitary operator that acts on the spin which represents a rotation through \( \varphi_0 \) about the axis \( \hat{e} \) is given by

\[
\hat{U}_{\hat{e}}(\varphi_0) = \exp \left[ -\varphi_0 \frac{i}{2} \hat{e} \cdot \sigma \right]
\]
\[
= \cos \frac{\varphi_0}{2} \sigma_0 - i \sin \frac{\varphi_0}{2} \hat{e} \cdot \sigma
\] (2166)

This unitary operator\(^{41}\) acts on the two-component spinor wave function. We should note that a rotation by \( 2 \pi \) does not leave the spinor invariant but changes

\(^{41}\)An arbitrary spin one half rotation operator can be represented by unitary \( 2 \times 2 \) matrices, with determinant +1. Hence, the matrices are the special unitary matrices of \( SU(2) \).
Figure 118: The Euler construction. The rotation \( R_{P_1}(\theta_1) \) through an angle \( \theta_1 \) about the axis \( OP_1 \) is to be combined with the rotation \( R_{P_2}(\theta_2) \) through an angle \( \theta_2 \) about the axis \( OP_2 \). Two auxiliary great circles are constructed from \( P_1 \) which subtend angles \( \frac{\theta_1}{2} \) to the great circle connecting \( P_1 \) and \( P_2 \). Likewise, two more auxiliary great circles are constructed emanating from point \( P_2 \). The points of intersection of the pairs of auxiliary great circles are labeled as \( P_3 \) and \( P_4 \). It is seen that \( R_{P_1}(\theta_1) \) shifts \( P_3 \) to position \( P_4 \), and is shifted back to \( P_3 \) by the subsequent application of \( R_{P_2}(\theta_2) \). Hence, \( P_3 \) is on the axis of the combined rotation. Also \( P_4 \) is on the axis of a combined rotation when the component rotations are combined in the opposite order.

Thus, for example, a rotation of a spin by \( \varphi_0 \) about the \( z \)-axis is produced by

\[
\hat{U}_z(\varphi_0) = \begin{pmatrix}
\exp[-i \frac{\varphi_0}{2}] & 0 \\
0 & \exp[i \frac{\varphi_0}{2}]
\end{pmatrix}
\]

That this operator produces a rotation of the spin state can be verified by letting it act on the eigenstate of the operator \( \frac{\eta}{2} \cdot \hat{S} \) with eigenvalue \( +\frac{\eta}{2} \). In this experiment, spin one half particles were sent through a two-channel interferometer. A magnetic field was used to rotate the particles in one channel. The interference pattern was periodic in the rotation angle, with period \( 4 \pi \). The experiment was described in A.W. Overhauser, A.R. Collela and S.A. Werner, Phys. Rev. Lett. 33, 1237 (1974).
Euler Construction

Figure 119: The Euler construction. The angle of the combined rotation can be found by considering the effect of the successive rotations on point $P_1$. Under the first transformation $P_1$ is invariant, since it is on the axis of rotation. Under the second transformation $P_1$ is swept to point $R$. Thus, under the combined rotation around $P_3$, the great circle segment $P_3P_1$ is swept to $P_3R$. Since $P_2P_3$ bisects the segments $P_2P_1$ and $P_3R$, the angle of the combined rotation is found to be $2(\pi - \frac{\theta}{2})$.

expression, $\eta$ is a unit vector that has the Cartesian components

$$\eta = \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix}$$  \hspace{1cm} (2168)

The $\eta$ component of the spin operator is given by

$$\eta \cdot \hat{S} = \frac{\hbar}{2} \begin{pmatrix} \cos \theta & \sin \theta \exp\left[-i \varphi\right] \\ \sin \theta \exp\left[i \varphi\right] & -\cos \theta \end{pmatrix}$$  \hspace{1cm} (2169)

and the eigenstate with eigenvalue $+\frac{\hbar}{2}$ is given by

$$\Psi_\eta = \begin{pmatrix} \cos \frac{\theta}{2} \exp\left[-i \frac{\varphi}{2}\right] \\ \sin \frac{\theta}{2} \exp\left[i \frac{\varphi}{2}\right] \end{pmatrix}$$  \hspace{1cm} (2170)

This eigenstate describes a spin pointing along the positive $\eta$ direction. The rotated spin state is then given by

$$\Psi'_{\eta} = \hat{U}_z(\varphi_0) \Psi_\eta$$
Hence, we deduce that $\Psi'$ is the eigenstate of $\eta' \cdot S$ with eigenvalue $+\hbar^2/2$, where the unit vector $\eta'$ is obtained by rotating $\eta$ around the $z$ axis through the angle $\phi_0$. That is, the spins now point along the positive $\eta'$ direction. The operator $\hat{U}_z(\phi_0)$ produced a rotation of the spin about the $z$-axis through an angle of $\phi_0$.

The combined rotation on the spin and spatial wave function of the spin one half particle

$$\Psi(r) = \left( \begin{array}{c} \Psi_+(r) \\ \Psi_-(r) \end{array} \right)$$

produces the transformed state

$$\Psi'(r) = \left( \begin{array}{c} \Psi_+'(r) \\ \Psi_-'(r) \end{array} \right) = \left( \begin{array}{cc} \exp[i \phi_0/2] & 0 \\ 0 & \exp[-i \phi_0/2] \end{array} \right) \left( \begin{array}{c} \Psi_+(R_z^{-1}r) \\ \Psi_-(R_z^{-1}r) \end{array} \right)$$

In this expression, the spinor wave function is transferred from the point $R_z^{-1}r$ to the rotated point $r$ and the direction of the spin is adjusted locally.

For a particle with spin one, the corresponding (local) spin rotation operator can be represented as

$$\hat{U}_z(\phi_0) = \exp\left[ -i \frac{\phi_0}{\hbar} \hat{e} \cdot \hat{S} \right] = \hat{I} - i \sin \phi_0 \left( \frac{\hat{e} \cdot \hat{S}}{\hbar} \right) + \left( \cos \phi_0 - 1 \right) \left( \frac{\hat{e} \cdot \hat{S}}{\hbar} \right)^2$$

For integer spins, a rotation of $2 \pi$ does not produce a change in the phase of spinor wave function. This is in contrast to the case of half integer spins where the phase of the wave function changes by $\pi$.

As an example, a spin is rotated through an angle $\phi_0$ about the $z$-axis by the transformation $\hat{U}_z(\phi_0)$ where

$$\hat{U}_z(\phi_0) = \left( \begin{array}{ccc} \exp[-i \phi_0/2] & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \exp[i \phi_0/2] \end{array} \right)$$

The state in which the direction of the classical spin is known to be along an arbitrary direction $\eta$ corresponds to the quantum state which is an eigenstate
of the component of the spin along $\vec{\eta}$ is $\hbar$. The relevant operator is given by

$$\left(\frac{\vec{\eta} \cdot \vec{S}}{\hbar}\right) = \begin{pmatrix} \cos \theta & \frac{1}{\sqrt{2}} \sin \theta \exp[-i \varphi] & 0 \\ \frac{1}{\sqrt{2}} \sin \theta \exp[i \varphi] & 0 & \frac{1}{\sqrt{2}} \sin \theta \exp[-i \varphi] \\ 0 & \frac{1}{\sqrt{2}} \sin \theta \exp[i \varphi] & -\cos \theta \end{pmatrix}$$

(2176)

where $\theta$ and $\varphi$ are the polar coordinates that specify the direction of the unit vector $\vec{\eta}$. The operator has an eigenstate with eigenvalue $\hbar$ which is given by

$$\Psi_{\eta} = \frac{1}{2} \left( \begin{array}{c} (1 + \cos \theta) \exp[-i \varphi] \\ \sqrt{2} \sin \theta \\ (1 - \cos \theta) \exp[i \varphi] \end{array} \right)$$

(2177)

Hence, this eigenstate describes a spin pointing in the direction of positive $\eta$. This result is consistent with the calculated expectation values of $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ for this state. It is simple to see that the transformation $\hat{U}_z(\varphi_0)$ results in a spin state $\hat{U}_z(\varphi_0) \Psi_{\eta}$ where the spin’s direction is rotated by $\varphi_0$.

4.9.7 Exercise 112

Show that the spin rotation operator $\hat{U}_c(\varphi_0)$, for a spin one half particle, satisfies the identity

$$\hat{U}_c(\varphi_0) = \exp \left[ -\varphi_0 \frac{i}{2} \hat{e} \cdot \vec{\sigma} \right] = \cos \frac{\varphi_0}{2} \sigma_0 - i \sin \frac{\varphi_0}{2} \hat{e} \cdot \vec{\sigma}$$

(2178)

4.9.8 Solution 112

First we expand the operator, and rearrange the series as a sum of even and odd terms

$$\hat{U}_c(\varphi_0) = \exp \left[ -i \frac{\varphi_0}{2} \hat{e} \cdot \vec{\sigma} \right] = \sum_{n=0}^{\infty} \frac{1}{n!} \left( -i \frac{\varphi_0}{2} \hat{e} \cdot \vec{\sigma} \right)^n$$

$$= \sum_{n=0}^{\infty} \frac{1}{2n!} \left( -i \frac{\varphi_0}{2} \hat{e} \cdot \vec{\sigma} \right)^{2n} + \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \left( -i \frac{\varphi_0}{2} \hat{e} \cdot \vec{\sigma} \right)^{(2n+1)}$$

(2179)
Then prove the identity
\[
\left( \hat{e} \cdot \vec{\sigma} \right)^2 = \sigma_0
\]  
which proceeds from the expansion of the scalar product
\[
\left( \hat{e} \cdot \vec{\sigma} \right)^2 = \left( \sum_i \hat{e} \cdot \hat{e}_i \sigma_i \right)^2
\]
\[
= \sum_{i,j} \left( \hat{e} \cdot \hat{e}_i \right) \left( \hat{e} \cdot \hat{e}_j \right) \sigma_i \sigma_j
\]
\[
= \sum_i \left( \hat{e} \cdot \hat{e}_i \right)^2 \sigma_i^2 + \sum_{i>j} \left( \hat{e} \cdot \hat{e}_i \right) \left( \hat{e} \cdot \hat{e}_j \right) \left( \sigma_i \sigma_j + \sigma_j \sigma_i \right)
\]
\[
= \sum_i \left( \hat{e} \cdot \hat{e}_i \right)^2 \sigma_0 + \sum_{i>j} \left( \hat{e} \cdot \hat{e}_i \right) \left( \hat{e} \cdot \hat{e}_j \right) \delta_{i,j}
\]
\[
= \left( \hat{e} \cdot \hat{e} \right) \sigma_0
\]
\[
= \sigma_0
\]  
(2180)

since the squares of the Pauli matrices are unity and the different Pauli matrices anti-commute. The last line follows as \( \hat{e} \) is a unit vector. On substituting the identity in the series expansion, one finds
\[
\hat{U}_e(\varphi_0) = \exp \left[ -i \frac{\varphi_0}{\hat{e} \cdot \vec{\sigma}} \right]
\]
\[
= \sum_{n=0}^{\infty} \frac{(-1)^n}{2n!} \left( \frac{\varphi_0}{2} \right)^{2n} \sigma_0 - i \left( \hat{e} \cdot \vec{\sigma} \right) \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!} \left( \frac{\varphi_0}{2} \right)^{2n+1}
\]  
(2182)

Since, the trigonometric functions are defined as
\[
\cos \left( \frac{\varphi_0}{2} \right) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} \left( \frac{\varphi_0}{2} \right)^{2n}
\]
\[
\sin \left( \frac{\varphi_0}{2} \right) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!} \left( \frac{\varphi_0}{2} \right)^{2n+1}
\]  
(2183)

one has proved the identity
\[
\hat{U}_e(\varphi_0) = \exp \left[ - \frac{\varphi_0}{2} \hat{e} \cdot \vec{\sigma} \right]
\]
\[
= \cos \left( \frac{\varphi_0}{2} \right) \sigma_0 - i \sin \left( \frac{\varphi_0}{2} \right) \hat{e} \cdot \vec{\sigma}
\]  
(2184)
4.9.9 Exercise 113

Consider the rotation of an arbitrary (spatially uniform) spin one half state $\Psi$. The rotation is represented by the unitary transformation $\hat{U}_z(\varphi_0)$. Express the expectation value of the $x$-component of spin in the transformed state $\Psi'$ in terms of the untransformed states. Hence, show that

$$ ( \Psi^\dagger \hat{S}_x \Psi' ) = \cos \varphi_0 \left( \Psi^\dagger \hat{S}_x \Psi \right) - \sin \varphi_0 \left( \Psi^\dagger \hat{S}_y \Psi \right) $$

(2185)

4.9.10 Solution 113

The transformed state is given by $\Psi'$ where

$$ \Psi' = \hat{U}_z(\varphi_0) \Psi $$

(2186)

Hence, the expectation value is given by

$$ \Psi'^\dagger \hat{S}_x \Psi' = \Psi^\dagger \hat{U}_z^\dagger(\varphi_0) \hat{S}_x \hat{U}_z(\varphi_0) \Psi $$

(2187)

In matrix form, we have

$$ \Psi'^\dagger \hat{S}_x \Psi' = \frac{\hbar}{2} \Psi^\dagger \left( \begin{array}{cc} \exp[+i\varphi_0] & 0 \\ 0 & \exp[-i\varphi_0] \end{array} \right) \left( \begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \right) \left( \begin{array}{cc} \exp[-i\varphi_0] & 0 \\ 0 & \exp[+i\varphi_0] \end{array} \right) \Psi $$

$$ = \Psi^\dagger \left( \begin{array}{cc} 0 & \exp[+i\varphi_0] \\ \exp[-i\varphi_0] & 0 \end{array} \right) \Psi $$

$$ = \cos \varphi_0 \left( \Psi^\dagger \hat{S}_x \Psi \right) - \sin \varphi_0 \left( \Psi^\dagger \hat{S}_y \Psi \right) $$

(2188)

The expectation value of $\hat{S}_y$ also changes like the $y$-component of a classical vector under rotation, as does the expectation value of $\hat{S}_z$. The expectation value of $\hat{S}_z$ doesn’t change since the rotation is about the $z$-axis. Hence, the expectation value of $\hat{S}$ of any arbitrary state transforms like a vector.

The Vector Character of Spin One Particles

For a particle with spin one, the corresponding (local) spin rotation operator can be represented as

$$ \hat{U}_e(\varphi_0) = \exp \left[ -\frac{i}{\hbar} \varphi_0 \hat{e} \cdot \hat{S} \right] $$

$$ = \hat{I} - i \sin \varphi_0 \left( \frac{\hat{e} \cdot \hat{S}}{\hbar} \right) + \left( \cos \varphi_0 - 1 \right) \left( \frac{\hat{e} \cdot \hat{S}}{\hbar} \right)^2 $$

(2189)
Therefore, the transformation $\hat{U}_z(\varphi_0)$ which produces a rotation of the spin of a spin one particle through the angle $\varphi_0$ about the $z$-axis is given by

$$\hat{U}_z(\varphi_0) = \begin{pmatrix} \exp[ -i \varphi_0 ] & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \exp[ + i \varphi_0 ] \end{pmatrix} \quad (2190)$$

in the basis formed by the set of eigenstates of $\hat{S}_z$. Likewise, the forms of the operators $\hat{U}_y$ and $\hat{U}_x$ that produce spin rotations about the $y$ and $x$ axes are given by

$$\hat{U}_y(\varphi_0) = \begin{pmatrix} \frac{1}{2} ( 1 + \cos \varphi_0 ) & \frac{1}{\sqrt{2}} \sin \varphi_0 & \frac{1}{2} ( 1 - \cos \varphi_0 ) \\ \frac{1}{\sqrt{2}} \sin \varphi_0 & \cos \varphi_0 & -\frac{1}{\sqrt{2}} \sin \varphi_0 \\ \frac{1}{2} ( 1 - \cos \varphi_0 ) & \frac{1}{\sqrt{2}} \sin \varphi_0 & \frac{1}{2} ( 1 + \cos \varphi_0 ) \end{pmatrix} \quad (2191)$$

and

$$\hat{U}_x(\varphi_0) = \begin{pmatrix} \frac{1}{2} ( 1 + \cos \varphi_0 ) & \frac{1}{\sqrt{2}} \sin \varphi_0 & \frac{1}{2} ( 1 - \cos \varphi_0 - 1 ) \\ -\frac{1}{\sqrt{2}} \sin \varphi_0 & \cos \varphi_0 & -\frac{1}{\sqrt{2}} \sin \varphi_0 \\ \frac{1}{2} ( \cos \varphi_0 - 1 ) & -\frac{1}{\sqrt{2}} \sin \varphi_0 & \frac{1}{2} ( 1 + \cos \varphi_0 ) \end{pmatrix} \quad (2192)$$

The operator $\hat{Q}$ given by

$$\hat{Q} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 0 & 1 \\ -i & 0 & -i \\ 0 & \sqrt{2} & 0 \end{pmatrix} \quad (2193)$$

represents a unitary transformation. This operator transforms states from the basis formed by the eigenstates of $\hat{S}_z$ ($\Psi$) to a new basis ($\tilde{\Psi}$) via

$$\begin{pmatrix} \tilde{\Psi}_x \\ \tilde{\Psi}_y \\ \tilde{\Psi}_z \end{pmatrix} = \hat{Q} \begin{pmatrix} \Psi_{+1} \\ \Psi_0 \\ \Psi_{-1} \end{pmatrix} \quad (2194)$$

The $z$-component of the transformed spin operator is given by

$$\tilde{\hat{S}}_z = \hat{Q} \hat{S}_z \hat{Q}^\dagger$$

$$= \frac{\hbar}{2} \begin{pmatrix} -1 & 0 & 1 \\ -i & 0 & -i \\ 0 & \sqrt{2} & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & i & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & i & 0 \end{pmatrix}$$

$$= \hbar \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad (2195)$$

On applying the unitary transform to the $y$-component of the spin operator

$$\tilde{\hat{S}}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad (2196)$$
one obtains the transformed operator as
\[
\tilde{S}_y = \hat{Q} \hat{S}_y \hat{Q}^\dagger
\]
\[
= \frac{\hbar}{2} \begin{pmatrix}
-1 & 0 & 1 \\
-\imath & 0 & -\imath \\
0 & \sqrt{2} & 0
\end{pmatrix}
\begin{pmatrix}
0 & -\frac{\imath}{\sqrt{2}} & 0 \\
\frac{\imath}{\sqrt{2}} & 0 & -\frac{\imath}{\sqrt{2}} \\
0 & \frac{\imath}{\sqrt{2}} & 0
\end{pmatrix}
\begin{pmatrix}
-1 & \imath & 0 \\
0 & 0 & 0 \\
\imath & 0 & 0
\end{pmatrix}
\]
\[
= \hbar \begin{pmatrix}
0 & 0 & \imath \\
0 & 0 & 0 \\
-\imath & 0 & 0
\end{pmatrix}
\]
(2197)

Likewise, applying the transformation to the \(x\)-component
\[
\tilde{S}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix}
\]
(2198)

one obtains the transformed operator
\[
\tilde{S}_x = \hat{Q} \hat{S}_x \hat{Q}^\dagger
\]
\[
= \frac{\hbar}{2} \begin{pmatrix}
-1 & 0 & 1 \\
-\imath & 0 & -\imath \\
0 & \sqrt{2} & 0
\end{pmatrix}
\begin{pmatrix}
0 & \frac{1}{\sqrt{2}} & 0 \\
\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\
0 & \frac{1}{\sqrt{2}} & 0
\end{pmatrix}
\begin{pmatrix}
-1 & \imath & 0 \\
0 & 0 & 0 \\
\imath & 0 & 0
\end{pmatrix}
\]
\[
= \hbar \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & \imath & 0
\end{pmatrix}
\]
(2199)

Therefore, the \((j, k)\) matrix element of the transformed spin operator \(\tilde{S}_i\) is simply given by
\[
(\tilde{S}_i)_{j,k} = -\imath \hbar \varepsilon^{i,j,k}
\]
(2200)

where \(\varepsilon^{i,j,k}\) is the Levi-Civita symbol. Since the transformed and untransformed operators are related via a unitary transformation, the transformed operators obey the same commutation relations as the untransformed operators. In particular, the squared magnitude of the transformed spin operator
\[
\tilde{S}^2 = \tilde{S}_x^2 + \tilde{S}_y^2 + \tilde{S}_z^2
\]
\[
= 2 \hbar^2 \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]
(2201)

is diagonal and, therefore, commutes with all other spin operators.

The form of the spin rotation operator \(\tilde{U}_e(\varphi_0)\) in the new basis is given by
\[
\tilde{U}_e(\varphi_0) = \hat{Q} \hat{U}_e(\varphi_0) \hat{Q}^\dagger
\]
(2202)
where
\[
\tilde{U}_e(\varphi_0) = \exp \left[ -i \frac{\varphi_0}{\hbar} \hat{e} \cdot \tilde{S} \right]
\]
\[
= \hat{1} - i \sin \varphi_0 \left( \frac{\hat{e} \cdot \tilde{S}}{\hbar} \right) + \left( \cos \varphi_0 - 1 \right) \left( \frac{\hat{e} \cdot \tilde{S}}{\hbar} \right)^2
\]
(2203)

In particular, the matrix which describes a rotation about the \(z\)-axis is given by
\[
\tilde{U}_z(\varphi_0) = \begin{pmatrix}
\cos \varphi_0 & -\sin \varphi_0 & 0 \\
\sin \varphi_0 & \cos \varphi_0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]
(2204)
The matrix which describes a rotation about the \(y\)-axis becomes
\[
\tilde{U}_y(\varphi_0) = \begin{pmatrix}
\cos \varphi_0 & 0 & \sin \varphi_0 \\
0 & 1 & 0 \\
-\sin \varphi_0 & 0 & \cos \varphi_0
\end{pmatrix}
\]
(2205)
and a rotation about the \(x\)-axis is produced by
\[
\tilde{U}_x(\varphi_0) = \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \varphi_0 & -\sin \varphi_0 \\
0 & \sin \varphi_0 & \cos \varphi_0
\end{pmatrix}
\]
(2206)

These transformations are recognized as being identical to the expressions for the transformations of vectors under rotations through a finite angle \(\varphi_0\) about the Cartesian axes. A more general (local) rotation of the spin one wave function can be built up from infinitesimal rotations about an arbitrary axis. Under an infinitesimal rotation \(\delta \varphi_0\) about an arbitrary axis \(\hat{e}\), the spin one wave function changes (locally) according to
\[
\begin{pmatrix}
\tilde{\Psi}'_x \\
\tilde{\Psi}'_y \\
\tilde{\Psi}'_z
\end{pmatrix} = \left[ \hat{1} - i \delta \varphi_0 \left( \frac{\hat{e} \cdot \tilde{S}}{\hbar} \right) \right] \begin{pmatrix}
\tilde{\Psi}_x \\
\tilde{\Psi}_y \\
\tilde{\Psi}_z
\end{pmatrix}
\]
(2207)

In terms of the components, the transformation is expressed as
\[
\tilde{\Psi}'_i = \sum_j \left[ \delta_{i,j} - i \sum_k \delta \varphi_0 \left( \frac{\hat{e}_k \cdot \tilde{S}_k}{\hbar} \right)_{i,j} \right] \tilde{\Psi}_j
\]
\[
= \sum_j \left[ \delta_{i,j} - \sum_k \delta \varphi_0 \hat{e}_k \varepsilon^{k,i,j} \right] \tilde{\Psi}_j
\]
(2208)

If one interprets the components of wave function of the spin one particle as a vector in the same space as ordinary vectors, then on re-labelling and re-arranging the indices, one finds
\[
- \sum_{j,k} \hat{e}_k \varepsilon^{k,i,j} \tilde{\Psi}_j = \sum_{j,k} \hat{e}_j \varepsilon^{i,j,k} \tilde{\Psi}_k
\]
Rotation of a Vector Field

Figure 120: The unitary operator $\hat{U}_z(\varphi)$ produces a rotation of the spin one wave function through an angle of $\varphi$ around the $z$-axis. The rotation operator $\hat{R}_z$ acts on the coordinates and transforms the point $\mathbf{r}$ to the point $\mathbf{r}'$, i.e. $\mathbf{r}' = \hat{R}_z \mathbf{r}$. Under the rotation, the vector wave function $\Psi(\mathbf{r})$ is transformed to $\Psi'(\mathbf{r})$, such that the value of $\Psi'$ at the point $\mathbf{r}'$ is the same as the value of $\Psi$ at the point $\mathbf{r}$. However, the rotation also rotates the direction of the vector field by $\varphi$. Therefore, $\Psi'(\mathbf{r}') = \exp[-i\varphi \hat{S}_z] \Psi(\mathbf{r})$ so, $\Psi'(\mathbf{r}) = \exp[-i\varphi \hat{S}_z] \Psi(\hat{R}_z^{-1} \mathbf{r})$.

The unitary operator which transforms the wave function is then determined by $\Psi'(\mathbf{r}) = \hat{U}(\varphi) \Psi(\mathbf{r}) = \exp[-i\varphi \hat{S}_z] \Psi(\hat{R}_z^{-1} \mathbf{r})$.

Therefore, the spin one wave function transforms under rotations via

$$\tilde{\Psi}' = \left[ \tilde{\Psi} + \delta\varphi_0 \left( \hat{e} \wedge \tilde{\Psi} \right) \right]$$

This is the same transformation law obeyed by a vector under a rotation through an infinitesimal angle $\delta\varphi_0$ about the axis $\hat{e}$. This suggests that the wave function of a spin one particle should be considered as a vector field.

If the spin one wave function $\Psi$ has a vector representation, then its decomposition in terms of Cartesian unit vectors $\hat{e}_i$ and the Cartesian components $\Psi_i$ is given by

$$\Psi = \hat{e}_x \Psi_x + \hat{e}_y \Psi_y + \hat{e}_z \Psi_z$$
Sometimes it may be convenient to express the vector field in terms of components $\Psi_m$ which have definite values of $\hat{S}_z$. The components of the vector in the two basis sets are related by

$$\Psi_m = \hat{Q} \Psi_i$$

(2212)

or, equivalently, in matrix form by

$$\begin{pmatrix} \Psi_{+1} \\ \Psi_0 \\ \Psi_{-1} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & i & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & i & 0 \end{pmatrix} \begin{pmatrix} \Psi_x \\ \Psi_y \\ \Psi_z \end{pmatrix}$$

(2213)

### 4.9.11 Exercise 114

Find the spin states that are the simultaneous eigenstates of the operators $\hat{S}_z$ and $\hat{S}^2$.

Show that, with an appropriate choice of phase, these states can be mapped onto the circularly polarized states $\tilde{\Psi}_m$ which are expressed in terms of the Cartesian basis by

$$\begin{align*}
\tilde{\Psi}_{+1} &= -\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix} \\
\tilde{\Psi}_0 &= \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \\
\tilde{\Psi}_{-1} &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}
\end{align*}$$

(2214)

### 4.9.12 Solution 114

On expressing the eigenvectors in the form

$$\tilde{\Psi}_m = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

(2215)
one finds that the form of the eigenstates trivially satisfy the eigenvalue equation for $\tilde{S}^2$. The eigenvalue equation for the operator $\tilde{S}_z$ is non-trivial and can be written as

$$\hat{h} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \lambda_m \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$ (2216)

The eigenvalues $\lambda_m$ are determined from the zeros of the determinant

$$\left| \begin{array}{ccc} -\lambda & -i & 0 \\ i & -\lambda & 0 \\ 0 & 0 & -\lambda \end{array} \right| = 0$$ (2217)

which yield the solutions for $\lambda_m$ as $(1, 0, -1)$. The eigenvectors for $\lambda = \pm 1$ are determined from the equations

$$\hat{h} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \alpha_{\pm 1} \\ \beta_{\pm 1} \\ \gamma_{\pm 1} \end{pmatrix} = \pm \begin{pmatrix} \alpha_{\pm 1} \\ \beta_{\pm 1} \\ \gamma_{\pm 1} \end{pmatrix}$$ (2218)

which yields the equations

$$-i \beta_{\pm 1} = \pm \alpha_{\pm 1}$$
$$i \alpha_{\pm 1} = \pm \beta_{\pm 1}$$
$$0 = \pm \gamma_{\pm 1}$$ (2219)

Since these are homogeneous linear equations, the (un-normalized) solutions can be found by choosing $\alpha_{\pm 1} = 1$. The eigenvector corresponding to $\lambda_m = 0$ is given by

$$-i \beta_0 = 0$$
$$i \alpha_0 = 0$$
$$0 = 0$$ (2220)

which can be solved by choosing $\gamma_0 = 1$. On normalizing the above set of eigenstates, one finds that they can be expressed in forms

$$\tilde{\Psi}_{+1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix}$$

$$\tilde{\Psi}_{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}$$

$$\tilde{\Psi}_0 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$ (2221)
These correspond to the given set of eigenstates, except for the difference in the choice of phase for $\Psi_1$. The desired phase could have been arrived at by choosing $\alpha_1 = -1$.

---

**Exercise 115**

Consider a general rotation of a vector through an angle $\theta$ in $d$ dimensions. Show that trace of the rotation operator $\hat{U}(\theta)$ is given by

$$\text{Trace} \; \hat{U}(\theta) = (d - 2) + 2 \cos \theta$$

---

When expressed in terms of the angular momentum basis, an arbitrary vector $\Psi$ has the decomposition

$$\Psi = \sum_{m=-1}^{m=+1} \hat{e}_m \Psi_m$$

which defines the appropriate angular momentum basis vectors $\hat{e}_m$. The basis vectors $\hat{e}_m$ are given in terms of the Cartesian basis vectors via

$$\hat{e}_{+1} = -\frac{1}{\sqrt{2}} (\hat{e}_x + i \hat{e}_y)$$
$$\hat{e}_0 = \hat{e}_z$$
$$\hat{e}_{-1} = \frac{1}{\sqrt{2}} (\hat{e}_x - i \hat{e}_y)$$

These complex basis vectors are the circular polarization vectors for a spin one particle. The set of complex basis vectors $\hat{e}_m$ for the angular momentum representation satisfy

$$\hat{e}_m^* = (-1)^m \hat{e}_{-m}$$

and their scalar products are given by

$$\hat{e}_m^* \cdot \hat{e}_{m'} = (-1)^m \hat{e}_{-m} \cdot \hat{e}_{m'} = \delta_{m,m'}$$

The components of the vector $\Psi$ would then be found from

$$\Psi_m = \hat{e}_m^* \cdot \Psi$$

A similar type of decomposition in terms of circularly polarized basis vectors is frequently applied to the vector wave function of the spin one photon.
4.9.13 Gauge Invariance

The Schrödinger equation for a charged particle in an electromagnetic field is given by

\[ i \hbar \frac{\partial}{\partial t} \Psi(r, t) = \left[ \frac{1}{2m} \left( -i \hbar \nabla - \frac{q}{c} A(r, t) \right)^2 + q \phi(r, t) \right] \Psi(r, t) \]  

(2228)

The vector and scalar potentials are invariant under the gauge transformations

\[ A(r, t) \rightarrow A'(r, t) = A(r, t) + \nabla \Lambda(r, t) \]
\[ \phi(r, t) \rightarrow \phi'(r, t) = \phi(r, t) - \frac{1}{c} \frac{\partial}{\partial t} \Lambda(r, t) \]  

(2229)

The primed and unprimed potentials are in different gauges, but represent the same physical system. The Schrödinger equation in the primed gauge is

\[ i \hbar \frac{\partial}{\partial t} \Psi'(r, t) = \left[ \frac{1}{2m} \left( -i \hbar \nabla - \frac{q}{c} A'(r, t) \right)^2 + q \phi'(r, t) \right] \Psi'(r, t) \]  

(2230)

where the primed wave function is given in terms of the unprimed wave function by

\[ \Psi(r, t) \rightarrow \Psi'(r, t) = \Psi(r, t) \exp \left[ i \frac{q}{\hbar c} \Lambda(r, t) \right] \]  

(2231)

and where the scalar field involved in the gauge transformation has been absorbed into the phase of the wave function.

The gauge transformation is produced by the unitary transformation \( U \) such that

\[ \Psi'(r, t) = U \Psi(r, t) \]
\[ U = \exp \left[ i \frac{q}{\hbar c} \Lambda(r, t) \right] \]  

(2232)

Then the Hamiltonians in the two gauges are connected via

\[ \hat{H}' = U \hat{H} U^\dagger - i \hbar U \frac{\partial}{\partial t} U^\dagger \]  

(2233)

as can be seen by examining

\[ i \hbar \frac{\partial}{\partial t} \Psi(r, t) = \hat{H} \Psi(r, t) \]  

(2234)

which on substituting

\[ \Psi(r, t) = U^\dagger \Psi'(r, t) \]  

(2235)
becomes
\[ U^\dagger i \hbar \frac{\partial}{\partial t} \Psi'(r, t) + i \hbar \left( \frac{\partial}{\partial t} U^\dagger \right) \Psi'(r, t) = \hat{H} U^\dagger \Psi'(r, t) \] (2236)

On utilizing the primed Schrödinger equation
\[ i \hbar \frac{\partial}{\partial t} \Psi'(r, t) = \hat{H}' \Psi'(r, t) \] (2237)

one has
\[ U^\dagger \hat{H}' \Psi'(r, t) + i \hbar \left( \frac{\partial}{\partial t} U^\dagger \right) \Psi'(r, t) = \hat{H} U^\dagger \Psi'(r, t) \] (2238)

This equation determines the time evolution of an arbitrary initial wave function \( \Psi'(r, t) \), and so we have an operator equation
\[ U^\dagger \hat{H}' + i \hbar \left( \frac{\partial}{\partial t} U^\dagger \right) = \hat{H} U^\dagger \] (2239)

which on pre-multiplying by \( U \) is identical to the relation between \( \hat{H} \) and \( \hat{H}' \).

We note that this gauge transformation leaves \( r \) and the velocity \( \hat{p} - \frac{q}{c} A(r, t) \) invariant. This can be seen as
\[ r' = U r U^\dagger = r \] (2240)

and
\[ \hat{p}' - \frac{q}{c} A'(r, t) = U \left( \hat{p} - \frac{q}{c} A(r, t) \right) U^\dagger \]
\[ = \hat{p} - \frac{q}{c} A(r, t) - \frac{q}{c} \nabla A(r, t) \]
\[ = \hat{p} - \frac{q}{c} A'(r, t) \] (2241)

Finally, as \( \hat{p}' = \hat{p} = -i \hbar \nabla \), the above quantity is gauge invariant as was to be proved. Thus, the Schrödinger equation is gauge invariant.

### 4.9.14 Exercise 116

Find the continuity equation for a charged particle in an electromagnetic field, and show that the appropriate probability current density \( j(r, t) \) and the charge density \( \rho(r, t) \) are gauge invariant.
4.9.15 Solution 116

The equation of motion for the wave function $\Psi$ is

\[
i \hbar \frac{\partial}{\partial t} \Psi = \left[ \frac{1}{2m} \left( \hat{p} - \frac{q}{c} A \right)^2 + q \phi \right] \Psi \quad (2242)
\]
or

\[
i \hbar \frac{\partial}{\partial t} \Psi = \left[ \frac{1}{2m} \left( - i \hbar \nabla - \frac{q}{c} A \right)^2 + q \phi \right] \Psi \quad (2243)
\]

and the complex conjugate $\Psi^*$ satisfies

\[-i \hbar \frac{\partial}{\partial t} \Psi^* = \left[ \frac{1}{2m} \left( + i \hbar \nabla - \frac{q}{c} A \right)^2 + q \phi \right] \Psi^* \quad (2244)\]

Multiplying the first equation by $\Psi^*$ and the second by $\Psi$, then subtracting the second from the first, one obtains

\[
i \hbar \frac{\partial}{\partial t} \left( \Psi^* \Psi \right) = -\frac{\hbar^2}{2m} \left[ \Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^* \right] + i \hbar \nabla \left( \frac{q}{mc} \Psi^* A(r,t) \Psi \right) \quad (2245)
\]

Thus, one has the continuity equation

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot j = 0 \quad (2246)
\]

but

\[
\rho(r,t) = \Psi^*(r,t) \Psi(r,t)
\]
\[
j(r,t) = \frac{\hbar}{mc} \Im \left[ \Psi^* \nabla \Psi - \Psi \nabla \Psi^* \right] - \frac{q}{mc} \Psi^*(r,t) A(r,t) \Psi(r,t) \quad (2247)
\]

The charge density $\rho(r,t)$ is gauge invariant, as under the gauge transformation one has

\[
\Psi(r,t) \rightarrow \Psi'(r,t) = \exp \left[ i \frac{q}{c \hbar} \Lambda(r,t) \right] \Psi(r,t) \quad (2248)
\]

and the phase factor drops out of the density.

In the current density, the gradient factor transforms as

\[
\Psi^* \nabla \Psi \rightarrow \Psi'^* \nabla \Psi' = \Psi^* \nabla \Psi + i \frac{q}{c \hbar} \Psi^* \left( \nabla \Lambda \right) \Psi \quad (2249)
\]
and the term involving the vector potential transform as

\[ \Psi^* A(r, t) \Psi \rightarrow \Psi'^* A'(r, t) \Psi' \quad (2250) \]

where

\[ \Psi'^* A'(r, t) \Psi' = \Psi^* A(r, t) \Psi + \Psi^* \nabla A(r, t) \Psi \quad (2251) \]

Thus, the factor in the current density involving \( \nabla A \) cancels, leaving \( j(r, t) \) gauge invariant.

### 4.9.16 Galilean Boosts

A transformation to a uniformly moving reference frame is represented by a time-dependent unitary transform. The (passive) transformation from a stationary reference frame to one moving with a velocity \( \vec{u} \) is represented by the unitary matrix \( \hat{U} \) defined by

\[ \hat{U} = \exp \left[ -\frac{i}{\hbar} \vec{u} \cdot (m \vec{r} - \hat{p} t) \right] \quad (2252) \]

The above Galilean transformation is derived as the non-relativistic limit of a Lorentz boost, which is just a (static) rotation in space-time. However, in the non-relativistic limit the operator \( \hat{H} \) is replaced by the rest mass energy \( mc^2 \).

The above transformation represents a Galilean boost since it has the effect that

\[ \begin{align*}
    r' &= \hat{U} r \hat{U}^\dagger = r + u t \\
    \hat{p}' &= \hat{U} \hat{p} \hat{U}^\dagger = \hat{p} + m u
\end{align*} \quad (2253) \]

as expected for a transformation to a reference frame moving with constant velocity.

The Hamiltonian is the generator of time-translations and, therefore, a state \( \Psi \) evolves according to the prescription

\[ \Psi^* \left( i \frac{\hbar}{\partial t} \right) \Psi = \Psi^* \hat{H} \Psi \quad (2254) \]

on transforming from \( \Psi \) to \( \Psi' \) via

\[ \Psi' = \hat{U} \Psi \quad (2255) \]

one finds that

\[ \Psi'^* \left( i \frac{\hbar}{\partial t} \right) \Psi' = \Psi'^* \hat{U} \hat{H} \hat{U}^\dagger \Psi' - i \hbar \Psi'^* \hat{U} \frac{\partial}{\partial t} \hat{U}^\dagger \Psi' \quad (2256) \]
which defines the transformed Hamiltonian $\hat{H}'$ as

$$\hat{H}' = \hat{U} \hat{H} \hat{U}^\dagger - i \hbar \hat{U} \frac{\partial}{\partial t} \hat{U}^\dagger$$

$$= \hat{U} \hat{H} \hat{U}^\dagger - u \cdot \hat{p}$$

(2257)

Thus, the energy eigenvalues are related via

$$E' = E - u \cdot \hat{p}$$

(2258)

which is recognized as the non-relativistic limit of the Lorentz transformation of the time-like component of a four-vector

$$E' = \frac{E - u \cdot \hat{p}}{\sqrt{1 - \left(\frac{u}{c}\right)^2}}$$

(2259)

For a Hamiltonian in the stationary reference frame of the form

$$\hat{H} = \frac{1}{2m} \left( \hat{p} - \frac{q}{c} A(r) \right)^2 + V(r)$$

(2260)

the Hamiltonian in the moving reference frame has the form

$$\hat{H}' = \frac{1}{2m} \left( \hat{p} + m u - \frac{q}{c} A(r + ut) \right)^2 + q \phi(r + ut) - u \cdot \hat{p}$$

$$= \frac{1}{2m} \left( \hat{p} - \frac{q}{c} A(r + ut) \right)^2 + q \phi(r + ut) - \frac{q}{c} u \cdot A(r + ut) + \frac{m u^2}{2}$$

(2261)

when expressed in terms of the untransformed position and momentum operators. In the above equations we have ignored any explicit time-dependence of the electromagnetic potentials. The transformed Hamiltonian is increased by an additive constant equal to the kinetic energy of the boost. Since we are working in the non-relativistic limit, this additive constant has no physical consequence. The vector potential is transformed according to

$$A(r) \rightarrow A'(r') = A(r + ut)$$

(2262)

which is the same as in the static reference frame (except that it is evaluated at the transformed position $r' = r + ut$), but the scalar potential is transformed according to

$$\phi(r) \rightarrow \phi'(r') = \phi(r') - \frac{1}{c} u \cdot A(r')$$

(2263)

This has the implication that the magnetic field in the moving frame defined by

$$B'(r') = \nabla \wedge A(r')$$

(2264)

is simply given by the magnetic field at the transformed position

$$B'(r') = B(r + ut)$$

(2265)
On the other hand, the transformed electric field defined by

\[
E'(\mathbf{r}') = -\nabla \phi'(\mathbf{r}') - \frac{1}{c} \frac{\partial}{\partial t} A'(\mathbf{r}')
\]  

is evaluated as

\[
E'(\mathbf{r}') = -\nabla \phi(\mathbf{r}') + \frac{1}{c} \nabla \left( \mathbf{u} \cdot A(\mathbf{r}') \right) - \frac{1}{c} \left( \mathbf{u} \cdot \nabla \right) A(\mathbf{r}') - \frac{1}{c} \frac{\partial}{\partial t} A(\mathbf{r}')
\]  

(2267)

where the last term is a partial derivative with respect to \( t \) at constant \( \mathbf{r}' = \mathbf{r} + \mathbf{u} t \).

On using the identity

\[
\nabla \left( \mathbf{u} \cdot A \right) - \left( \mathbf{u} \cdot \nabla \right) A = \mathbf{u} \wedge \left( \nabla \wedge A \right)
\]  

(2268)

one obtains the transformed electric field as

\[
E'(\mathbf{r}') = E(\mathbf{r}') + \frac{1}{c} \mathbf{u} \wedge B(\mathbf{r}')
\]  

(2269)

which is as might have been expected.

5 The Rotating Planar Oscillator

To end this first semester of quantum mechanics, we shall look at a simple system and show that there are still some surprises to be found in separable systems. Usually systems are neither separable, nor can their excitations be found analytically. Most systems have to be solved numerically and it is expected that their dynamics may sometimes show chaotic motion.

We shall consider a two-dimensional simple harmonic oscillator, that is slowly being rotated about the origin with frequency \( \Omega \). The classical Lagrangian is given by

\[
L = \frac{m}{2} \left( \dot{r}^2 + r^2 (\dot{\varphi} - \Omega)^2 \right) - \frac{m}{2} \omega^2 r^2
\]  

(2270)

The generalized momenta are given by

\[
p_r = m \dot{r} \\
p_{\varphi} = m r^2 (\dot{\varphi} - \Omega)
\]  

(2271)

Therefore, the classical Hamiltonian can be expressed as

\[
H = p_r \dot{r} + p_{\varphi} \dot{\varphi} - L \\
= \frac{p_r^2}{2m} + \frac{p_{\varphi}^2}{2m r^2} + p_{\varphi} \Omega + \frac{m}{2} \omega^2 r^2
\]  

(2272)
In two dimensions, the angular momentum $p_\varphi$ (which we shall now denote by $L$) is masquerading as a scalar. Hence, we shall write the Hamiltonian as

$$H = \frac{p_\varphi^2}{2m} + \frac{L^2}{2mr^2} + L\Omega + \frac{m}{2}\omega^2 r^2$$  \hspace{1cm} (2273)

We shall quantize this classical Hamiltonian and shall determine the energy eigenfunctions in the form

$$\Psi_{n,l}(r,\varphi) = R_{n,l}(r) \frac{1}{\sqrt{2\pi}} \exp\left(i l \varphi\right)$$  \hspace{1cm} (2274)

where $l$ is a positive or negative integer. The radial part of the energy eigenvalue equation takes the form

$$-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial R_{n,l}}{\partial r} \right) + \left( \frac{\hbar^2 l^2}{2mr^2} + \hbar l \Omega + \frac{m}{2}\omega^2 r^2 \right) R_{n,l} = E_{n,l} R_{n,l}$$  \hspace{1cm} (2275)

We shall introduce a dimensionless variable $\rho$ via the definition

$$\rho = \sqrt{\frac{m\omega}{\hbar}} r$$  \hspace{1cm} (2276)

and re-write the radial equation as

$$\frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial R_{n,l}}{\partial \rho} \right) + \left( \frac{l^2}{\rho^2} + 2\frac{l}{\omega} + \rho^2 \right) R_{n,l} = \frac{2}{\hbar\omega} E_{n,l} R_{n,l}$$  \hspace{1cm} (2277)

For $\Omega = 0$, the radial equation can easily be solved by using the operator algebra of raising and lowering operators. The raising operators are expressed as

$$\hat{A}_{\uparrow}^l = -\left( \frac{\partial}{\partial \rho} + \frac{1}{2\rho} \right) + \left( \rho - \frac{2l+1}{2\rho} \right)$$  \hspace{1cm} (2278)

and the lowering operators are defined as the Hermitean conjugate operators\textsuperscript{43}

$$\hat{A}_l = \left( \frac{\partial}{\partial \rho} + \frac{1}{2\rho} \right) + \left( \rho - \frac{2l+1}{2\rho} \right)$$  \hspace{1cm} (2279)

The commutator of the raising and lowering operator is evaluated as

$$[\hat{A}_{\uparrow}^l, \hat{A}_l] = -2 - \frac{2l+1}{\rho^2}$$  \hspace{1cm} (2280)

\textsuperscript{43}The operators contain terms that depend on the dimensionality. In $d$ dimensions, the corresponding pair of Hermitean conjugate operators are given by

$$\hat{A}_{\uparrow}^l = -\left( \frac{\partial}{\partial \rho} + \frac{d-1}{2\rho} \right) + \left( \rho - \frac{2l+d-1}{2\rho} \right)$$

and

$$\hat{A}_l = \left( \frac{\partial}{\partial \rho} + \frac{d-1}{2\rho} \right) + \left( \rho - \frac{2l+d-1}{2\rho} \right)$$
The product of the lowering and raising operators is evaluated as
\[
\hat{A}_l^\dagger \hat{A}_l = -\frac{\partial^2}{\partial \rho^2} - \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{l^2}{\rho^2} + \rho^2 - 2 \left( l + 1 \right) \tag{2281}
\]
which has a form similar to the left-hand side of the radial equation\textsuperscript{44}. On using the commutator in eqn(2280), one finds that the product of the lowering and raising operators taken in opposite order is given by
\[
\hat{A}_l \hat{A}_l^\dagger = -\frac{\partial^2}{\partial \rho^2} - \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{(l + 1)^2}{\rho^2} + \rho^2 - 2 \tag{2283}
\]
The dimensionless form of radial equation is expressed as
\[
\hat{H}_l R_{n_r,l} = 2 \frac{E_{n_r,l}}{\hbar \omega} R_{n_r,l} \tag{2284}
\]
where the dimensionless effective Hamiltonian for angular momentum \( l \) is given by
\[
\hat{H}_l = \left( \hat{A}_l^\dagger \hat{A}_l + 2 \left( l + 1 \right) \right) \tag{2285}
\]
and the effective Hamiltonian for angular momentum \( l + 1 \) is given by
\[
\hat{H}_{l+1} = \left( \hat{A}_l \hat{A}_l^\dagger + 2 \right) \tag{2286}
\]
By using the radial equation in the form
\[
\hat{H}_l \left( \hat{A}_l^\dagger \hat{A}_l + 2 \left( l + 1 \right) \right) R_{n_r,l} = 2 \frac{E_{n_r,l}}{\hbar \omega} \hat{A}_l R_{n_r,l} \tag{2287}
\]
and then on pre-multiplying by \( \hat{A}_l \), one finds
\[
\hat{A}_l \left( \hat{A}_l^\dagger \hat{A}_l + 2 \left( l + 1 \right) \right) R_{n_r,l} = 2 \frac{E_{n_r,l}}{\hbar \omega} \hat{A}_l R_{n_r,l} \tag{2288}
\]
\textsuperscript{44}In \( d \) dimensions, the commutator of the raising and lowering operators is evaluated
\[
\left[ \hat{A}_l^\dagger, \hat{A}_l \right] = -2 - \frac{2 l + d - 1}{\rho^2}
\]
and the product of the operators is given by
\[
\hat{A}_l^\dagger \hat{A}_l = -\frac{\partial^2}{\partial \rho^2} - \frac{d-1}{\rho} \frac{\partial}{\partial \rho} + \frac{l \left( l + d - 2 \right)}{\rho^2} + \rho^2 - \left( 2 l + d \right) \tag{2282}
\]
Hence, we have shown that $\hat{A}_l R_{n_r,l}$ is an eigenstate of $\hat{H}_{l+1}$ since

$$\hat{H}_{l+1} \hat{A}_l R_{n_r,l} = 2 \left( \frac{E_{n_r,l}}{\hbar \omega} - 1 \right) \hat{A}_l R_{n_r,l} \quad (2289)$$

Therefore, the lowering operator $\hat{A}_l$ acting on $R_{n_r,l}$ produces another energy eigenfunction with indices $(n_r - 1, l + 1)$

$$\hat{A}_l R_{n_r,l} \propto R_{n_r-1,l+1} \quad (2290)$$

and with energy eigenvalue given by

$$E_{n_r-1,l+1} = E_{n_r,l} - \hbar \omega \quad (2291)$$

Since the energy is bounded from below there is a minimum value of $n_r$ (defined as $n_r = 0$), so that the lowering operator acting on this state with $n_r = 0$ vanishes

$$\hat{A}_l R_{0,l} = 0 \quad (2292)$$

On using this condition in eqn(2287), one finds the energy eigenvalue equation simplifies to

$$(l + 1) R_{0,l} = \frac{E_{0,l}}{\hbar \omega} R_{0,l} \quad (2293)$$

Hence, the energy eigenvalues for the states with $n_r = 0$ are given by

$$E_{0,l} = \hbar \omega \left( l + 1 \right) \quad (2294)$$

The radial eigenfunctions are found from the condition

$$\hat{A}_l R_{0,l} = 0$$

$$(\frac{\partial}{\partial \rho} + \rho - \frac{l}{\rho}) R_{0,l} = 0 \quad (2295)$$

which can be re-expressed as

$$\frac{(\partial R_{0,l})}{R_{0,l}} = -\rho + \frac{l}{\rho} \quad (2296)$$

This can be integrated to yield

$$R_{0,l} = C \rho^l \exp \left[ -\frac{\rho^2}{2} \right] \quad (2297)$$

The above form of the energy eigenfunction is also found for the isotropic $d$-dimensional harmonic oscillator, and the energy eigenvalue corresponding to this eigenfunction is given by

$$E_{0,l} = \hbar \omega \left( l + \frac{d}{2} \right) \quad (2298)$$
The radial eigenfunctions for larger values of \( n_r \) can be obtained from the action of the raising operators. This can be seen by considering the radial equation with angular momentum \( l + 1 \)

\[
\hat{H}_{l+1} R_{n_r, l+1} = 2 \frac{E_{n_r, l+1}}{\hbar \omega} R_{n_r, l+1}
\]

\[
\left( \hat{A}_l \hat{A}_l^\dagger + 2 l \right) R_{n_r, l+1} = 2 \frac{E_{n_r, l+1}}{\hbar \omega} R_{n_r, l+1}
\] (2299)

and then pre-multiplying by the raising operator \( \hat{A}_l^\dagger \)

\[
\hat{A}_l^\dagger \left( \hat{A}_l \hat{A}_l^\dagger + 2 l \right) R_{n_r, l+1} = 2 \frac{E_{n_r, l+1}}{\hbar \omega} \hat{A}_l^\dagger R_{n_r, l+1}
\]

\[
\left( \hat{A}_l^\dagger \hat{A}_l + 2 l \right) \hat{A}_l^\dagger R_{n_r, l+1} = 2 \frac{E_{n_r, l+1}}{\hbar \omega} \hat{A}_l^\dagger R_{n_r, l+1}
\]

\[
\left( \hat{H}_l - 2 \right) \hat{A}_l^\dagger R_{n_r, l+1} = 2 \frac{E_{n_r, l+1}}{\hbar \omega} \hat{A}_l^\dagger R_{n_r, l+1}
\] (2300)

Hence, we have

\[
\hat{H}_l \hat{A}_l^\dagger R_{n_r, l+1} = 2 \left( \frac{E_{n_r, l+1}}{\hbar \omega} + 1 \right) \hat{A}_l^\dagger R_{n_r, l+1}
\] (2301)

so the raising operator acting on a radial eigenfunction with quantum numbers \((n_r, l+1)\) produces an eigenstate with quantum numbers \((n_r + 1, l)\) and eigenvalue

\[
E_{n_r+1, l} = E_{n_r, l+1} + \frac{\hbar \omega}{2}
\] (2302)

Therefore, the eigenfunctions with higher values of \( n \) are found from

\[
R_{n_r+1, l} \propto \hat{A}_l^\dagger R_{n_r, l+1}
\] (2303)

The energy eigenvalues are found as

\[
E_{n_r, l} = \hbar \omega \left( 2 n_r + \left| l \right| + 1 \right)
\] (2304)

This completely solves for the energy spectrum and the energy eigenfunctions when \( \Omega = 0 \). The classical states can be recovered as coherent states, since the ratios of the rotational frequencies to the vibrational frequencies are rational\(^{45}\).

In the more general case, one finds

\[
E_{n_r, l} = \hbar \omega \left( 2 n_r + \left| l \right| + \frac{l \Omega}{\omega} + 1 \right)
\] (2305)

In the general case, the ratios of the frequencies are not rational. The energy spectrum can be plotted as a function of the de-tuning parameter $\nu$ defined by

$$\nu = \left( \frac{\Omega - \omega}{2\omega} \right)$$

(2306)

The spectrum is shown in fig(121). For negative rational values of $\nu$ the spectrum shows gaps. These gaps are related to the occurrence of periodic orbits. The gaps are easily seen in the higher energy portions of the spectrum, shown in fig(122). For $\nu = 0$ a catastrophe occurs, all the energy levels become infinitely degenerate and each group of levels is separated by the energy difference $2\hbar\omega$.

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Figure 122: The higher-energy eigenvalues for the rotated planar harmonic oscillator as a function of the de-tuning.

6 Dirac Formulation

Schrödinger introduced wave mechanics in which a quantum state was described in terms of a wave function and physical measurements were described by differential operators. On the other hand, Heisenberg introduced matrix mechanics in which states were represented by column vectors, similar to the column vectors used in our discussion of spin, and measurements were treated as matrices similar to the spin matrices. These two formulations of quantum mechanics are identical in physical content. The equivalence was first seen by Dirac and this led to his abstract formulation.

6.1 Dirac Notation

Dirac introduced an abstract notation for states and their duals, and also for the operators.
6.1.1 Bracket Notation

In the Dirac formulation, physical states are represented by the so-called kets, which are written as
\[ | \Psi > \] (2307)
These kets obey the principle of linear superposition
\[ | \Psi > = \sum_n C_n | \phi_n > \] (2308)
where \( C_n \) are complex numbers. Generally, if the discrete index \( n \) is supplemented by a continuous index\(^{47}\) denoted by \( \xi_n \), the superposition can be expressed in terms of a sum and an integral
\[ | \Psi > = \sum_n C_n | \phi_n > + \int d\xi C_\xi | \phi_\xi > \] (2309)

Dirac also introduced a dual space of bras. The bras are denoted as \( < \Psi | \) and are defined as the duals to the kets \( | \Psi > \). They are the mirror image of the ket states. More precisely, they are defined by the scalar products with the kets defined as a complex number given by
\[ ( < \Phi | ) | \Psi > = < \Phi | \Psi > \] (2310)
The scalar product is linear, so that
\[ < \Phi | ( C_1 | \Psi_1 > + C_2 | \Psi_2 > ) = C_1 < \Phi | \Psi_1 > + C_2 < \Phi | \Psi_2 > \] (2311)
A bra vector is completely defined when the scalar product with every ket is known. Thus, if the scalar product with every ket vector is zero, then the bra vector is also zero.
\[ < \Phi | \Psi > = 0 \quad \text{for all} \quad | \Psi > \] (2312)
then
\[ < \Phi | = 0 \] (2313)

We assume that there is a one to one correspondence between the bras and the kets. That is, the bra corresponding to the sum of the kets \( | \phi_1 > + | \phi_2 > \)
\(^{47}\)For example, if the set of states \( | \phi_n > \) corresponds to the eigenstates of some operator, the eigenvalue may have both discrete and continuous portions of its spectrum.
is the sum of the equivalent bras $< \phi_1 | + < \phi_2 |$. Also, the bra corresponding to the ket $C | \phi >$ is given by $C^* < \phi |$, which involves complex conjugation.

Because of this assumption, every physical state can also be represented by a bra as much as it can be represented by a ket.

The scalar product is defined such that the complex number equal to the scalar product

$$< \Phi | \Psi >$$  \hspace{1cm} (2314)

is related to the number given by the scalar product of the dual vectors

$$< \Psi | \Phi >$$  \hspace{1cm} (2315)

via complex conjugation. That is, we require that the scalar product satisfies

$$< \Phi | \Psi > = < \Psi | \Phi >^*$$  \hspace{1cm} (2316)

In particular, the normalization of a state can be defined as the scalar product with itself,

$$< \Psi | \Psi > = < \Psi | \Psi >^*$$  \hspace{1cm} (2317)

which must be real. We shall require that the scalar product be defined such that the normalization is both real number and positive

$$< \Psi | \Psi > \geq 0$$  \hspace{1cm} (2318)

Two states $| \Phi >$ and $| \Psi >$ are defined to be orthogonal if their scalar product is zero

$$< \Phi | \Psi > = 0$$  \hspace{1cm} (2319)

### 6.1.2 Operators

A physical measurement is described by an operator $\hat{A}$ which is defined by its effect on a ket, and in general, transforms a ket to another ket,

$$\hat{A} | \Psi > = | \Phi >$$  \hspace{1cm} (2320)
The operators are linear in that its effect on a linear superposition is expressed as a linear combination on the individual states

\[ \hat{A} \mid \Psi \rangle = \sum_n C_n \hat{A} \mid \phi_n \rangle \quad (2321) \]

The effect of an operator on a bra can be defined via the scalar product

\[ < \Phi \mid (\hat{A} \mid \Psi \rangle) = < \Phi \mid \hat{A} \mid \Psi \rangle \\
= ( < \Phi \mid \hat{A} \rangle \mid \Psi \rangle \quad (2322) \]

This defines the effect of the operator \( \hat{A} \) on the bra \( < \Phi \mid \),

\[ < \Phi \mid \hat{A} \]

6.1.3 Adjoint and Hermitean Operators

The Hermitean conjugate of an operator \( \hat{A} \) is defined as the operator \( \hat{A}^\dagger \) such that the bra

\[ < \Psi \mid \hat{A} \]

is equivalent to the ket

\[ \hat{A}^\dagger \mid \Psi \rangle \quad (2324) \]

for any state \( \mid \Psi \rangle \). In particular, this means that

\[ < \Psi \mid \hat{A} \mid \Phi \rangle = < \Phi \mid \hat{A}^\dagger \mid \Psi \rangle^* \quad (2326) \]

Physical operators are represented by Hermitean operators such that

\[ \hat{A}^\dagger = \hat{A} \]

(2327)

The eigenvalue equation of an operator \( \hat{A} \) is

\[ \hat{A} \mid \phi_n \rangle = a_n \mid \phi_n \rangle \quad (2328) \]

where \( a_n \) are the eigenvalues and \( \mid \phi_n \rangle \) are the eigenstates. It can be proved that the eigenstates of a Hermitean operator form a complete orthogonal set and their eigenvalues are real.
An arbitrary state can be represented as a linear superposition of a complete orthonormal set of states $|\phi_n\rangle$. That is, an arbitrary state $|\Psi\rangle$ is re-written in terms of the expansion

$$|\Psi\rangle = \sum_n C_n |\phi_n\rangle$$

(2329)

where, due to orthonormality of the complete set, the expansion coefficient is evaluated as

$$C_n = <\phi_n|\Psi>$$

(2330)

Thus, we have

$$|\Psi\rangle = \sum_n <\phi_n|\Psi>|\phi_n\rangle$$

(2331)

which can be re-arranged as

$$|\Psi\rangle = \sum_n |\phi_n\rangle <\phi_n|\Psi>$$

(2332)

Since $|\Psi\rangle$ is completely arbitrary, the relation is independent of $|\Psi\rangle$. Omitting the arbitrary state leads to the completeness relation, in which the identity operator $\hat{I}$ is written as

$$\hat{I} = \sum_n |\phi_n\rangle <\phi_n|$$

(2333)

**6.1.4 Representation of Operators**

An arbitrary operator $\hat{A}$ can be represented in much the same way. We define the operator via its effect on an arbitrary state $|\Psi\rangle$

$$\hat{A}|\Psi\rangle = |\Phi\rangle$$

(2334)

Then, with the analogous expression for $|\Phi\rangle$ with expansion coefficients $B_m$, we find that the effect of the operator is given by

$$\hat{A} \sum_n C_n |\phi_n\rangle = \sum_m B_m |\phi_m\rangle$$

(2335)

Taking the scalar product of the above equation with the bra $<\phi_m|$, one finds that the matrix elements of the operator $<\phi_m|\hat{A}|\phi_n\rangle$ satisfy the equation

$$<\phi_m|\hat{A}|\Psi\rangle = \sum_n <\phi_m|\hat{A}|\phi_n\rangle C_n$$

$$= B_m$$

(2336)
Inserting the expression for $C_n$, one finds that the effect of an operator on an arbitrary state $|\Psi>\rangle$ can be expressed directly in terms of the matrix elements

$$<\phi_m | \hat{A} | \Psi>\rangle = \sum_n \left( <\phi_m | \hat{A} | \phi_n>\right) <\phi_n | \Psi>\rangle = B_m$$

(2337)

Hence, we can use the expression for $B_m$ in the equation defining the effect of the operator

$$\hat{A} | \Psi>\rangle = \sum_m B_m | \phi_m>\rangle$$

$$= \sum_{m,n} | \phi_m>\rangle \left( <\phi_m | \hat{A} | \phi_n>\right) <\phi_n | \Psi>\rangle$$

(2338)

Thus, as $| \Psi>\rangle$ is arbitrary the above equation is independent of the choice of $| \Psi>\rangle$, so we may omit it. Hence, the operator $\hat{A}$ can be decomposed as

$$\hat{A} = \sum_{m,n} | \phi_m>\rangle \left( <\phi_m | \hat{A} | \phi_n>\right) <\phi_n |$$

(2339)

The operator is completely defined by its matrix elements between a complete set of states.

### 6.2 Representations

The position space states $|\mathbf{r}>\rangle$ are eigenstates of the Hermitean position operator $\hat{\mathbf{r}}$,

$$\hat{\mathbf{r}} | \mathbf{r}>\rangle = \mathbf{r} | \mathbf{r}>\rangle$$

(2340)

Due to the Hermiticity, the eigenvalues of $\hat{\mathbf{r}}$ are real. The orthogonality of the eigenstates are expressed as

$$<\mathbf{r} | \mathbf{r'}>\rangle = \delta^3(\mathbf{r} - \mathbf{r'})$$

(2341)

The completeness condition is expressed in terms of the identity operator $\hat{I}$, where

$$\hat{I} = \int d^3\mathbf{r} |\mathbf{r}>\rangle <\mathbf{r} |$$

(2342)

The position space representation associates a complex number $\Psi(\mathbf{r})$ (the wave function) with every scalar product of a state represented by a ket $| \Psi>\rangle$ and the bra representing a position state $<\mathbf{r} |$

$$<\mathbf{r} | \Psi>\rangle = \Psi(\mathbf{r})$$

(2343)
alternatively, one obtains the complex conjugate of the wave function from
\[
< \Psi | r > = \Psi^*(r) \quad \text{(2344)}
\]

A general scalar product can be evaluated using the completeness relation for the position states, which involves the identity operator
\[
\hat{I} = \int d^3 \mathbf{r} | \mathbf{r} > < \mathbf{r} |
\quad \text{(2345)}
\]
as
\[
< \Phi | \Psi > = \int d^3 \mathbf{r} < \Phi | \mathbf{r} > < \mathbf{r} | \Psi > = \int d^3 \mathbf{r} \Phi^*(\mathbf{r}) \Psi(\mathbf{r}) \quad \text{(2346)}
\]
Thus, the scalar product has a position space representation as the overlap operator.

The position space representation of an operator \( \hat{A} \) can also be found from the matrix elements between two arbitrary states, by inserting complete sets of states
\[
< \Phi | \hat{A} | \Psi > = \int d^3 \mathbf{r} < \Phi | \mathbf{r} > < \mathbf{r} | \hat{A} | \Psi > = \int d^3 \mathbf{r} \int d^3 \mathbf{r}' < \Phi | \mathbf{r} > < \mathbf{r} | \hat{A} | \mathbf{r}' > < \mathbf{r}' | \Psi > \quad \text{(2347)}
\]
The position space representation of the operator \( \hat{A} \) is given by
\[
< \mathbf{r} | \hat{A} | \mathbf{r}' >
\quad \text{(2348)}
\]
For a local operator, the operator only depends on the position variable and the derivative at one point in space, so we have
\[
< \mathbf{r} | \hat{A} | \mathbf{r}' > = \delta^3(\mathbf{r} - \mathbf{r}') A(\mathbf{r}'; - i \hbar \nabla') \quad \text{(2349)}
\]
Thus, on integrating over \( \mathbf{r} \) one obtains the usual expression
\[
< \Phi | \hat{A} | \Psi > = \int d^3 \mathbf{r}' < \Phi | \mathbf{r}' > A( \mathbf{r}'; - i \hbar \nabla') < \mathbf{r}' | \Psi > = \int d^3 \mathbf{r} \Phi^*(\mathbf{r}) A(\mathbf{r}'; - i \hbar \nabla') \Psi(\mathbf{r}) \quad \text{(2350)}
\]
In this expression, the differential operator \( A( \mathbf{r}'; - i \hbar \nabla') \) is that which appears in the usual formulation of Schrödinger’s wave mechanics.
6.3 Gram-Schmidt Orthogonalization

Given a complete set of normalized states $| \phi_m >$, that are not orthogonal, one can construct an orthonormal set $| \Psi_n >$ via the process of Gram-Schmidt orthogonalization.

This is achieved by taking the first state as

$$| \Psi_0 > = | \phi_0 >$$ (2351)

which is normalized to unity. The second state in our orthogonal set is constructed as

$$| \Psi_1 > = N_1 \left( | \phi_1 > - | \Psi_0 > < \Psi_0 | \phi_1 > \right)$$ (2352)

This second state is orthogonal to $| \Psi_0 >$ as can be seen by forming the scalar product, and noting that the first state is normalized to unity. The normalization of the second state $N_1$ is chosen such that this state is also normalized to unity.

The higher order states are found by orthogonalizing to the properly normalized states found earlier, i.e.,

$$| \Psi_n > = N_n \left( | \phi_n > - \sum_{m=0}^{m=n-1} | \Psi_m > < \Psi_m | \phi_n > \right)$$ (2353)

and finding the normalization $N_n$ constants before proceeding to find the next state. The normalization constants are given by

$$N_n^{-2} = 1 - \sum_{m=0}^{m=n-1} | < \Psi_m | \phi_n > |^2$$ (2354)

Hence, given any complete set of states, it is possible to transform them into an orthonormal set.
7 Appendices

A: Non-spreading probability densities

The spreading of a wave packet (such as a Gaussian) is a feature which is often found in quantum mechanics. Normalizable wave functions are interpretable in terms of the motion of a single particle. Non-normalizable wave functions should be thought of describing an ensemble of particles. There are only two non-spreading wave functions, the plane wave which corresponds to a uniform beam of particles with momentum $\hbar k$, and the Airy wave function which we shall discuss below.

The Airy wave function is given at $t = 0$ by

$$\Psi(x; 0) = \text{Ai}\left[ \frac{B x}{\hbar^3} \right]$$

which has the Fourier transform

$$\Phi(k; 0) = \frac{1}{\sqrt{2\pi}} \frac{\hbar^{\frac{2}{3}}}{B} \exp\left[i \frac{\hbar^2 k^3}{3 B^3} \right]$$

Hence, in momentum representation, the time-dependent wave function for free particles is given by

$$\Phi(k; t) = \frac{1}{\sqrt{2\pi}} \frac{\hbar^{\frac{2}{3}}}{B} \exp\left[i \left( \frac{\hbar^2 k^3}{3 B^3} - \frac{\hbar k^2}{2 m} t \right) \right]$$

Therefore, we find that the real-space wave function is given by the inverse Fourier transform

$$\Psi(x; t) = \frac{1}{2\pi} \frac{\hbar^{\frac{2}{3}}}{B} \int_{-\infty}^{\infty} dk \exp\left[i \left( k x + \frac{\hbar^2 k^3}{3 B^3} - \frac{\hbar k^2}{2 m} t \right) \right]$$

On changing the variable of integration from $k$ to $k'$

$$k \rightarrow k' = k - \frac{B^3}{2 m \hbar} t$$

one finds that the integration results in another Airy function. The result is

$$\Psi(x; t) = \text{Ai}\left[ \frac{B}{\hbar^2} \left( x - \frac{B^3 t^2}{4 m^2} \right) \right] \exp\left[i \frac{B^3 t}{2 m \hbar} \left( x - \frac{B^3 t^2}{6 m^2} \right) \right]$$

Therefore, the probability density is given by

$$|\Psi(x; t)|^2 = \text{Ai}^2\left[ \frac{B}{\hbar^2} \left( x - \frac{B^3 t^2}{4 m^2} \right) \right]$$
Figure 123: The initial probability density \(|\Psi(x;0)|^2\) for an Airy wavepacket. The wavepacket does not disperse with increasing \(t\), but it does accelerate.

which propagates without distortion and has an uniform acceleration given by

\[
\frac{B^3}{2 m^2}
\]  

(2362)

This peculiar result can be understood on the basis of a comparison of the semi-classical form of the wave function with a family of classical trajectories\(^{48}\). The semi-classical limit of the Airy function is given by

\[
\Psi(x;0) \sim \frac{1}{\sqrt{\pi}} \left( \frac{\hbar^2}{B x} \right)^{\frac{1}{4}} \sin \left[ \frac{2}{3} \left( \frac{-B x}{\hbar^2} \right)^{\frac{3}{2}} + \frac{\pi}{4} \right]
\]  

(2363)

The semi-classical wave function is interpreted as a superposition of forward and backward travelling particles with actions \(S_{\pm}\) given by

\[
S_{\pm} = \pm \frac{2}{3} \left( -B x \right)^{\frac{3}{2}}
\]  

(2364)

From Hamilton-Jacobi theory, the momenta are given by

\[
p_{\pm} = \frac{\partial S_{\pm}}{\partial x} = \pm \left( -B x \right)^{\frac{1}{2}}
\]  

(2365)

This implies that there is a phase-space relationship given by

\[ X_0(p) = -\frac{p^2}{B^3} \]  

(2366)

The Airy function can be considered as resembling an infinite ensemble of classical particles, with initial positions given by \( X_0(p) \) and each particle is parameterized by its momentum \( p \). These particles map out straight-line trajectories given by

\[ X(p; t) = X_0(p) + \frac{p}{m} t \]  

(2367)

The envelope of the family of trajectories is a parabola. This can be seen by

Figure 124: The family of trajectories represented by an Airy wave packet, and its parabolic envelope.

noting that at fixed value of \( t \), the maximum value of \( X(p, t) \) corresponds to the value \( p_t \) determined from

\[ \left. \frac{\partial X(p, t)}{\partial p} \right|_{p_t} = 0 \]  

(2368)

which yields the relation

\[ p_t = \frac{B^3}{2m} t \]  

(2369)

Since the family of trajectories touch the envelope at \( p_t \), the envelope \( x(t) \) is given by

\[ x(t) = X(p_t, t) = -\frac{p_t^2}{B^3} + \frac{p_t}{m} t \]  

(2370)
or
\[ x(t) = -\frac{B^3}{4m^2} t^2 + \frac{B^2}{2m^2} t^2 = \frac{B^3}{4m^2} t^2 \]  
(2371)
Hence the envelope is parabolic. This parabolic envelope represents the boundaries of classical motion and closely follows the motion of the maximum value of the quantum mechanical probability density.

**B: Bound States within the Continuum**

von Neumann and Wigner found that it is possible to construct potentials which have bound states at energies that are higher than the lowest energy of the continuum spectra\(^{49}\). However, in these unusual examples, the potential contains infinitely many oscillations. The method used is based on the solution of the field-free energy eigenvalue equation, with any fixed values of the angular momentum and energy. The energy eigenvalue equation for a free particle with angular momentum \(l\) has the form
\[
- \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R_l}{\partial r} \right) + \frac{l(l+1)}{r^2} R_l = k^2 R_l \]  
(2372)
where the energy eigenvalue \(E\) is positive and is related to \(k\) via
\[
E = \frac{\hbar^2 k^2}{2m} > 0 \]  
(2373)
The radial equation has the non-normalizable solution
\[
R_l(r) = j_l(kr) \]  
(2374)
corresponding to the spherical Bessel function. This energy eigenstate is extended and corresponds to the continuous portion of the energy spectrum.

von Neumann and Wigner suggested that any continuum state may be modified so as to produce a localized or normalizable state, by multiplying by some function \(f(r)\) which vanishes faster than \(r^{-2}\) as \(r \to \infty\). As they showed, it is possible to construct a potential such that the modified state is an eigenstate of the Hamiltonian with the same value of the energy. Extending these results to finite values of \(l\), Stillinger and Herrick\(^{50}\) expressed the radial function as
\[
R_l(r) = j_l(kr) f(r) \]  
(2375)
Since this wave function is required to satisfy the energy eigenvalue equation with fixed quantum numbers \(l\) and \(E\)
\[
- \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R_l}{\partial r} \right) \left( \frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2} V(r) \right) R_l = k^2 R_l \]  
(2376)
the potential is specified in terms of derivatives of the eigenfunction

\[ \frac{2m}{\hbar^2} V(r) = 2k \left( \frac{j'_l(kr)}{j_l(kr)} + \frac{1}{kr} \right) \frac{f'(r)}{f(r)} + \frac{f''(r)}{f(r)} \]  

(2377)

The potential falls to zero at infinity, if both \( \frac{f'(r)}{f(r)} \) and \( \frac{f''(r)}{f(r)} \) vanish as \( r \to \infty \). For an arbitrary decaying form of \( f(r) \), the potential would have poles at the zeros of \( j_l(kr) \). If the potential is required to be finite, then the poles originating from the zeros of \( j_l(kr) \) should be suppressed by the zeros of \( \frac{f'(r)}{f(r)} \), and furthermore \( f(r) \) should have no zeros. This suggests that the function \( f(r) \) should be an analytic function of the variable \( s(r) \), where

\[
 s(r) = k \int_0^r dr' (kr')^{2l+3} j_l^2(kr') \\
 = \frac{1}{4(l+1)} (kr)^{2l+4} \left[ j_l^2(kr) + j_{l+1}^2(kr) \right]
\]

(2378)

This has the effect that derivative of \( s(r) \) vanishes at the zeros of \( j_l(kr) \), but \( s(r) \) never decreases. The function \( f(r) \) may be chosen as

\[
 f(r) = \frac{1}{A^2 + s(r)}
\]

(2379)

so that \( f(r) \) vanish at infinity and \( R_l(r) \) is normalizable. Due to the multiplicative factor of \( j_l(kr) \) the wave function has an infinite number of nodes. The potential is then found as

\[
 V(r) = k^2 \left[ \frac{(kr)^{4l+6} j_l^4(kr)}{(A^2 + s(r))^2} - \frac{2(kr)^{2l+3} j_l(kr) j'_l(kr)}{A^2 + s(r)} + \frac{(l + \frac{1}{2}) (kr)^{2l+2} j_l^2(kr)}{A^2 + s(r)} \right]
\]

(2380)

The long-ranged behavior of the potential is then found to be given by

\[
 V(r) \sim (-1)^l 8 (l+1) k^2 \frac{\sin 2kr}{2kr}
\]

(2381)

The absence of an outgoing “spherical” wave at infinity can be thought of as being caused by the infinite sequence of reflections by subsequent maxima in the potential. At each maximum, there is always some reflection, even though the particle may have an energy greater than the potential barriers. Indeed, the energy of the bound state may even exceed the maximum value of the potential. In this truly exceptional case, even a classical particle would never be localized.

---

C: The Symmetric Rotor

We shall consider the quantum mechanics describing the rotation of a rigid body. Initially, the body is assumed to have non-identical moments of inertia
Radial wave function for $l = 0$

Figure 125: The radial wave function $R_0(r)$ for an $l = 0$ bound state with positive energy considered by von Neumann and Wigner.

$I_1$, $I_2$ and $I_3$. We shall describe the orientation of the rigid body by the Euler angles $(\alpha, \beta, \gamma)$ which describe the orientation of a set of axes embedded in the body with respect to an external fixed frame of reference.

The Euler angles are angles which describe three successive rotations of the body, which bring it from a configuration in which the axes embedded in the body coincide with the axes of the fixed reference frame. The first angle $\alpha$ describes the first rotation of the body about the $z$-axis. This rotation rotates the $x$ and $y$ axes embedded in the body into new positions, $x'$ and $y'$. The second rotation usually is prescribed as a rotation about the $y'$-axis, through the angle $\beta$. The second rotation brings the $z$-axis into the position $z''$. The $z''$-axis has polar coordinates $(\beta, \alpha)$. The last rotation is a rotation through an angle $\gamma$ about the $z''$-axis.

The rotation can be represented by three by three matrices which acts on the Cartesian coordinates $(x_1, x_2, x_3)$ of a vector. Under the rotation, the point $\vec{r}$ rigidly attached to the body is transformed to the point $\vec{r}'$, by

$$
\vec{r}' = \hat{R}(\alpha, \beta, \gamma) \vec{r} = R_{z''}(\gamma) R_y(\beta) R_z(\alpha) \vec{r}
$$

(2382)

The rotation through the angle $\alpha$ about the $z$-axis is represented by the three
Figure 126: The oscillating potential $V(r)$ of von Neumann and Wigner that produces an $l = 0$ bound state with positive energy.

by three matrix

$$\hat{R}_z(\alpha) = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$ (2383)

The rotation through an angle $\beta$ about the $y'$-axis is described by

$$\hat{R}_{y'}(\beta) = \hat{R}_z(\alpha) \hat{R}_{y}(\beta) \hat{R}_z(\alpha)^{-1}$$ (2384)

where

$$\hat{R}_{y}(\beta) = \begin{pmatrix} \cos \beta & 0 & \sin \beta \\ 0 & 1 & 0 \\ -\sin \beta & 0 & \cos \beta \end{pmatrix}$$ (2385)

The final rotation is the rotation about the angle $\gamma$ about the $z''$ axis. This is represented by

$$\hat{R}_{z''}(\gamma) = \hat{R}_{y'}(\beta) \hat{R}_z(\alpha) \hat{R}_z(\gamma) \hat{R}_z(\alpha)^{-1} \hat{R}_{y'}(\beta)^{-1}$$

$$= \hat{R}_z(\alpha) \hat{R}_{y}(\beta) \hat{R}_z(\gamma) \hat{R}_y(\beta)^{-1} \hat{R}_z(\alpha)^{-1}$$ (2386)

where

$$\hat{R}_z(\gamma) = \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}$$ (2387)
Hence, the combined rotation is given by the product of the rotations about the fixed axes as
\[ \hat{R}(\alpha, \beta, \gamma) = \hat{R}_z(\alpha) \hat{R}_y(\beta) \hat{R}_z(\gamma) \] (2388)
and has the representation
\[
\hat{R}(\alpha, \beta, \gamma) = \begin{pmatrix}
\cos \alpha & -\sin \alpha & 0 \\
\sin \alpha & \cos \alpha & 0 \\
0 & 0 & 1
\end{pmatrix} \begin{pmatrix}
\cos \beta & \cos \gamma & -\cos \beta \sin \gamma & \sin \beta \\
\sin \beta & \cos \gamma & \sin \beta \sin \gamma & \cos \beta \\
-\sin \beta & \cos \gamma & \sin \beta \sin \gamma & \cos \beta \\
\end{pmatrix}
\]
(2389)
The angle of rotation \( \psi \) can be found by evaluating the trace. The trace is found as
\[ \cos \beta + \cos(\alpha + \gamma) \left( 1 + \cos \beta \right) \] (2389)
which is equal to \( 1 + 2 \cos \psi \). Hence,
\[ \cos \psi = \cos^2 \frac{\beta}{2} \cos(\alpha + \gamma) - \sin^2 \frac{\beta}{2} \] (2390)

The kinetic energy of the symmetric rotor is described by the Lagrangian
\[ L = \frac{1}{2} \left( I_3 \omega_3^2 + I_2 \omega_2^2 + I_1 \omega_1^2 \right) \] (2391)
where \( \omega_1, \omega_2 \) and \( \omega_3 \) are the components of the angular velocity of rotation about the three body-fixed principal axes. We shall first express this Lagrangian in terms of the Euler angles and then determine the Hamiltonian. The angular velocity vector \( \omega \) can be expressed as
\[ \omega = \dot{\alpha} \hat{e}_\alpha + \dot{\beta} \hat{e}_\beta + \dot{\gamma} \hat{e}_\gamma \] (2392)
The unit vectors \( \hat{e}_\alpha, \hat{e}_\beta, \hat{e}_\gamma \) are to be expressed in terms of the unit vectors in the body-fixed coordinate system. Since the angular velocity \( \dot{\gamma} \) takes place around the body fixed \( z \)-axis (\( z' \)), one has
\[ \hat{e}_\gamma = \hat{e}_3 \] (2393)
The angular velocity \( \dot{\beta} \) occurs around the \( y' \)-axis. The \( y' \)-axis is in the \( \hat{e}_1 - \hat{e}_2 \) plane, since the rotation \( \gamma \) is around \( \hat{e}_3 \) and keeps the \( \hat{e}_1 - \hat{e}_2 \) plane invariant. The azimuthal angle of the \( y' \) axis is \( \frac{\pi}{2} - \gamma \). Hence
\[ \hat{e}_\beta = \hat{e}_1 \cos(\frac{\pi}{2} - \gamma) + \hat{e}_2 \sin(\frac{\pi}{2} - \gamma) \]
\[ = \hat{e}_1 \sin \gamma + \hat{e}_2 \cos \gamma \] (2394)
The final component of the rotation is around the $\alpha$ axis, which is aligned along the original $z$-axis. The $\hat{e}_\alpha$ axis has polar angle $\beta$ and azimuthal angle $\pi - \gamma$ relative to the fixed body axes.

$$\hat{e}_\alpha = \sin \beta \left( - \cos \gamma \hat{e}_1 + \sin \gamma \hat{e}_2 \right) + \hat{e}_3 \cos \beta$$  \hspace{1cm} (2395)

Hence, the components of the angular velocity with respect to the body-fixed axes are expressed in terms of the Euler angles via

$$\begin{align*}
\omega_1 &= - \sin \beta \cos \gamma \hat{\alpha} + \sin \gamma \hat{\beta} \\
\omega_2 &= \sin \beta \sin \gamma \hat{\alpha} + \cos \gamma \hat{\beta} \\
\omega_3 &= \cos \beta \hat{\alpha} + \hat{\gamma}
\end{align*}$$  \hspace{1cm} (2396)

Hence, the Lagrangian is given as

$$L = \frac{1}{2} \left[ I_1 \left( - \sin \beta \cos \gamma \hat{\alpha} + \sin \gamma \hat{\beta} \right)^2 + I_2 \left( \sin \beta \sin \gamma \hat{\alpha} + \cos \gamma \hat{\beta} \right)^2 + I_3 \left( \cos \beta \hat{\alpha} + \hat{\gamma} \right)^2 \right]$$  \hspace{1cm} (2397)

For the symmetric top, one has $I_1 = I_2$, therefore, the Lagrangian simplifies to

$$L = \frac{1}{2} \left[ I_1 \left( \sin^2 \beta \hat{\alpha}^2 + \hat{\beta}^2 \right) + I_3 \left( \cos \beta \hat{\alpha} + \hat{\gamma} \right)^2 \right]$$  \hspace{1cm} (2398)

The momenta are given by

$$p_\alpha = \frac{\partial L}{\partial \hat{\alpha}} = I_1 \sin^2 \beta \hat{\alpha} + I_3 \cos \beta \left( \cos \beta \hat{\alpha} + \hat{\gamma} \right)$$  \hspace{1cm} (2399)

and

$$p_\beta = \frac{\partial L}{\partial \hat{\beta}} = I_1 \hat{\beta}$$  \hspace{1cm} (2400)

and finally

$$p_\gamma = \frac{\partial L}{\partial \hat{\gamma}} = I_3 \left( \cos \beta \hat{\alpha} + \hat{\gamma} \right)$$  \hspace{1cm} (2401)

The Hamiltonian $H$ is given by

$$H = p_\alpha \hat{\alpha} + p_\beta \hat{\beta} + p_\gamma \hat{\gamma} - L$$

$$= \frac{1}{2 I_1} p^2_\beta + \frac{1}{2 I_1 \sin^2 \beta} \left( p_\alpha - \cos \beta p_\gamma \right)^2 + \frac{1}{2 I_3} p^2_\gamma$$  \hspace{1cm} (2402)

This Hamiltonian is quantized as

$$\hat{H} = \frac{1}{2 I_1} \hat{p}^2_\beta + \frac{1}{2 I_1 \sin^2 \beta} \left( \hat{p}_\alpha - \cos \beta \hat{p}_\gamma \right)^2 + \frac{1}{2 I_3} \hat{p}^2_\gamma$$  \hspace{1cm} (2403)
It is seen that \( \hat{p}_\alpha \) and \( \hat{p}_\gamma \) commute with the Hamiltonian and, therefore, one can find simultaneous eigenstates of \( \hat{p}_\alpha \), \( \hat{p}_\gamma \) and \( \hat{H} \). The simultaneous eigenfunctions are written in the form

\[
\Psi(\alpha, \beta, \gamma) = \left( \frac{1}{2\pi} \right) \exp \left[ \frac{i}{\hbar} \left( \alpha \hat{p}_\alpha + \gamma \hat{p}_\gamma \right) \right] \phi(\beta) \tag{2404}
\]

Since the wave functions are required to be single-valued, the quantum numbers are determined to be \( \hat{p}_\alpha = m_\alpha \hbar \) and \( \hat{p}_\gamma = m_\gamma \hbar \) where \((m_\alpha, m_\gamma)\) are either both integers or they are both half-integers. On substituting the above form, the expression for the eigenvalue equation reduces to

\[
\frac{1}{2 \, I_1} \left[ \hat{p}_\beta^2 + \frac{1}{\sin^2 \beta} \left( \hat{p}_\alpha - \cos \beta \hat{p}_\gamma \right)^2 \right] \phi(\beta) = \left( E - \frac{1}{2 \, I_3} \hat{p}_\gamma^2 \right) \phi(\beta) \tag{2405}
\]

Since \( \beta \) is a polar angle, the above equation takes the explicit form

\[
-\frac{\hbar^2}{2 \, I_1} \frac{1}{\sin \beta} \frac{\partial}{\partial \beta} \left( \sin \beta \frac{\partial \phi}{\partial \beta} \right) + \frac{\hbar^2}{2 \, I_1} \sin^2 \beta \left( m_\alpha - \cos \beta m_\gamma \right)^2 \phi(\beta) = \left( E - \frac{\hbar^2 m_\gamma^2}{2 \, I_3} \right) \phi(\beta) \tag{2406}
\]

or

\[
-\sin \beta \frac{\partial}{\partial \beta} \left( \sin \beta \frac{\partial \phi}{\partial \beta} \right) + \left[ \left( m_\alpha - \cos \beta m_\gamma \right)^2 + \sin^2 \beta \left( \frac{I_1}{I_3} m_\gamma^2 - \frac{2 \, I_1 \, E}{\hbar^2} \right) \right] \phi(\beta) = 0 \tag{2407}
\]

Clearly, this can be rewritten as an eigenvalue equation in terms of the variable \( z = \cos \beta \), where \( z \) is restricted to the range \( 1 \geq z \geq -1 \). Therefore, we have

\[
- (1 - z^2) \frac{\partial}{\partial z} \left( (1 - z^2) \frac{\partial \phi(\beta)}{\partial z} \right) + \left[ m_\alpha^2 + m_\gamma^2 - \lambda - 2 m_\alpha m_\gamma z + \lambda z^2 \right] \phi(\beta) = 0 \tag{2408}
\]

where \( \lambda \) is related to the energy eigenvalue via

\[
\lambda = \frac{2 \, I_1 \, E}{\hbar^2} + \left( 1 - \frac{I_1}{I_3} \right) m_\gamma^2 \tag{2409}
\]

The eigenvalue equation has regular singular points at \( z = \pm 1 \). Near these points, the solution has a non-analytic form, and is expressed as

\[
\phi(\beta) = (1 - z)^\mu (1 + z)^\nu F(z) \tag{2410}
\]

where \( F(z) \) is an analytic function, and the indices \( \mu \) and \( \nu \) are to be determined. The indices are determined by considering the most singular terms, and are found to be given by

\[
\mu = \pm \left( \frac{m_\alpha - m_\gamma}{2} \right) \tag{2411}
\]

and

\[
\nu = \pm \left( \frac{m_\alpha + m_\gamma}{2} \right) \tag{2412}
\]
The solutions with the negative values for the exponents are discarded since the solution is required to be finite and normalizable. The function $F(z)$ then must satisfy an equation of the form

$$- (1 - z^2) \frac{\partial^2 F}{\partial z^2} + 2 \left[ (1 + m_\alpha) z - m_\gamma \right] \frac{\partial F}{\partial z} + \left( m_\alpha (m_\alpha + 1) - \lambda \right) F = 0$$

(2413)

For convenience, we have assumed that $m_\alpha$ and $m_\gamma$ are both positive and that $m_\alpha > m_\gamma$. The eigenvalue $\lambda$ is found by using the Frobénius method, expanding in powers about a singular point and requiring that the series expansion terminates, yielding a polynomial for $F(z)$. This requires that

$$\left( m_\alpha + \frac{1}{2} \right) \pm \sqrt{\frac{1}{4} + \lambda}$$

(2414)

is a positive integer. Hence, we find that

$$\lambda = j (j + 1)$$

(2415)

and the energy eigenvalue is given by

$$E = \frac{\hbar^2}{2 I_1} j (j + 1) + \frac{\hbar^2 m_\alpha^2}{2 I_3} - \frac{\hbar^2 m_\alpha^2}{2 I_1}$$

(2416)

as could have been expected.