

### Theory of intermediate-valence solids

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A realistic Hamiltonian which involves the electronic interactions among the  $f$  and  $d$  electrons and the interaction of the  $f$  and  $d$  electrons with the lattice is considered for studying valence change transitions in intermediate-valence systems. The eigenstates of the Hamiltonian are obtained by employing a self-consistent method, which consists of four steps. First, the  $f$ - $f$  and  $f$ - $d$  interactions are considered for a fixed lattice constant by employing multiple single-site scattering theory [R. Lal, Phys. Rev. B **27**, 2535 (1983)]. Second, the lattice problem is solved by considering the effect of the interactions of the  $f$  and  $d$  electrons. Third, the effect of the interactions of the  $f$  electron and the lattice are considered on the  $d$  band structure. And finally, interactions among the  $f$ -electron impurities are incorporated. The main feature of the method is that it provides a source which stabilizes the  $f$ -state occupation at a noninteger value and the lattice in an equilibrium state with a changed lattice constant. Other general features of the method are also discussed.

Despite efforts from various studies<sup>1</sup> the theory of mixed valence is still at an unsatisfactory stage.<sup>2</sup> The main reason for the poor understanding of the mixed-valence problem is that the interactions which exist in the system are not employed to obtain the state of the system. A treatment in terms of true interactions is the real way for studying a system, and we expect<sup>3,4</sup> that only such a treatment can provide the understanding of the nature of the valence-change transitions. Although some qualitative ideas regarding the roles of the interactions have come up,<sup>5,6</sup> a theoretical effort has not yet been made. In this Rapid Communication we intend to make such an effort by investigating the roles of the electronic interactions among the  $f$  and  $d$  electrons, the interactions of the  $f$  and  $d$  electrons with the lattice, and the phonon-phonon interaction. Our main objective is to derive the mechanism which is governed by these interactions, and to study the stabilization under such a mechanism.

We start with the following total Hamiltonian:

$$H = H_f + H_d + H_l + H_{fd} + H_{fl} + H_{dl} + U_r. \quad (1)$$

Here  $H_f$ ,  $H_d$ , and  $H_l$  are Hamiltonians, respectively, for the  $f$  electrons,  $d$  electrons, and the lattice. In atomic units we have

$$H_f = \sum_{i, M_j} E_f f_{iM_j}^\dagger f_{iM_j} + \frac{1}{2} \sum_{iM_j} U_{ff} f_{iM_j}^\dagger f_{iM_j} f_{iM_j}^\dagger f_{iM_j}, \quad (2)$$

$$H_d = \sum_{\mathbf{k}, \sigma_d} \epsilon_{\mathbf{k}} d_{\mathbf{k}\sigma_d}^\dagger d_{\mathbf{k}\sigma_d}, \quad (3)$$

$$H_l = \sum_{\mathbf{w}, \mathbf{K}} w \left( \frac{1}{2} + b_{\mathbf{w}\mathbf{K}}^\dagger b_{\mathbf{w}\mathbf{K}} \right) + H_{\text{anh}}. \quad (4)$$

In Eq. (2) the  $z$  components of the total angular momentum  $M_j$  and  $M_j^-$  correspond to opposite spins. In Eq. (4)  $H_{\text{anh}}$  represents the anharmonic part of the ion-ion interaction. Its origin lies in the interactions  $|\mathbf{R}_i - \mathbf{R}_j|^{-1}$ , where  $\mathbf{R}_i$  is the position coordinate of the  $i$ th site. The strength of  $H_{\text{anh}}$  varies like  $Z_f^2 u^3 a^{-4}$ , where  $Z_f$  (depending upon the  $f$ -state occupation) is the charge

number of the ion,  $u$  is the amplitude of the lattice oscillations, and  $a$  is the lattice constant.

In Eq. (1)  $U_r$  is the vector potential which causes decay of the excited state via photon emission. The term  $H_{fd}$  corresponds to the  $f$ - $d$  interaction. Its origin lies in the Coulombic interactions  $|\mathbf{r}_{fi} - \mathbf{r}_{dj}|^{-1}$  and the exchange interactions  $-2J_{ij} \mathbf{s}_{fi} \cdot \mathbf{s}_{dj}$ . Here  $\mathbf{r}_{fi}$  and  $\mathbf{s}_{fi}$  denote the position and spin coordinates, respectively, of the  $i$ th  $f$  electron, and  $J_{ij}$  is the exchange integral. The term  $H_{fl}$  in Eq. (1) represents the interaction of  $f$  electrons with other lattice ions. It is given by

$$-Z_f \sum_i \left( \sum_j |\mathbf{r}_{fi} - \mathbf{R}_j|^{-1} - |\mathbf{r}_{fi} - \mathbf{R}_i^0|^{-1} \right).$$

Here  $\mathbf{R}_j^0$  is the equilibrium position of the  $j$ th site. The last term of Eq. (1),  $H_{dl}$ , denotes the interaction of the  $d$  electrons with the lattice potential difference

$$-Z_d \sum_{i,j} (|\mathbf{r}_{di} - \mathbf{R}_j|_a^{-1} - |\mathbf{R}_{di} - \mathbf{R}_j|_{a_{in}}^{-1}),$$

where  $|\mathbf{A}|_a$  means value of  $\mathbf{A}$  for the lattice of lattice constant  $a$ . The lattice constant  $a_{in}$  corresponds to  $n_f = 1$ . Here  $Z_d$  denotes the ionic charge seen by the  $d$  electron.

The Hamiltonian of Eq. (1) involves much more detail than any other Hamiltonian used so far in the study of mixed valence systems. In fact, most of the existing methods are divided into two<sup>7</sup> classes—one for which  $H_{fl} + H_{dl} = 0$ , and the other for which  $H_{fd} + H_{dl} = 0$ . The former class is based upon the electronic mechanism,<sup>7</sup> while the latter class is based upon the lattice mechanism.<sup>7</sup> There exists some, but very few methods,<sup>8-10</sup> which consider the joint effects of the electronic and the lattice interactions on the stabilization of the mixed valence phase. But, such methods treat the electronic and the lattice interactions in a highly parametric way so that it is not possible to gain information on the detailed roles of the true interactions.

Exact solution of the eigenvalue problem of the Hamiltonian  $H$  will be of formal importance only. For practical

purposes we have to employ approximation methods. In order to develop a useful method we divide the Hamiltonian  $H$  into two parts—one, say  $H_1$ , corresponding to noninteracting  $f$  electron impurities, and the other, say  $H_2$ , corresponding to interaction among various ( $f$  electron) impurities.  $H_1$  is given by

$$H_1 = H_f + H_d + H_l + H'_{fd} + H'_{fl} + U_r . \quad (5)$$

Here “prime” on  $H'_{fd}$  and  $H'_{fl}$  implies that  $H'_{fd}$  and  $H'_{fl}$  affect only the  $f$  electrons and not the  $d$ -band electrons or the lattice ions.

In order to specify the interaction  $H_2$ , we first construct the Hamiltonians of the  $d$ -band electrons and the phonons by considering the effect of the interactions  $H'_{fd}$ ,  $H'_{fl}$ , and  $H_{dl}$ . Let  $\tilde{H}_d$  and  $\tilde{H}_l$  denote these Hamiltonians; we then construct them in the following way:

$$\tilde{H}_d = H_d + H'_d + H^l_d , \quad (6)$$

$$\tilde{H}_l = H_l + H^f_l + H^d_l . \quad (7)$$

Here the interactions  $H^f_d$ ,  $H^l_d$ ,  $H^f_l$ , and  $H^d_l$  are defined as follows:

$$H^f_d = \text{Tr}(\rho_f H'_{fd}), \quad H^l_d = \text{Tr}(\rho_l H_{dl}) , \quad (8)$$

$$H^f_l = \text{Tr}(\rho_f H'_{fl}), \quad H^d_l = \text{Tr}(\rho_d H_{dl}) .$$

The density operators  $\rho_f$  and  $\rho_d$  correspond to the spatial parts of the Hamiltonians  $H_f$  and  $H_d$ , respectively, and  $\rho_l$  corresponds to the lattice Hamiltonian  $H_l$ . The purpose of such definitions of  $\rho_f$  and  $\rho_d$  is as follows. For practical purposes we have to consider the interactions in an approximate way. If we also include the spin part in defining  $\rho_f$  and  $\rho_d$  it will be difficult to obtain proper symmetrization of the wave functions (of the interacting  $f$  and  $d$  electrons). To retain proper symmetry of the wave functions we first consider the electric interactions and then incorporate symmetrization by taking a spin structure of the type  $\mathbf{s}_1 \cdot \mathbf{s}_2$ . The details of the interactions are included in the exchange integral  $J_{12}$  through the wave functions. Since the value of  $J_{12}$  is more important from the viewpoint of magnetic properties of the system, we expect that the present method will enable us to obtain a deep understanding of the magnetic character of the system.

We are now able to define the impurity-impurity interaction  $H_2$ . The contributions of  $H'_{fd}$  and  $H'_{fl}$  to  $H_2$ , denoted, respectively, by  $H^d_f$  and  $H^l_f$ , may be defined as follows:

$$H^d_f = \text{Tr}(\tilde{\rho}_d H'_{fd}) - \text{Tr}(\rho_d H'_{fd}) , \quad (9)$$

$$H^l_f = \text{Tr}(\tilde{\rho}_l H'_{fl}) - \text{Tr}(\rho_l H'_{fl}) , \quad (10)$$

where  $\tilde{\rho}_d$  is the density operator corresponding to the spatial part of  $\tilde{H}_d$ , and  $\tilde{\rho}_l$  is the density operator corresponding to the lattice Hamiltonian  $\tilde{H}_l$ .

It is clear from Eqs. (9) and (10) that  $H^d_f$  and  $H^l_f$  are small from the viewpoint of their strengths. But their symmetry properties are important from the viewpoint of the impurity-impurity interaction. The exchange interactions involved in  $H^d_f$  are, as discussed above, of the type  $J_{ij} \mathbf{s}_{if} \cdot \mathbf{s}_{jf}$ . The exchange interaction in  $H^l_f$  is also of the same type. This means that the exchange interactions

used here are different from the so-called RKKY interactions.

Let the density operator corresponding to the approximate Hamiltonian  $\tilde{H} = H_1 + H_2$  be denoted by  $\tilde{\rho}$ . Since  $H_2$  is a small perturbation, we can assume that

$$\tilde{\rho} = \rho_1 + \rho_2 , \quad (11)$$

where  $\rho_1$  is the density operator of the state of the noninteracting impurities. Treating  $H_2$  within the first-order perturbation theory, we find that  $\rho_2$  is given by

$$i \frac{d\rho_2}{dt} = [H_1, \rho_2] + [H_2, \rho_1] . \quad (12)$$

To obtain an expression for the density operator  $\rho_1$  we employ the time-dependent collision theory developed earlier.<sup>3,4</sup> The interaction term  $H'_{fd}$  of  $H_1$  [Eq. (5)] causes the  $d$ -band electron to make multiple single-site scatterings with the impurity ion, so that the impurity will undergo  $f \rightarrow d$  and  $d \rightarrow f$  transitions. The role of the interaction  $H'_{fl}$  is to cause multiple emissions and absorptions of phonons by the impurity, so that again the impurity makes  $f \rightarrow d$  and  $d \rightarrow f$  transitions. We describe the joint effect of these two types of processes formally by a single, multiple single-site scattering matrix  $M_s(t_s)$ , where  $t_s$  is the time when the  $s$ th scattering is completed. The  $s$ th scattering may correspond to a scattering by a  $d$ -band electron or to an absorption of a phonon. To specify  $t_s$  precisely we first realize that, in general, the magnitudes of the group velocities of the  $d$ -band electron and the phonon will be different. Thus, the time of the multiple scatterings by the  $d$  electron will, in general, be different from the times of the multiple absorptions of the phonon. Let the number of scatterings made by the  $d$  electron and the phonon up to the time  $t_s$  be given, respectively, by  $n$  and  $m$ . Then  $s = m + n$  will be the total number of scatterings made jointly by the  $d$ -band electron and the phonon. The times  $t_s$  follow the order  $t_1 < t_2 < t_3 \dots$

The multiple single-site scattering matrix  $M_s(t_s)$  can be expressed in terms of the single-site scattering matrix  $S_p(t_p)$  formally in the same way as in Ref. 3. The scattering matrix  $S_p(t_p)$  is contributed by two matrices—one corresponding to the interaction  $H'_{fd}$ , the other corresponding to  $H'_{fl}$ . That is to say

$$S_p(t_p) = S_{p,fd}(t_p) + S_{p,fl}(t_p) , \quad (13)$$

where the scattering matrix  $S_{p,fd}$  describes the  $p$ th single-site interaction process which may be either a scattering of the  $d$ -band electron (due to the interaction  $H'_{fd}$ ) or an absorption of a phonon (due to the interaction  $H'_{fl}$ )—whichever is possible at the time  $t_p$ . The multiple scatterings made by the  $d$ -band electron generate coherence between the  $f$  and  $d$  states.<sup>3</sup> To see how far the multiple absorptions of phonons generate coherence between the  $f$  and  $d$  states we consider the time taken by the excited state (which is a mixture of  $f$  and  $d$  states) to decay via phonon emission. This time, say  $T_p$ , is given by  $T_p = \Gamma_p^{-1}$ , where  $\Gamma_p$  is the energy width of the excited state caused by the phonon absorption.  $\Gamma_p$  is described in terms of the multiple single-site absorption matrix  $M_{fl}$  as follows:

$$\Gamma_p = 2\pi \sum_g | \langle g' | M_{fl}(t_s) | g \rangle |^2 . \quad (14)$$

Here  $g$  denotes collectively the  $f$  state and the  $d$  states, and  $g'$  runs over all these states. If  $T_p \gg \tau_p$ , where  $\tau_p$  is the time difference between two successive absorptions of a phonon, the excited state produced by phonon absorptions will be a coherent mixture of the various  $f$  and  $d$  states.

The joint effect of the above two processes prepares an impurity in a state described by the density operator  $\rho_1$  as

$$\rho_{1,g'',g'}(t) = \left\langle \sum_{g,\mathbf{k},\sigma_d,w,\mathbf{K}} (g''; \mathbf{k}'\sigma_d''; p_{w\mathbf{K}}'' | M_s | g; \mathbf{k}\sigma_d; p_{w\mathbf{K}}) (g; \mathbf{k}\sigma_d; p_{w\mathbf{K}} | M_s | g'; \mathbf{k}'\sigma_d'; p_{w\mathbf{K}}') \right\rangle_{av}. \quad (16)$$

Here  $|\mathbf{k}\sigma_d\rangle$  is the  $d$ -band state corresponding to the wave vector  $\mathbf{k}$  and spin  $\sigma_d$ ,  $p_{w\mathbf{K}}$  is the number of phonons in the state  $|w\mathbf{K}\rangle$  of energy  $w$  and wave vector  $\mathbf{K}$ , and  $\langle \dots \rangle_{av}$  denotes average over the various scatterings at the time  $t_s$ .

It must be noted that the contribution of the scattering of the  $d$  electron and the absorption of the phonon to the

follows:

$$\rho_1(t_s) = \sum_{g'',g'} \rho_{1,g'',g'}(t_s) B_g^\dagger B_{g'}. \quad (15)$$

Here  $B_g^\dagger$  and  $B_g$  are the creation and destruction operators corresponding to the state  $|g\rangle$ .

The matrix elements of the density operator  $\rho_1$  at a time  $t$  are given by

strength of the coherence which makes the off-diagonal elements of  $\rho_1$  nonzero will be different. This is because the  $d$  electron and the phonon differ in their velocities. The net contribution to the coherence is better understood in terms of the collision-generated hybridization which is given by

$$V_{h,\text{coll}} = \sum_{\substack{g,g',\mathbf{k},\mathbf{k}' \\ d,d',w,w' \\ \mathbf{K},\mathbf{K}'}} (g'; \mathbf{k}'\sigma_d'; p_{w\mathbf{K}}' | (H_{fd} + H_{fl}) | g; \mathbf{k}\sigma_d; p_{w\mathbf{K}}) \text{Tr} \langle [f_{i\sigma}^\dagger d_{\mathbf{k}\sigma} \tilde{\rho}(t_s)] \rangle_{av}. \quad (17)$$

The above method for finding out the density operator of the state of the  $f$ -electrons under the interactions  $H_{fd}$ ,  $H_{fl}$ , and  $H_{dl}$  is a self-consistent method having four steps. In the first step we have considered only the noninteracting impurities and have obtained the density operator  $\rho_1$ . The second step corresponds to the lattice dynamics under the interactions  $H_{\text{anh}}$ ,  $H_f^f$ , and  $H_f^d$  [cf. Eq. (7)]. The average interactions  $H_f^f$  and  $H_f^d$  are basically attractive<sup>11</sup> in nature since their origin lies in the interaction of an electron with positive ions. Therefore, the effect of  $H_f^f$  and  $H_f^d$  will be to contract the lattice. But since the anharmonic term  $H_{\text{anh}}$  causes expansion of the lattice, the net effect will be that the lattice will assume an equilibrium position with a changed lattice constant. This mechanism is consistent with that of Anderson and Chui.<sup>12</sup>

The third step of the self-consistency lies in the perturbation of the  $d$  band. Since in the second step the lattice constant has changed, the  $d$ -band energies will also change. This will induce changes in the density operator  $\rho_1$ . In the final step of the self-consistency of the method, the  $f$  electron impurities interact with each other so that the final state of the  $f$  electron is characterized by the den-

sity operator  $\tilde{\rho}$ ; and in particular, the  $f$ -state occupation is given by

$$n_{ff} = \text{Tr}(f_{i\sigma}^\dagger f_{i\sigma} \tilde{\rho}). \quad (18)$$

In conclusion, we have formulated a method which takes both the electron-electron and the electron-lattice interactions into account in an approximate but realistic way. The method is capable of providing information on the roles of the electron-electron and the electron-phonon interactions in driving and stabilizing the valence-change transition. The method suggests a mechanism of stabilization of the mixed valence phase. The mechanism is governed by the joint effect of the electronic and lattice interactions. The collision-generated hybridization is an experimentally measurable<sup>3</sup> quantity. Moreover, the method opens a way for realistic calculations of the exchange integral, whose value finds importance in determining the magnetic behavior of the mixed-valence system.

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<sup>1</sup>See various contributions in *Proceedings of the International Conference on Valence Fluctuations in Solids, Cologne, West Germany, August 27-30, 1984* [J. Magn. Mater. **47 & 48** (1985)].

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