

## AN EXACT LIMIT OF A LOCAL MIXED VALENCE MODEL

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Recently, Khomskii and Kocharjan have considered a local mixed valence model and, in a generalized linear Hartree–Fock approximation, found solutions which, when generalized to the many site problem, displayed continuous and discontinuous transitions from ground states of integral to intermediate valence. The transitions were due to an energy dependence of the virtual bound state width and persisted in the limit of zero hybridization. We examine the model of Khomskii and Kocharjan and demonstrate that in the limit of zero hybridization an exact solution may be found for the valence behaviour. The generalization of this result to the case of a small but finite concentration of localized level sites, exhibits intermediate valence only as a consequence of the pinning of the Fermi level to the narrow localized levels and the transitions between the ground states of integral and intermediate valence are continuous.

KHOMSKII AND KOCHARJAN [1] have considered a local mixed valence model in which there is a single highly correlated localized level of  $4f$  character and itinerant band states. These are coupled by a hybridization matrix element  $V_{fd}$  and a repulsive on site localized electron–itinerant electron repulsion  $U_{fd}$ . The Hamiltonian for the system is given by:

$$\begin{aligned} \hat{H} = & \sum_{\sigma} E_{fd} f_{\sigma}^{\dagger} f_{\sigma} + \sum_{\sigma} U_{fd} f_{\sigma}^{\dagger} f_{\sigma} f_{\sigma}^{\dagger} f_{\sigma} + \sum_{\mathbf{k}\sigma} \epsilon_d(\mathbf{k}) d_{\mathbf{k}\sigma}^{\dagger} d_{\mathbf{k}\sigma} \\ & + \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} U_{fd} f_{\sigma}^{\dagger} f_{\sigma} d_{\mathbf{k}'\sigma'}^{\dagger} d_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma} V_{fd}(\mathbf{k}) \\ & \times \{ f_{\sigma}^{\dagger} d_{\mathbf{k}\sigma} + d_{\mathbf{k}\sigma}^{\dagger} f_{\sigma} \} \end{aligned} \quad (1)$$

where the operator  $f_{\sigma}^{\dagger}$  creates an electron of spin  $\sigma$  in the localized level and  $d_{\mathbf{k}\sigma}^{\dagger}$  creates an electron of spin  $\sigma$  in the  $d$  band in the  $\mathbf{k}$ th Bloch state. Khomskii and Kocharjan neglected the spin dependence of the problem and treated in a mean field manner by taking the most general linearization of the screened repulsion terms, i.e.

$$\sum_{\mathbf{k}\mathbf{k}'} U_{fd} \{ d_{\mathbf{k}}^{\dagger} d_{\mathbf{k}'} \langle f^{\dagger} f \rangle + \langle d_{\mathbf{k}}^{\dagger} d_{\mathbf{k}'} \rangle f^{\dagger} f + d_{\mathbf{k}}^{\dagger} f d_{\mathbf{k}'} f^{\dagger} + \langle f d_{\mathbf{k}}^{\dagger} \rangle f^{\dagger} d_{\mathbf{k}'} \}.$$

The correlation terms  $\sum_{\mathbf{k}'} U_{fd} \langle d_{\mathbf{k}}^{\dagger} f^{\dagger} \rangle$  add to the hybridization elements giving an increased width to the quasi particle states,  $\Gamma$ , which is given by

$$\Gamma = \sum_{\mathbf{k}} \frac{\pi}{W} \left| \left\{ V_{fd}(\mathbf{k}) + U_{fd} \sum_{\mathbf{k}'} \langle d_{\mathbf{k}'}^{\dagger} f \rangle \right\} \right|^2$$

where  $\langle d_{\mathbf{k}}^{\dagger} f \rangle$  has to be determined self consistently and  $W$  is the itinerant band width.

They analyze the case in which the hybridization matrix elements are zero  $V_{fd}(\mathbf{k}) = 0$ . The number of localized electrons  $\langle f^{\dagger} f \rangle$ , itinerant electrons  $\sum_{\mathbf{k}} \langle d_{\mathbf{k}}^{\dagger} d_{\mathbf{k}} \rangle$  and the width of the localized level are found self consistently. Depending on the value of the itinerant electron–localized electron repulsion  $U_{fd}$ , they find continuous and discontinuous transitions to intermediate valence states. Their results are depicted diagrammatically in Fig. 1. For a certain range of  $U_{fd}$ , they find two discontinuous jumps in the number of the valence electrons and suggest that the approximate solution in this regime may be used to explain the intermediate valence behaviour of cerium under pressure [2].

Their analysis does not provide a clear description of the mechanism that can produce two discontinuous valence transitions, nor is it clear under what circumstances their approximation is reliable. The zero hybridization limit of their model can be solved exactly for the behaviour of the valence, and this can be used to test both the conclusions of Khomskii and Kocharjan and the nature of the approximations involved.

From the equations of motion one may obtain the exact Greens function for the itinerant band of electrons due to the closure of the equations of motion for the

where  $\epsilon_d(\mathbf{k})$  are the energy levels in the unperturbed itinerant electron band and  $\epsilon_d(l)$  are the energy levels in the itinerant band when the localized  $4f$  level is occupied by a single electron  $\Sigma_\sigma \langle f_\sigma^\dagger f_\sigma \rangle = 1$  and  $\epsilon_d(m)$  are the energy levels when  $\Sigma_\sigma \langle f_\sigma^\dagger f_\sigma \rangle = 2$ . These energy levels are obtained from the poles of the Greens Function for the itinerant electrons (5). We may re-express (7) as:

$$\frac{\sum_\sigma \langle f_\sigma^\dagger f_\sigma \rangle}{\sigma} = \frac{2\{\exp[-\beta(\epsilon_f - \mu)]D_1(\beta) + \exp[-\beta(2\epsilon_f + U_{ff} - 2\mu)]D_2(\beta)\}}{1 + 2\exp[-\beta(\epsilon_f - \mu)]D_1(\beta) + \exp[-\beta(2\epsilon_f + U_{ff} - 2\mu)]D_2(\beta)}$$

where

$$D_\alpha(\beta) = \exp\left[-\int_{-\infty}^{\infty} \Delta\rho_\alpha(\omega) \log_e\{1 + \exp[-\beta(\omega - \mu)]\} d\omega\right] \quad (8)$$

and the change in the itinerant band density of states  $\Delta\rho_\alpha(\omega)$  is given by:

$$\Delta\rho_\alpha(\omega) = \frac{1}{N\pi} \text{Im} \sum_{\mathbf{k}\sigma} \{G_{\mathbf{k}\sigma}^\alpha(\omega) - G_{\mathbf{k}\sigma}^0(\omega)\} \quad \left\{ \sum_\sigma \langle f_\sigma^\dagger f_\sigma \rangle = \alpha \right\} \quad \left\{ \sum_\sigma \langle f_\sigma^\dagger f_\sigma \rangle = 0 \right\} \quad (9)$$

We shall generalize this model from the case in which instead of only having one localized  $4f$  level in the sample there are  $N_1$  localized  $4f$  level sites, which means that the chemical potential  $\mu$  must be found self-consistently. For small, but finite concentrations  $N_1/N$  of such localized levels, the self consistency equation for the chemical potential  $\mu$  is given by:

$$N_{\text{tot}} = N \int_{-\infty}^{\infty} f(\omega) \rho_0(\omega) d\omega + \sum_\sigma NN_1 \{ \langle f_\sigma^\dagger f_\sigma \rangle - \langle f_\sigma^\dagger f_\sigma f_\sigma^\dagger f_\sigma \rangle \} \\ \times \int_{-\infty}^{\infty} f(\omega) \Delta\rho_1(\omega) d\omega + NN_1 \sum_\sigma \langle f_\sigma^\dagger f_\sigma f_\sigma^\dagger f_\sigma \rangle \\ \times \int_{-\infty}^{\infty} f(\omega) \Delta\rho_2(\omega) d\omega + N_1 \sum_\sigma \langle f_\sigma^\dagger f_\sigma \rangle \quad (10)$$

where  $N_{\text{tot}}$  is the total number of electrons in the sample. For rare earth materials the Coulomb interaction between two electrons in a  $4f$  level  $U_{ff}$ , is extremely large. This has the effect of reducing the probability that a  $4f$  level is doubly occupied to a negligible value, as seen from equation (6). Thus we shall set

$$\langle f_\sigma^\dagger f_\sigma f_\sigma^\dagger f_\sigma \rangle = 0.$$

In this limit the self-consistency condition may then be rewritten as

$$\sum_\sigma \langle f_\sigma^\dagger f_\sigma \rangle = \frac{1}{N_1} \frac{N_{\text{tot}} - N \int_{-\infty}^{\infty} f(\omega) \rho_0(\omega) d\omega}{1 + N \int_{-\infty}^{\infty} f(\omega) \Delta\rho_1(\omega) d\omega} \quad (11)$$

In choosing a flat band for the unperturbed density of states

$$\rho_0(\omega) = \begin{cases} 2/W & \text{for } 0 < \omega < W \\ 0 & \text{otherwise} \end{cases}$$

we note that one state will be split off the top of the band whenever the localized level is occupied i.e.  $\Sigma_\sigma \langle f_\sigma^\dagger f_\sigma \rangle \neq 0$ , whatever the strength of  $U_{fd}$ . This is due to the discontinuities of the band edges. The change in the itinerant

band density of states which occurs when  $\Sigma_\sigma \langle f_\sigma^\dagger f_\sigma \rangle = 1$  is given by

$$\Delta\rho_1(\omega) = \frac{1}{W} \left[ \delta(E - E_B) - \frac{1}{\pi} \frac{\partial}{\partial \omega} \tan^{-1} \left\{ \frac{\pi U_{fd}/W}{1 - (U_{fd}/W) \log(\omega/\omega - W)} \right\} \right]$$

where  $E_B$  is the energy of the bound state, and is given by

$$E_B = \frac{W}{\exp[W/U_{fd}] - 1}$$

An alternative choice for the unperturbed itinerant band is the elliptical density of states.

$$\rho_0(\omega) = \frac{4}{\pi W} \sqrt{1 - 4\left(\frac{\omega}{W}\right)^2}.$$

The change in the  $d$  band density of states is given by

$$\Delta\rho_1(\omega) = \frac{1}{\pi W} \frac{1}{\sqrt{1 - 4(\omega/W)^2}} \\ \times \left[ 1 + \frac{\left(\frac{4U_{fd}}{W}\right)^2 - 1}{1 + \left(\frac{4U_{fd}}{W}\right)^2 - \frac{16U_{fd}\omega}{W^2}} \right].$$

A bound state splits off the top of the itinerant band, only if

$$U_{fd} \geq \frac{W}{4}$$

Equation (11) is solved graphically for  $T = 0$  by plotting the left hand side (a) and the right hand side (b) of the equation, as a function of  $\mu$ , as is shown in Fig. 2.

The values of  $\Sigma_\sigma \langle f_\sigma^\dagger f_\sigma \rangle$  and  $\mu$  are calculated from the point of intersection of these curves for given values of  $\epsilon_f$ ,  $U_{fd}$  and  $W$ . There are three phases according to which portion of the curve (a) is intersected by the curve (b):  $\Sigma_\sigma \langle f_\sigma^\dagger f_\sigma \rangle = 0$ ,  $\Sigma_\sigma \langle f_\sigma^\dagger f_\sigma \rangle = 1$  or some value intermediate between 0 and 1. The intermediate valence regime is small but increases as the number of  $4f$  sites increases,

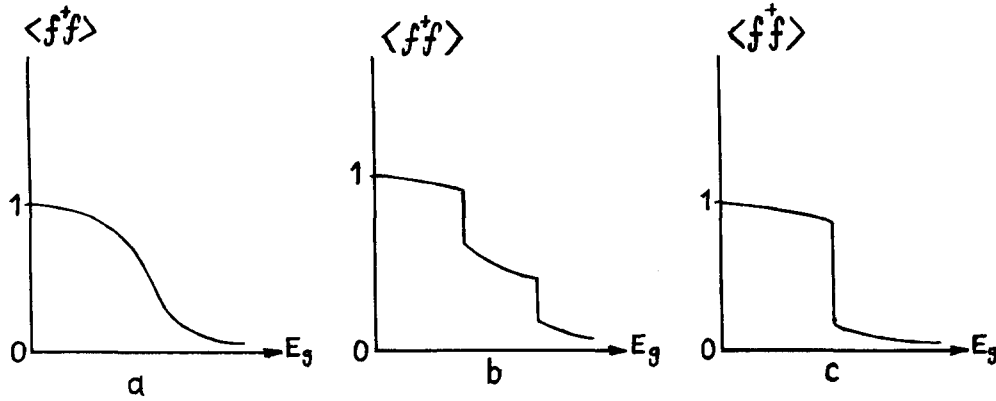


Fig. 1. The variation of the total occupation number  $\langle f^\dagger f \rangle$  of the localized levels with the energy difference between the  $4f$  level and the bottom of the band ( $E_g$ ) as obtained by Khomskii and Kocharjan. Figures (a), (b), (c) indicate the different types of behaviour found as the strength of the electron-electron repulsion  $U_{fd}$  is increased.

three particle correlation functions.

The Greens function defined by:

$$G_{\mathbf{k}\mathbf{k}'}^\sigma(\omega) = \int_{-\infty}^{\infty} \ll d_{\mathbf{k}'\sigma}(t); d_{\mathbf{k}\sigma}^\dagger(0) \gg e^{i\omega t} \frac{dt}{2\pi}$$

satisfies the equation:

$$[\omega - \epsilon_d(\mathbf{k})] G_{\mathbf{k}\mathbf{k}'}^\sigma(\omega) = \delta_{\mathbf{k}\mathbf{k}'} + \sum_{\sigma'\mathbf{k}''} U_{fd} F_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega) \quad (2)$$

where

$$F_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega) = \int_{-\infty}^{\infty} \ll d_{\mathbf{k}'\sigma}(t) f_{\sigma'}^\dagger(t) f_{\sigma'}(t); d_{\mathbf{k}\sigma}^\dagger(0) \gg e^{i\omega t} \frac{dt}{2\pi}$$

is a two particle correlation function.

The two particle correlation function  $F_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega)$  satisfies the equation:

$$[\omega - \epsilon_d(\mathbf{k}'')] F_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega) = \delta_{\mathbf{k}''\mathbf{k}'} \langle f_{\sigma'}^\dagger f_{\sigma'} \rangle + U_{fd} \times \sum_{\mathbf{k}'''} \{ F_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega) + H_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega) \} \quad (3)$$

where

$$H_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega) = \int_{-\infty}^{\infty} \ll d_{\mathbf{k}'\sigma}(t) f_{\sigma'}^\dagger(t) f_{\sigma'}(t) f_{-\sigma'}^\dagger(t) f_{-\sigma'}(t); d_{\mathbf{k}\sigma}^\dagger(0) \gg e^{i\omega t} \frac{dt}{2\pi}$$

The equations of motion for the three particle cor-

relation function  $H_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega)$  complete the set of equations:

$$[\omega - \epsilon_d(\mathbf{k}'')] H_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega) = \delta_{\mathbf{k}''\mathbf{k}'} \langle f_{\sigma'}^\dagger f_{\sigma'} f_{-\sigma'}^\dagger f_{-\sigma'} \rangle + 2U_{fd} \times \sum_{\mathbf{k}'''} H_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(\omega). \quad (4)$$

The property that closes the equations of motion is the idempotency of the number of electrons in the localized level

$$f_{\sigma'}^\dagger f_{\sigma'} f_{\sigma'}^\dagger f_{\sigma'} \equiv f_{\sigma'}^\dagger f_{\sigma'}$$

On solving these three coupled equations, for the single particle Greens Function  $G_{\mathbf{k}\mathbf{k}'}^\sigma(\omega)$  we have:

$$G_{\mathbf{k}\mathbf{k}'}^\sigma(\omega) = [\omega - \epsilon_d(\mathbf{k})]^{-1} \times \left[ \delta_{\mathbf{k}\mathbf{k}'} + \frac{U_{fd} \sum_{\sigma'} \{ \langle f_{\sigma'}^\dagger f_{\sigma'} \rangle - \langle f_{\sigma'}^\dagger f_{\sigma'} f_{-\sigma'}^\dagger f_{-\sigma'} \rangle \}}{1 - \sum_{\mathbf{k}''} \frac{U_{fd}}{\omega - \epsilon_d(\mathbf{k}'')}} [\omega - \epsilon_d(\mathbf{k}')]^{-1} + \frac{U_{fd} \sum_{\sigma'} \langle f_{\sigma'}^\dagger f_{\sigma'} f_{-\sigma'}^\dagger f_{-\sigma'} \rangle}{1 - \sum_{\mathbf{k}''} \frac{2U_{fd}}{\omega - \epsilon_d(\mathbf{k}'')}} [\omega - \epsilon_d(\mathbf{k}')]^{-1} \right]. \quad (5)$$

The number of  $4f$  electrons can be found directly from the definition of the thermal average of an operator.

$$\sum_{\sigma} \langle f_{\sigma}^\dagger f_{\sigma} \rangle = \frac{\sum_{\sigma} \text{Trace} \{ \exp [-\beta(\hat{H} - \mu\hat{N})] f_{\sigma}^\dagger f_{\sigma} \}}{\text{Trace} \{ \exp [-\beta(\hat{H} - \mu\hat{N})] \}} \quad (6)$$

The trace is evaluated using the appropriate set of eigenstates of the Hamiltonian (1) with  $V_{fd}(\mathbf{k}) \equiv 0$ .

$$\sum_{\sigma} \langle f_{\sigma}^\dagger f_{\sigma} \rangle = \frac{2[\exp[-\beta(\epsilon_f - \mu)] \prod_l \exp[-\beta[\epsilon_d(l) - \mu]] + \exp[-\beta(2\epsilon_f + U_{ff} - 2\mu)] \prod_m \exp\{-\beta[\epsilon_d(m) - \mu]\}] \prod_{\mathbf{k}} \exp\{-\beta[\epsilon_d(\mathbf{k}) - \mu]\} + 2 \exp[-\beta(\epsilon_f - \mu)] \prod_l \exp\{-\beta[\epsilon_d(l) - \mu]\} + \exp[-\beta(2\epsilon_f + U_{ff} - 2\mu)] \prod_m \exp\{-\beta[\epsilon_d(m) - \mu]\}]}{\prod_{\mathbf{k}} \exp\{-\beta[\epsilon_d(\mathbf{k}) - \mu]\} + 2 \exp[-\beta(\epsilon_f - \mu)] \prod_l \exp\{-\beta[\epsilon_d(l) - \mu]\} + \exp[-\beta(2\epsilon_f + U_{ff} - 2\mu)] \prod_m \exp\{-\beta[\epsilon_d(m) - \mu]\}} \quad (7)$$

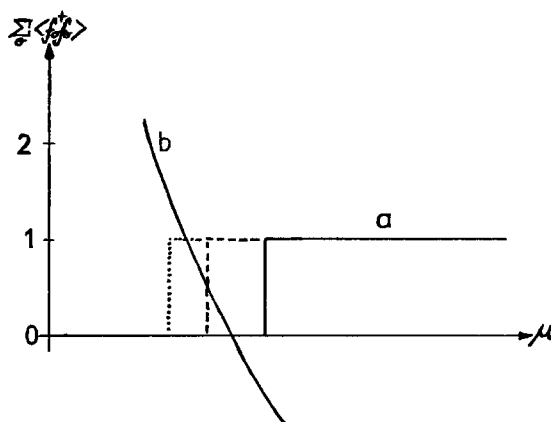


Fig. 2. The graphical solution of equation (11) for the chemical potential  $\mu$ . The intersection of the curves gives both the values of the chemical potential and the occupation number of the localized level  $\Sigma_{\sigma}\langle f_{\sigma}^{\dagger}f_{\sigma}\rangle$ . The dotted lines indicate the effect of decreasing  $E_g$ .

because the curve (b) lowers and flattens. This is the pinning effect of the Fermi level to the localized  $4f$  states [3]. The transitions between states of integral and intermediate valence are continuous, and there is only one

transition to an intermediate state as  $\epsilon_f$  varies.

In the treatment of the single  $4f$  site case we have taken the  $f$ - $d$  correlation into an account exactly and the results are quite different from the approximate ones of Khomskii and Kocharjan. This leads one to question the validity of their approximate solutions. Our treatment, as well as that of Khomskii and Kocharjan, cannot sensibly be extrapolated to the many site or Falicov Kimball model [4]. However, CPA [5] calculations for the Falicov Kimball model at  $T = 0$  also give continuous rather than discontinuous transitions and the intermediate valence phase only as a consequence of the pinning of the Fermi level to the  $4f$  states. The CPA allows the band to change shape and ought to take reasonable account of the correlation effects in the many site case. The intermediate valence state of Khomskii and Kocharjan may be due to the fact that the number of  $4f$  electrons is not conserved in their approximation which is incorrect for  $V_{fd} = 0$ .

For non-zero hybridization  $V_{fd} \neq 0$  there can be significant energy dependences of the width of the  $4f$  levels due to the  $k$  dependence of  $V_{fd}(k)$ , apart from many body effects, as has been shown by Iglesias Sicardi *et al.* [6].

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