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Competing hybridization and consequences for magnetic ordering in ternary and quaternary correlated-electron systems

Carlos Sanchez-Castro
Department of Physics, West Virginia University, Morgantown, West Virginia 26506-6315
and Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Bernard R. Cooper
Department of Physics, West Virginia University, Morgantown, West Virginia 26506-6315

Kevin S. Bedell
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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We present a method for calculating the hybridization induced f-f interionic interaction in systems where a d-electron species also hybridizes with the same Fermi sea. For the ternary and quaternary physical systems of interest, typically the f species is a light rare earth (e.g., Ce or Pr) or a light actinide (U) involving a partially filled f shell, and there may be experimental evidence of competition between magnetic ordering of the f- and d-electron systems (e.g., when f is U and d is Mn in UMn_2Si_2 or UMn_2Ge_2) or between magnetic ordering for the f-ionic system and superconductivity (e.g., when f is Pr and d is Cu in $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$). The method treats first the strong hybridization between the d and the conduction electrons to obtain a new ground state with delocalized d electrons. Then it calculates the f-f interionic interaction by perturbation theory. We find that the d electrons affect the f-f ion interaction by modifying the conduction electron spectral function. This process is quite sensitive to the degree of correlations among the d electrons.

I. INTRODUCTION

In recent years there has been considerable interest in the behavior of partially delocalized light rare-earth and actinide systems where cooperative hybridization between a lattice of somewhat delocalized f-electron ions and the non-f band electrons gives rise to orbitally driven magnetic ordering phenomena. These materials are characterized by extremely high anisotropy in the equilibrium, excitation and critical magnetic behavior, and often by anomalously strong damping of the excitations.[1,2] The theory of this magnetic ordering and associated behavior is by now well developed[1-7] when a lattice of only a single f-electron species, such as cerium or uranium, is present. Interest in generalizing this understanding to the situation where there is a d-electron species also present is strongly motivated by the magnetic competition[8,9] between d and f electrons that occurs in ternary and quaternary compounds such as the compounds of the $ThCr_2S_2$-type structure of the type UMn_2X_2 and RMn_2X_2 (where R is a rare earth [Ce, Pr, Nd] and X is Si, [Ge]). In these compounds, if the Mn is replaced by another transition metal, there is no magnetic ordering of the transition metal. For the light rare-earth/Mn compounds[8] there is magnetic ordering of Mn moments, with ordering temperatures above 300 K, that either is ferromagnetic or is antiferromagnetic with Mn planes that are ferromagnetic in alternating directions; and the rare-earth sublattices show no ordering. Quite different magnetic ordering behavior occurs for the corresponding heavy rare-earth compounds where the more localized f electrons presumably have negligible hybridization, and where typically there is evidence of magnetic ordering on the rare-earth site. For the UMn_2X_2 compounds[9] the magnetic ordering of the uranium sublattice is strongly coupled with that of the Mn sublattices.

Competition effects between d and f electrons are also observed in the study of the influence of praseodymium[10-14] and curium[14] on the superconducting properties of the CuO-based high-T_c superconductors of the type $RBa_2Cu_3O_7$ (R = Y, rare earth). $PrBa_2Cu_3O_7$ is unique among the members of the isostructural orthorhombic $RBa_2Cu_3O_7$ series in not being a superconductor. As Pr is substituted for Y, superconductivity disappears at somewhat over 60% Pr. Furthermore, at the Pr-rich end the magnetic ordering temperature is anomalously high, being 17 K for $PrBa_2Cu_3O_7$. Substitution of the actinide curium for Y has quite similar effects,[14] destroying superconductivity and with apparent magnetic ordering at 22 K.

There has been much interest in the possible mechanism for the ability of praseodymium to quench the superconductivity, with two different mechanisms being proposed.[15] One of these[10,11] envisions the praseodymium as going in as Pr^{4+}, and thus by charge-transfer filling oxygen p holes, thereby quenching the pairing interaction. The other point of view[16] considers hybridization between copper d electrons and oxygen p electrons as being essential for the pairing mechanism, and that the competing hybridization of the copper d electrons with the oxygen p electrons destroys this pairing mechanism. (The Pr can be either trivalent or tetravalent in this pic-

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ture.) In connection with this latter competing hybridization viewpoint, it is interesting that the magnetic ordering in $PrBa_2Cu_3O_7$ shows key characteristics of orbitally driven (hybridizing) magnetic ordering,[16] i.e., anomalously high ordering temperature, reduced ordered moment, and anomalously broadened magnetic excitations.[14,17] The competing hybridization picture also receives strong support from the neutron inelastic scattering results,[18,19] taken in conjunction with the specific heat and susceptibility behavior, showing that the crystal-field splitting is completely or predominantly that of trivalent Pr (at least 90% Pr^{3+}), which would rule out the charge-transfer/hole filling mechanism. It is also interesting that the ordering for both the orbitally driven magnetism and the CuO-type superconductivity develops its main strength in a planar unit. (For the orbitally driven magnetism this is typically a ferromagnetic unit that may be coupled to other planar units ferromagnetically or antiferromagnetically.) Given the present understanding of orbitally driven magnetism,[1,2] this evokes the picture of two sublattices (i.e., of Pr with partially filled f shell, and of Cu with partially filled d shell) competing to cooperatively hybridize (form weak covalent bonds) with oxygen p states in a sheetlike fashion. The valence fluctuations as electrons jump in and out of the f-electron shell provide the interionic coupling mechanism for the orbitally driven magnetism;[1,2] and presumably the same is true for the d-electron superconductivity. The matter of deciding which mechanism explains the ability of Pr to destroy superconductivity may be important in lending support to, or in eliminating, mechanisms proposed for the high-temperature superconductivity in the ceramic cuprates. For example, as discussed recently by Gao and Zhang,[20] a superconductivity mechanism based on bipolaron effects may provide a natural framework yielding the full range of behavior in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ system; and it might be illuminating to try to base such a model on calculations starting from fundamental theory in a manner analogous to the treatment herein. It would be extremely interesting to see if a detailed calculation based on the present formulation provides a hybridized state of the type envisioned in the model of Fehrenbacher and Rice.[21] In that model the absence of superconductivity would be explained by Pr immobilizing mobile holes in the Cu-O planes by the existence of a local Pr($4f$)-O($2p\pi$) hybridized state which binds holes to the Pr sites. The existence of this state implies a percentage of Pr^{4+} somewhat larger than the maximum indicated by the experimental behavior,[19] but sufficiently close as not to preclude this model subject to fully quantitative verification.

The first development necessary in an effort to understand the magnetic behavior of these d-f electron systems is the construction of an effective Hamiltonian. This task is in general a very difficult one since the three types of electrons, i.e., conduction, d and f electrons can interact with each other, and a full self-consistent approach which takes into account all feedback effects is necessary. Some progress along these lines has been made in the so-called parquet approximations to the quasiparticle interactions.[22,23] In the present paper we show that by properly identifying the most important feedback effects in the systems just described, a more practical and tractable approach is possible. We argue that when the f-electron ions show local magnetic moments the most significant renormalizations of the conduction band are due to the hybridization with the d electrons. Thus, we propose a method that treats first the strong hybridization between the d and the conduction electrons to obtain a new ground state with delocalized d electrons. Then it calculates the f-f ion interaction by an established procedure using perturbation theory.[4–7] We find that the d electrons affect the f-f ion interaction by modifying the conduction-electron spectral function. This process is quite sensitive to the degree of correlations among the d electrons.

The paper is organized as follows: In Sec. II, we present some technical background and generalize the existing theory[3,4] to compute the two-ion interactions in a system with two localized f species in each unit cell by summing all contributions coming from the interchange of particle-hole excitations in the conduction band and from kinetic superexchange. Then in Sec. III, we introduce a method to calculate the f-f ion interaction in a d-f electron system with strongly delocalized d electrons, *the situation of interest as discussed above*. In Sec. IV we apply this formalism to a d-f system interacting with a free-electron conduction band; and show that the f-f ion interaction is substantially affected by the correlations (Coulomb repulsion effects) among the d electrons. Finally, Sec. V contains our concluding remarks. A brief preliminary report of the work has appeared in Ref. 24.

II. TECHNICAL BACKGROUND AND THE CASE OF TWO WEAKLY HYBRIDIZING LOCALIZED SPECIES

In this article, we will be mostly concerned with the construction of an effective Hamiltonian for studying the magnetic properties of a system that contains two different species of partially delocalized electrons in a lattice hybridizing with a sea of conduction electrons. This system is described by an Anderson lattice Hamiltonian given by

$$H = H_c + \sum_{\alpha} H_{\alpha} , \tag{2.1a}$$

where $H_c = \sum_{\mathbf{k}n\sigma} \epsilon_{\mathbf{k}n} c^{\dagger}_{\mathbf{k}n\sigma} c_{\mathbf{k}n\sigma}$ is the conduction band Hamiltonian and $c^{\dagger}_{\mathbf{k}n\sigma}$ is a creation operator for a conduction electron with wave vector $\mathbf{k}$ located in the first Brillouin zone, band index n, and spin σ. Here

$$H_{\alpha} = \sum_{im} \epsilon_{\alpha} l^{\dagger}_{i\alpha m} l_{i\alpha m} + \frac{1}{2} \sum_{\substack{imm' \\ m \neq m'}} U_{\alpha} l^{\dagger}_{i\alpha m} l_{i\alpha m} l^{\dagger}_{i\alpha m'} l_{i\alpha m'} + \frac{1}{\sqrt{N_s}} \sum_{\substack{im \\ \mathbf{k}n\sigma}} \left(V^{(\alpha)}_{\mathbf{k}n\sigma m} e^{-i\mathbf{k}\cdot\mathbf{R}_{i\alpha}} c^{\dagger}_{\mathbf{k}n\sigma} l_{i\alpha m} + \text{c.c.} \right) \tag{2.1b}$$

and $l^{\dagger}_{i\alpha m}$ is a creation operator for a localized electron centered at $\mathbf{R}_{i\alpha} = \mathbf{R}_i + \mathbf{r}_{\alpha}$ in the ith unit cell. This localized electron has orbital angular momentum l_{α} and total angular momentum j_{α} and projection of the latter along the quantization axis m. Here c.c. stands for the complex conjugate of the previous expression, N_s is the number of unit cells in the crystal, and all single particles energies are taken with respect to the chemical potential. We have implicitly assumed the strong single-electron spin-orbit coupling limit, and j_α refers to the lowest lying spin-orbit coupled state. In the case where the spin-orbit coupling is weak, one must sum over both $j_\alpha = l_\alpha \pm 1/2$ terms in the Hamiltonian. This last procedure is equivalent to working in the uncoupled representation given in terms of (m_l, m_s).

The approach to follow in the calculation of an effective magnetic Hamiltonian starting from Eq. (2.1) varies depending on the physical system in consideration. In the most general case the different localized electrons can strongly interact with each other by modifying the electron gas and a self-consistent treatment is necessary. In other cases[4] as in CeSb such a treatment is not necessary. To explore the great diversity of physical behaviors possible, let us first consider a conduction-electron–f-electron system. For nearly localized f-electron ions one can, through a canonical transformation,[25,26] transform the hybridization Hamiltonian into a conduction-electron–f-electron ion scattering term with a dimensionless coupling $\tilde{J} = N(0) V_f^2 U_f / [(U_f + \epsilon_f)\epsilon_f]$, where $N(0)$ is the conduction density of states per spin and site at the Fermi surface.

In what has been the conventional picture for some years, the behavior of the hybridizing f system[27] is determined by a competition between Ruderman-Kittel-Kasuya-Yosida (RKKY) magnetic ordering between two local moments with energy scale $\tilde{J}^2/N(0)$ and conduction-electron-f-electron singlet formation with energy scale $e^{-1/|\tilde{J}|}/N(0)$. The deep Kondo regime occurs when $|\tilde{J}| \ll 1$ and the RKKY interaction dominates. For somewhat larger $|\tilde{J}|$, the heavy fermion regime appears with the formation of conduction-f-electron singlets and reduced magnetic moments. In the mixed-valence regime, it is not possible to map the Anderson lattice Hamiltonian to the Kondo Hamiltonian.

In an alternative picture,[1,2] supported by *ab initio* calculations,[6,7] the moment reduction results from the restructuring of the interionic magnetic interaction associated with the hybridization process in the presence of f-electron correlation effects for these systems with large orbital moments. It is the resulting extreme anisotropy of the interionic interaction which forces the hybridized f-ionic ground state to have a small or even vanishing value of the moment.

In contrast to the hybridizing f system described above, a hybridizing d system with a conduction-d-electron hybridization matrix element an order of magnitude larger than for an f-electron system usually exhibits delocalized behavior. Spontaneous magnetism is favored when spin polarization of the bands is made energetically favorable by some residual interaction.

The calculation of an effective Hamiltonian for a system with two f species at different sites in the unit cell both in the deep Kondo regime can be treated by a straightforward generalization of a well established approach.[3–5,25,26] This approach obtains an effective magnetic Hamiltonian by first performing a canonical transformation, a Schrieffer-Wolff transformation (SWT) on the Anderson lattice Hamiltonian and then applying perturbation theory (see the Appendix). Implicit in this approach is the assumption that the conduction Fermi sea is not significantly renormalized by either species. In other words, there are no feedback effects and a self-consistent treatment is unnecessary. Among the many terms in the Hamiltonian obtained from the SWT there is a scattering term between the conduction and the localized ions (Coqblin-Schrieffer interaction), a hopping or banding Hamiltonian between the localized electrons induced by hybridization and a term that when projected into the model space will give a direct two-ion interaction. By applying perturbation theory one sums over induced contributions to the two ion interaction due to (1) the exchange of particle-hole excitations in the conduction band (Coqblin-Schrieffer two-ion interaction) and (2) a kinetic superexchange contribution due to the hopping of the localized electrons between sites induced by the hybridization with the conduction electrons and involving intermediate ionic configurations.[3–5] [See discussion of Eqs. (A19)–(A22) in the Appendix.] Explicitly, the two-ion interaction between single-electron ions located at $\mathbf{R}_{i,\alpha}$ and $\mathbf{R}_{j,\alpha'}$, both in a given configuration (not necessarily identical) up to fourth order in the hybridization, has the form

$$h(\mathbf{R}_{i\alpha}, \mathbf{R}_{j\alpha'}) = -\sum_{\substack{m_1, m_1' \\ m_2, m_2'}} E^{\alpha\alpha'}_{m_1' m_1; m_2' m_2}(\mathbf{R}_{i\alpha} - \mathbf{R}_{j\alpha'}) \times l^\dagger_{i\alpha m_1'} l_{i\alpha m_1} l^\dagger_{j\alpha' m_2'} l_{j\alpha' m_2}, \tag{2.2a}$$

where the range function $E^{\alpha\alpha'}$ is given by

$$E^{\alpha\alpha'}_{m_1' m_1; m_2', m_2}(\mathbf{R}) = -\frac{1}{N_s^2} \sum_{\substack{\mathbf{k} n\sigma \\ \mathbf{k}' n'\sigma'}} V^{(\alpha)}_{\mathbf{k} n\sigma m_1} V^{(\alpha)*}_{\mathbf{k}' n'\sigma' m_1'} V^{(\alpha')}_{\mathbf{k}' n'\sigma' m_2} \times V^{(\alpha')*}_{\mathbf{k} n\sigma m_2'} e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} \times F^{\alpha\alpha'}(\epsilon_{\mathbf{k}n}, \epsilon_{\mathbf{k}'n'}) . \tag{2.2b}$$

Here $F^{\alpha\alpha'}$ is a function of the unrenormalized conduction band energies and is given by Eq. (A25c). The range function contains both ferromagnetic and antiferromagnetic contributions at short ranges, a point discussed after Eq. (A27) in the Appendix. The competition between these contributions, and the extreme anisotropy inherent with this interaction as discussed in the following paragraph, leads to a fascinating variety of unusual magnetic phenomena. The extension of this theory to multielectronic f ions is fully discussed by Sheng, Cooper, and Lim[7] and briefly summarized in Eq. (A27) of the Appendix. As expected, the interaction of two ions of the same species is not affected by the presence of the other localized species up to fourth order in perturbation theory; i.e., feedback effects where species α significantly modifies the electron gas and induces a change in the ion α'-ion α' interaction ($\alpha \neq \alpha'$) are clearly sixth- or higher-order effects. At this level of approximation, the two ionic species can only interact through the cross term in the Hamiltonian involving ions of different species. This cross term in the Hamiltonian can lead to competition between different magnetic interactions, frustration effects and complicated magnetic ordering.

To characterize the angular dependence of the cross term in the two-ion interaction, given by Eq. (2.2), we must generalize the analysis done by Cooper and coworkers[3,4] in the case of one localized species. To do that we assume a spherically symmetric hybridization potential with hybridization matrix element given by[28]

$$V_{\mathbf{k}n\sigma m}^{(\alpha)}=\sqrt{4\pi}V_{kn}^{(\alpha)}Y_{l_\alpha m-\sigma}(\hat{k})\times\langle l_\alpha,1/2,m-\sigma,\sigma|l_\alpha,1/2,j_\alpha,m\rangle\ , \qquad (2.3)$$

where $Y_{l_\alpha m-\sigma}(\hat{k})$ is a spherical harmonic for $l=l_\alpha$ and $\langle l_\alpha,1/2,m-\sigma,\sigma|l_\alpha,1/2,j_\alpha,m\rangle$ is a Clebsch-Gordon coefficient for a spin-orbit coupled state with $j=j_\alpha$ and $l=l_\alpha$. Furthermore, we simplify the analysis by considering the case of a conduction band with an isotropic dispersion relation. In this case, one can show that the asymptotic behavior of the range function for a quantization axis along the interatomic separation vector $\hat{R}=\mathbf{R}/R$ (abbreviated ba for bonding axis) is given by

$$E_{m_1'm_1;m_2'm_2}^{\alpha\alpha'}(\mathbf{R})|_{\mathrm{ba}}=(-1)^{(m_1-m_2)(j_\alpha-l_\alpha-j_{\alpha'}+l_{\alpha'})}\times\delta_{m_1,m_2'}\delta_{m_2,m_1'}\delta_{|m_1|,1/2}\times\delta_{|m_2|,1/2}E^{\alpha\alpha'}(R)\ , \qquad (2.4a)$$

where

$$E^{\alpha\alpha'}(R)=-\sum_{nn'}(j_\alpha+1/2)(j_{\alpha'}+1/2)\times\Omega^2\int dk\frac{k^2}{2\pi^2}\int dk'\frac{k'^2}{2\pi^2}V_{kn}^{(\alpha)}V_{kn}^{(\alpha')*}V_{k'n'}^{(\alpha')}V_{k'n'}^{(\alpha)*}g_t(kR)g_t(k'R)F^{\alpha\alpha'}(\epsilon_{kn},\epsilon_{k',n'})\ , \qquad (2.4b)$$

the region of integration is the first Brillouin zone, Ω is the primitive unit-cell volume, $g_t(kR)=\sin(kR-t\pi/2)/(kR)$, and $t=l_\alpha+l_{\alpha'}$. It is clear from Eq. (2.4) that the highly anisotropic two-ion interaction favors having two ions "point" their charge forming a "disk" along the bonding axis (the $m_j=\pm1/2$ states, i.e., $m_l=0$) thereby developing a small covalent bonding energy and causing the ionic orbital moments to align perpendicular to the bonding axis.[1] The angular dependence of the two-ion interaction implicit in Eq. (2.4) can be shown explicitly[4] by expressing the two-ion interaction in the fixed crystal frame. To do that we use the unitary transformation relating the creation operators for a localized ion at $\mathbf{R}_{i,\alpha}$ with total angular j_α and projection m' along the interionic axis (primed) and the corresponding projection in the fixed crystal frame (unprimed), i.e.,

$$l_{iam'}^{\prime\dagger}=\sum_m D_{mm'}^j(\phi,\theta,0)l_{iam}^\dagger\ . \qquad (2.5)$$

Here $D_{mm'}^j(\phi,\theta,0)=\langle jm|e^{-i(j_z/\hbar)\phi}e^{-i(j_y/\hbar)\theta}|jm'\rangle$ is a rotation matrix and (θ,ϕ) are the spherical angles that specify the direction of $\hat{R}$ in the crystal frame. Substituting Eq. (2.5) into Eq. (2.4), we obtain that the range function in the fixed crystal frame (abbreviated cf) is given by

$$E_{m_1',m_1;m_2',m_2}^{\alpha\alpha'}(\mathbf{R})|_{\mathrm{cf}}=\sum_{\substack{\mu_1,\mu_1'\\ \mu_2,\mu_2'}}E_{\mu_1'\mu_1;\mu_2'\mu_2}^{\alpha\alpha'}(R)|_{\mathrm{ba}}\times e^{-i(m_1'+m_2'-m_1-m_2)\phi}d_{m_1'\mu_1'}^{j_\alpha}(\theta)\times d_{m_1\mu_1}^{j_\alpha}(\theta)d_{m_2'\mu_2'}^{j_{\alpha'}}(\theta)d_{m_2\mu_2}^{j_{\alpha'}}(\theta)\ , \qquad (2.6)$$

where $d_{mm'}^j=\langle jm|e^{-i(j_y/\hbar)\theta}|jm'\rangle$.

In conclusion, a fourth-order treatment of the Anderson lattice Hamiltonian with two distinct ionic species predicts a magnetic Hamiltonian with cross terms between ions belonging to the different species. These terms have a different angular dependence from the interactions between ions of the same species when $j_\alpha\neq j_{\alpha'}$. This Hamiltonian is adequate for treating a number of systems, but is inadequate to study competition effects between the two hybridizers as the delocalization and hence the hybridization, of one of the species strengthens. This, in fact, is the situation for the two motivating examples discussed in the Introduction, and this leads us to treat the situation discussed in the next section. In addition, while it is possible to have the situation where magnetic ordering is destroyed by state mixing (giving a nonmagnetic, i.e., singlet state) even for a single weakly hybridizing species,[1,2,29] we do not believe that a straightforward generalization of that possibility provides an adequate representation of the mechanism for the destruction of magnetic ordering involved in the two examples discussed in the Introduction. That is, in principle, while the new cross-term for $l_\alpha\neq l_{\alpha'}$ introduced here (together with the overall decrease of Pr hybridization as Pr concentration decreases in $\mathrm{Pr}_x\mathrm{Y}_{1-x}\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_7$) could provide an overall interaction giving a nonmagnetic state for Pr, we do not believe that would adequately capture the essential features of the physics. Rather, we believe that there is a fundamental change in the Pr-Pr interaction itself (or in the R-R interaction for $R\mathrm{Mn}_2X_2$), and the physics developed in the next section allows us to treat that possibility.

III. THE *f*-*f* ION INTERACTION IN THE PRESENCE OF A MORE DELOCALIZED *d* HYBRIDIZER

A. Model Hamiltonian

Now we consider the problem described in the Introduction of obtaining an effective magnetic Hamiltonian for the f ions in a system where the d electrons are strongly hybridized with the conduction band. Evidence for the strong hybridization of the d electrons comes in part from band-structure calculations.[30] These calculations clearly show an enhanced density of states (DOS) near the Fermi level due to the d electrons. In many cases, the enhanced DOS plus various residual interactions between the d electrons could lead to a spontaneous magnetic moment for the d species.[8] We assume this does not happen here, and the d species remains paramagnetic. For the f species we assume that they are in the RKKY interaction dominated regime with local magnetic moments, i.e., the deep Kondo regime. For such a system, the most significant renormalizations of the conduction band is due to the d electrons. Thus, we propose a method where we first treat the hybridization of the d electrons with the conduction electrons in a mean-field approximation to obtain renormalized bands and enhanced DOS. Then, we proceed to treat the f-electron hybridization through the well established treatment of a SWT and perturbation theory. Since we explicitly incorporate the effects of the d hybridization in the unperturbed Hamiltonian used in the SWT, the resulting f-f ion interaction is explicitly dependent on the renormalizations effects of the conduction band due to the d electrons.

In practice, for the sake of simplicity, we consider a system with a single conduction band and we neglect the orbital degeneracy of the d system. Thus, our Hamiltonian is given by Eq. (2.1) with a slight change in notation $l^{\dagger}_{idm} \rightarrow d^{\dagger}_{i\sigma}$, $l^{\dagger}_{ifm} \rightarrow f^{\dagger}_{im}$ and from now on we will omit the band index identifying the conduction band, i.e., $c^{\dagger}_{\mathbf{k}n\sigma} \rightarrow c^{\dagger}_{\mathbf{k}\sigma}$. We take the d ions to be located at the origin of the unit cell and assume a constant d-electron hybridization matrix element $V^{(d)}_{\mathbf{k}\sigma m} = V_d$. The f-electron hybridization matrix element is given by Eq. (2.3) as

$$V^{(f)}_{\mathbf{k}\sigma m} = \sqrt{4\pi} V_f Y_{3m-\sigma}(\hat{k}) \times \langle 3, 1/2, m-\sigma, \sigma | 3, 1/2, j_f, m \rangle , \tag{3.1}$$

where we assumed a constant V_f. With this model Hamiltonian, in Sec. III B we consider the mean-field treatment of $H_{c-d} \equiv H_c + H_d$ and then proceed in Sec. III C to calculate the f-f ion interactions.

B. Mean-field treatment of the d-electron hybridization with the conduction-electron gas

In this subsection, we treat the hybridization of the d electrons with the conduction band to obtain renormalized bands. To do this, we diagonalize H_{c-d}, defined in Sec. III A, in a mean-field approximation. The d hybridization is different than for simple metals since electron-correlation effects between the narrow d-band electrons are significant and the intra-atomic d-d Coulomb interaction must be explicitly taken into account. *In order to compare the effect of d-electron correlations in the hybridization process, we will diagonalize* H_{c-d} *in two extreme cases: the case of no d-electron correlations, i.e.,* U_d *equals to zero and the limit of* U_d *infinite.*

Considering first the strong correlation case (U_d infinite), we adopt a slave-boson treatment of the Anderson lattice Hamiltonian.[31–33] In the slave-boson formalism, we have that H_{c-d} is written as

$$\begin{aligned} H_{c-d} = {} & \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \sum_{i\sigma} \epsilon_d \hat{d}^{\dagger}_{i\sigma} \hat{d}_{i\sigma} \\ & + \frac{1}{\sqrt{N_s}} \sum_{i\mathbf{k}\sigma} (V_d e^{-\mathbf{k}\cdot\mathbf{R}_i} c^{\dagger}_{\mathbf{k}\sigma} b^{\dagger}_i \hat{d}_{i\sigma} + \text{c.c.}) \\ & + \sum_i \lambda_i \left[\sum_{\sigma} \hat{d}^{\dagger}_{i\sigma} \hat{d}_{i\sigma} + b^{\dagger}_i b_i - 1 \right] . \end{aligned} \tag{3.2}$$

Here we have represented $d^{\dagger}_{i\sigma}$ as a bilinear product

$$d^{\dagger}_{i\sigma} = \hat{d}^{\dagger}_{i\sigma} b_i , \tag{3.3}$$

where $\hat{d}^{\dagger}_{i\sigma}$ is a slave fermion creation operator representing the $|d^{(1)}_{\sigma}\rangle_i$ configuration and $b^{\dagger}_i$ is a slave-boson creation operator representing the $|d^{(0)}\rangle_i$ configuration. We have also added a time-independent auxiliary boson field λ_i that couples to the system through a Hamiltonian

$$H_{\text{aux}} = \sum_i \lambda_i \left[\sum_{\sigma} \hat{d}^{\dagger}_{i\sigma} \hat{d}_{i\sigma} + b^{\dagger}_i b_i - 1 \right] \tag{3.4}$$

and acts as a local Lagrange multiplier to enforce the constraint of no multiple occupancy of a d site in the infinite U_d limit. In the mean-field approximation to the slave-boson Hamiltonian, one replaces the boson fields by their expectation values over their coherent equilibrium states, namely, $r = \langle b_i \rangle$ and $\Lambda = \langle \lambda_i \rangle$. The resulting Hamiltonian H^{MF}_{c-d} is one of hybridizing bands but with a renormalized hybridization matrix element $\tilde{V}_d = V_d r$ and a renormalized d level position $\tilde{\epsilon}_d = \epsilon_d + \Lambda$.

The above Hamiltonian is diagonalized by first changing to the Bloch representation for the d electrons given by $\hat{d}^{\dagger}_{\mathbf{k}\sigma} = \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} \hat{d}^{\dagger}_{i\sigma} / \sqrt{N_s}$ and then performing a canonical transformation to hybridized band creation operators given in terms of the orthogonal matrix $\hat{\gamma}$ as

$$\begin{bmatrix} a^{\dagger}_{\mathbf{k}1\sigma} \\ a^{\dagger}_{\mathbf{k}2\sigma} \end{bmatrix} = \begin{bmatrix} \alpha_{\mathbf{k}} & \beta_{\mathbf{k}} \\ -\beta_{\mathbf{k}} & \alpha_{\mathbf{k}} \end{bmatrix} \begin{bmatrix} \hat{d}^{\dagger}_{\mathbf{k}\sigma} \\ c^{\dagger}_{\mathbf{k}\sigma} \end{bmatrix} , \tag{3.5}$$

where

$$\alpha^2_{\mathbf{k}} = \frac{1}{2} \left[1 + \frac{\epsilon_{\mathbf{k}} - \tilde{\epsilon}_d}{E_{\mathbf{k}}} \right] , \quad \beta^2_{\mathbf{k}} = \frac{1}{2} \left[1 - \frac{\epsilon_{\mathbf{k}} - \tilde{\epsilon}_d}{E_{\mathbf{k}}} \right] ,$$

$\alpha_{\mathbf{k}} \beta_{\mathbf{k}} = -\tilde{V}_d / E_{\mathbf{k}}$, and $E_{\mathbf{k}} = [(\epsilon_{\mathbf{k}} - \tilde{\epsilon}_d)^2 + 4\tilde{V}^2_d]^{1/2}$. In terms of the hybridized band operators, H^{MF}_{c-d} simplifies to

$$H^{\text{MF}}_{c-d} = \sum_{\mathbf{k}n\sigma} \epsilon_{\mathbf{k}n} a^{\dagger}_{\mathbf{k}n\sigma} a_{\mathbf{k}n\sigma} + N_s \Lambda (r^2 - 1) , \tag{3.6a}$$

where $n = 1, 2$, is a band index, $\epsilon_{\mathbf{k}n}$ are the hybridized band energies given by

$$\epsilon_{\mathbf{k}n} = \frac{1}{2} [\epsilon_{\mathbf{k}} + \tilde{\epsilon}_d + (-1)^n E_{\mathbf{k}}] . \tag{3.6b}$$

For each band n, we can obtain the corresponding density of states per site (DOS) by evaluating the expression $\rho_n(\omega) = \sum_{\mathbf{k}\sigma} \delta(\omega - \epsilon_{\mathbf{k}n\sigma})$. The resulting DOS can also be decomposed into a projected d-band contribution $\rho_d(\omega)$ and a projected conduction-band contribution, $\rho_c(\omega)$

given by

$$\rho_{d(c)}(\omega)=\frac{1}{N_s}\sum_{\mathbf{k}n\sigma}\gamma^2_{n,1(2)}\delta(\omega-\epsilon_{\mathbf{k}n\sigma}) \ . \tag{3.7}$$

From Eqs. (3.5), (3.6), and (3.7), it can be shown that

$$\rho_c(\omega)=\frac{1}{N_s}\sum_{\mathbf{k}\sigma}\delta\left[\omega-\frac{\widetilde{V}_d^2}{\omega-\widetilde{\epsilon}_d}-\epsilon_{\mathbf{k}}\right] \tag{3.8a}$$

is the conduction-band density of states per site evaluated at $\omega-\widetilde{V}_d^2/(\omega-\widetilde{\epsilon}_d)$ and

$$\rho_d(\omega)=\frac{\widetilde{V}_d^2}{(\omega-\widetilde{\epsilon}_d)^2}\rho_c(\omega) \ . \tag{3.8b}$$

These results, Eqs. (3.6), (3.7), and (3.8) are formally valid for the case of U_d equals to zero by neglecting Coulomb renormalization effects, i.e., by setting $\widetilde{\epsilon}_d=\epsilon_d$ and $\widetilde{V}_d=V_d$. The $U\rightarrow\infty$ ground state differs from the $U=0$ ground state in that in the former all configurations with doubly occupied d sites have been projected out.

The equations for determining the expectation value of the boson fields are obtained by minimizing the mean-field energy with respect to r and Λ. The resulting equations are[32]

$$n_d\equiv\sum_n\int_{\epsilon_n^{(-)}}^{\epsilon_n^{(+)}}d\omega\,\rho_d(\omega)n_F(\omega)=1-r^2 \ , \tag{3.9a}$$

$$\Lambda=-\sum_n V_d^2\int_{\epsilon_n^{(-)}}^{\epsilon_n^{(+)}}d\omega\frac{\rho_c(\omega)n_F(\omega)}{\omega-\widetilde{\epsilon}_d} \ , \tag{3.9b}$$

where $\epsilon_n^{(-)}$ and $\epsilon_n^{(+)}$ are the lower and upper bands edges of the nth hybridized band and $n_F(\omega)=[\exp(\omega/(k_BT))+1]^{-1}$ The chemical potential μ is determined simultaneously with the evaluation of r, Eq. (3.9a) and Λ, Eq. (3.9b), from the conservation of charge equation

$$n_{\text{total}}=\sum_n\int_{\epsilon_n^{(-)}}^{\epsilon_n^{(+)}}d\omega[\rho_d(\omega)+\rho_c(\omega)]n_F(\omega) \ , \tag{3.9c}$$

where n_{total} is the total number of electrons per site contributed by both the d and the conduction bands. From Eq. (3.9a), it is evident that the average occupation in a d site in the infinite U_d limit is $n_d=1-r^2$, i.e., in the mean-field approximation the constraint given by H_{aux}, Eq. (3.4), is enforced in an average way. The fact that r also renormalizes the hybridization matrix element can be physically understood[33] by noting that in the infinite U_d limit, an electron can jump from a site to another site only if the final state is empty and this results in a phase space factor $1-n_d$ in the transition rate.

C. Calculation of the modified *f*-*f* ion interaction due to species *d* hybridization

To obtain the f-f ion interaction, we first derive a single species Anderson Hamiltonian where the f electrons hybridize with the two renormalized bands obtained in Sec. III B. This is obtained by replacing $H_c+H_d\rightarrow H^{\text{MF}}_{c-d}$ in the Hamiltonian in Eq. (2.1), and using the inverse transformation, $c^\dagger_{\mathbf{k}\sigma}=\sum_n\gamma_{n,2}a^\dagger_{\mathbf{k}n\sigma}$, [see Eq. (3.5)] to express the f hybridization with the conduction band in terms of the renormalized band operators. We obtain

$$H=H^{\text{MF}}_{c-d}+\sum_{i,m}\epsilon_f f^\dagger_{im}f_{im}+\frac{1}{2}\sum_{\substack{imm'\\ m\neq m'}}U_f f^\dagger_{im}f_{im}f^\dagger_{im'}f_{im'}$$
$$+\frac{1}{\sqrt{N_s}}\sum_{im\mathbf{k}n\sigma}(\widetilde{V}^{(f)}_{\mathbf{k}n\sigma m}e^{-i\mathbf{k}\cdot\mathbf{R}_{if}}a^\dagger_{\mathbf{k}n\sigma}f_{im}+\text{c.c.}) \ , \tag{3.10}$$

where $\widetilde{V}^{(f)}_{\mathbf{k}n\sigma m}=V^{(f)}_{\mathbf{k}\sigma m}\gamma_{n,2}$ are renormalized matrix elements and the unrenormalized hybridization matrix element $V^{(f)}_{\mathbf{k}\sigma m}$ is given by Eq. (3.1). This Hamiltonian is an Anderson lattice Hamiltonian where the f electrons hybridize with two renormalized bands that already contain the effects of the d-electron hybridization. The renormalized f hybridization matrix element takes into account the mixed-valence nature of the renormalized bands, i.e., an electron in a state $|\mathbf{k}n\sigma\rangle$ with energy $\epsilon_{\mathbf{k}n}$ has a probability $\gamma_{n,2}(k)^2$ of being in a conduction-band state and hopping into the localized f state.

The method just described for calculating the renormalized f Anderson Hamiltonian is a many-body generalization of the block perturbation theory method or "down-folding treatment" used in muffin-tin orbital theory[7,33] to obtain an effective Anderson Hamiltonian with two important differences. First, we include the d bands in the conduction-band block of the Hamiltonian. Second, we explicitly keep the intrasite Coulomb interactions for both d and f electrons, i.e., the two-body terms in the Hamiltonian. However, the basic idea of applying a unitary transformation that diagonalizes the conduction-band block and the f-electron block in the Hamiltonian to obtain an effective f Anderson Hamiltonian is the same.

Since the Anderson Hamiltonian in Eq. (3.10) has a conduction-electron band structure that has been renormalized by the d electrons, the established treatment using a SWT and perturbation theory as described in Sec. II yields an f-f ion interaction that does depend on the modifications of the Fermi sea by the d electrons including *d*-*d* *correlations*. Carrying out this procedure, we obtain that the f-f ion interaction for an $\prod_i|f^{(1)}\rangle i$ configuration is given by Eq. (2.2) as

$$E^{ff}_{m_1'm_1;m_2'm_2}(\mathbf{R})=-\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\left[\frac{1}{N_s^2}\sum_{\substack{\mathbf{k}\sigma\\ \mathbf{k}'\sigma'}}V^{(f)}_{\mathbf{k}\sigma m_1}V^{(f)*}_{\mathbf{k}'\sigma' m_1'}V^{(f)}_{\mathbf{k}'\sigma' m_2}V^{(f)*}_{\mathbf{k}\sigma m_2'}e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}A_c(\mathbf{k},\sigma,\omega)\right.$$
$$\left.\times A_c(\mathbf{k}',\sigma',\omega')F^{ff}(\omega,\omega')\right] \ , \tag{3.11}$$

where $F^{ff}(\omega,\omega')$ is given by Eq. (A26) and the $V^{(f)}_{\mathbf{k}\sigma m}$ are the bare hybridization matrix elements. Here $A_c(\mathbf{k},\sigma,\omega)$ is the conduction-electron spectral function[34] in the mean-field approximation. This function is defined as the probability of finding a conduction electron with momentum $\mathbf{k}$, spin σ, and energy $\hbar\omega$. In this mixed-valence ground state, the spectral function at the mean-field level is given by

$$A_c(\mathbf{k},\sigma,\omega)=\sum_n \gamma_{n,2}^2\delta(\omega-\epsilon_{\mathbf{k}n\sigma})\ . \tag{3.12}$$

The same formula is formally valid for the case of no d hybridization but with the corresponding spectral function $A_c(\mathbf{k},\sigma,\omega)=\delta(\omega-\epsilon_{\mathbf{k}})$. Thus, we find that by hybridizing with the conduction electrons, the d electrons change the ground state of the system to a mixed valence state thereby modifying the conduction-electron spectral function. Furthermore, this change in the conduction electron spectral function induces a change in the f-f ion interaction. The results of a practical implementation of this method for the illustrative case of a free-electron conduction band is presented in the next section, where we contrast the results with those in the $U_d=0$ limit.

IV. RESULTS FOR A FREE-ELECTRON CONDUCTION BAND

Here we present the results of a calculation of the ion f-ion f interaction in the d and f system just described. As discussed above, the calculation proceeds in two steps: (1) the calculation of the renormalized band structure due to species d hybridization, (2) the calculation of the ion f-ion f interaction using the renormalized f Hamiltonian. For simplicity, we model the conduction band by a parabolic dispersion relation, which we parametrize as

$$\epsilon_{\mathbf{k}}=\epsilon_0+W\left[\frac{k}{k_{\mathrm{BZ}}}\right]^2 , \tag{4.1}$$

where $0\le k\le k_{\mathrm{BZ}}$. Here $\epsilon_0=3$ eV is a constant reference energy, $W=5$ eV is the bandwidth, and k_{BZ} corresponds to the radius of a spherical Brillouin zone[35] chosen such that its volume equals the true Brillouin-zone volume, i.e., $k_{\mathrm{BZ}}=(6\pi^2/\Omega)^{1/3}$. Here all single-particle energies are expressed in an absolute energy scale to facilitate the comparison between band structures with different chemical potentials. In order to obtain the renormalized band structure in the infinite U_d limit, we must first evaluate the slave-boson averages. We have chosen a system such that before hybridization the d band holds one electron per site and the conduction band holds 0.6 electrons per site; and therefore after hybridization, the lower hybridized band holds $n_{\mathrm{total}}=1.6$ electrons per site. In a real material, there would be several relevant partially filled bands and this represents the effects of one of them. For a hybridization matrix element $V_d=1$ eV and $\epsilon_d=0.3$ eV below $\epsilon^0_{k_F}=5.24$ eV, the conduction Fermi level [see Fig. 1(a)], we obtain that the slave-boson averages are $r^2=0.33$, $\Lambda=1.07$ eV, and the chemical potential is $\mu=5.79$ eV. For the hybridization model with no correlations, we have $\tilde{\epsilon}_d=\epsilon_d$, $\tilde{V}=V$, and $\mu=4.57$ eV. The calculated band structures as functions of the ratio of the wave vector to the Brillouin-zone boundary wave vector are shown in Fig. 1 for three different situations: (a) unhybridized bands, (b) hybridized bands neglecting correlation effects between the d electrons, (c) hybridized bands including correlation (Coulomb repulsion) effects for the d electrons. The corresponding d and c projected DOS as a function of energy are shown in Fig. 2. To understand these results, we focus first on the d- and c-electron projected DOS. We first observe that the d hybridization broadens the d resonance and this effect is proportional to $\tilde{V}_d^2$. The conduction-electron DOS is only modified significantly in the region of the d resonance. As we fill the electrons into the renormalized bands, we find that the d resonance with its associated high DOS pins the chemical potential[36] at an energy $k_BT_K=0.37$ eV below the d-level position and as shown

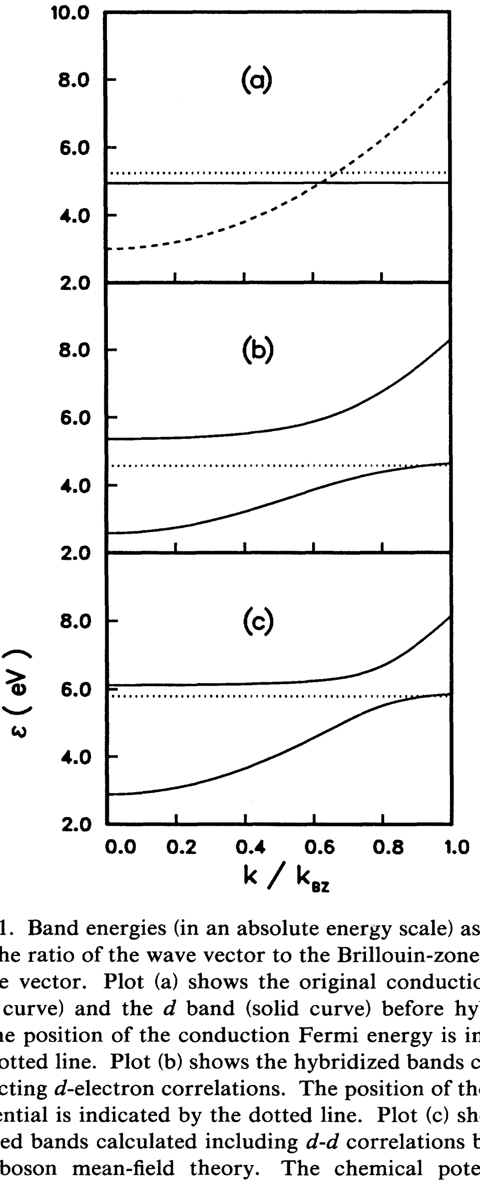

FIG. 1. Band energies (in an absolute energy scale) as a function of the ratio of the wave vector to the Brillouin-zone boundary wave vector. Plot (a) shows the original conduction band (dashed curve) and the d band (solid curve) before hybridization. The position of the conduction Fermi energy is indicated by the dotted line. Plot (b) shows the hybridized bands calculated neglecting d-electron correlations. The position of the chemical potential is indicated by the dotted line. Plot (c) shows the hybridized bands calculated including d-d correlations by using a slave-boson mean-field theory. The chemical potential is shown by a dotted line.

in Fig. 2(b) a band gap opens such that the lower band holds two electrons per site. As we turn on the Coulomb repulsion between the *d* electrons two additional effects appear: (1) As shown in Figs. 2(c) and 1(c), respectively, the *d* resonance gets narrower due to the renormalized hybridization and the renormalized band structure abruptly flattens in this region. (2) As shown in Fig. 2(c), the *d* resonance is pushed up above the conduction Fermi surface to avoid multiple occupancy of the *d* site. This movement of the *d* band while the conduction and *f* bands are essentially stationary causes electrons to spill from the *d* band into the conduction band and gives a reduced average occupation of a *d* site $n_d = 0.67$, compared with $n_d = 0.99$ for the case of $U_d = 0$. The renormalized hybridization also reduces the indirect band gap between the two bands to $\Delta = 0.26$ eV [see Fig. 2(c)] from a value of $\Delta = 0.72$ eV for $U_d = 0$ [see Fig. 2(b)]. As before, for the $U_d = 0$ case the high DOS of the *d* resonance pins the chemical potential at an energy $k_B T_K = 0.22$ eV below the renormalized *d* level position.

Having calculated the renormalized band structure, we proceed to calculate the *f*-*f* ion interaction. Due to the isotropy of our band structure, we have from Eq. (2.4) that the angular dependence of the *f*-*f* ion interaction is unchanged for all the bands structures considered, however, the radial dependence is different. To study this effect, we considered a *f* system with $j_f = 5/2$, $V_f = 0.1414$ eV, $U_f = 3$ eV, and $\epsilon_f = 1.0$ eV below the conduction Fermi surface. In Fig. 3 we show the *f*-*f* ion interaction range function calculated using different band structures: (1) the range function $E^{ff}_{V,U}$ (solid curve) was calculated using a band structure that takes into account the hybridization and correlations between the *d* electrons (slave-boson band structure) (2) the range function E^{ff}_V (dashed curve) was obtained using a band structure that treats the hybridization but neglects the correlations between the *d* electrons, and (3) the range function E^{ff}_0 (dotted curve) was calculated using a band structure that neglects both the hybridization and the correlations between the *d* electrons. The arrows in Fig. 3 indicate the nearest-neighbor distances for a fcc lattice. It is evident from these results that a large hybridization of the *d* electrons has a significant effect in the *f*-*f* ion interaction E^{ff}. Our calculations show a trend of $E^{ff}_{V,U}$ and E^{ff}_V to oscillate more rapidly than E^{ff}_0 with distance but with a smaller amplitude as we increase the *d* hybridization strength. The difference between $E_{V,U}$ and E_V shows that the renormalizations in the conduction-band structure due to *d* electron correlations have a significant effect on the *f*-*f* ion interaction.

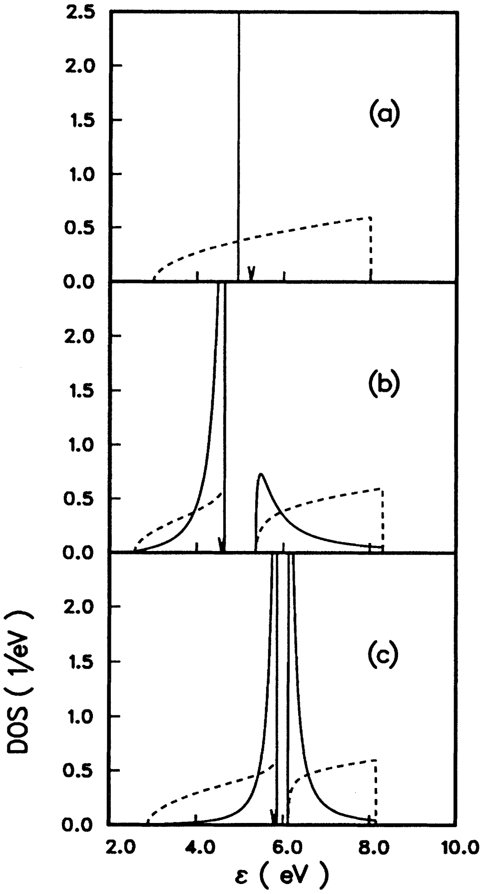

FIG. 2. The projected conduction electron DOS per site (dashed curve) and the projected *d*-electron DOS per site (solid curve) as a function of the energy (absolute energy scale). The arrow indicates the position of the corresponding chemical potential. Cases (a), (b), and (c) correspond to cases (a), (b), and (c) in Fig. 1.

V. CONCLUDING REMARKS

We have presented a two-step method for calculating the *f*-*f* ion interaction in systems where a *d*-electron species also hybridizes with the same Fermi sea. The

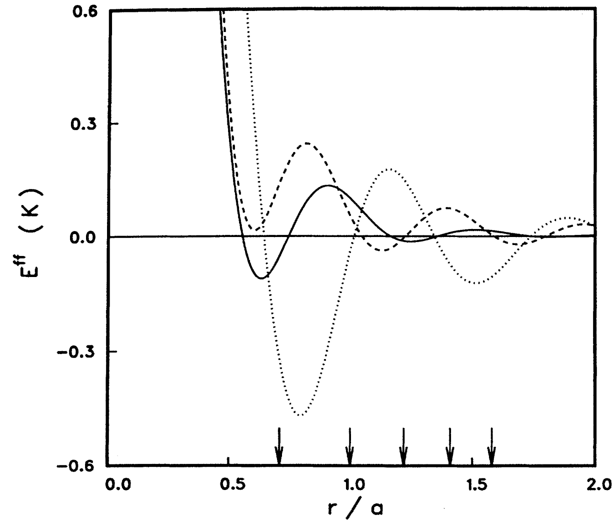

FIG. 3. The range function (intersite coupling strength) as a function of the ratio of the distance between two *f* sites to the unit-cell fcc lattice constant, *a*. Here $E_{V,U}$ (solid curve), E_V (dashed curve), and E_0 (dotted curve) were calculated with band structures (c), (b), and (a) of Fig. 1, respectively. The arrows indicate the nearest-neighbor distances for a fcc lattice.

method first diagonalizes the terms in the Hamiltonian involving the conduction and the *d* electrons to obtain a renormalized *f*-electron Anderson lattice Hamiltonian. This step is a many-body generalization of the "downfolding" treatment used in muffin-tin orbital theory[7,33] to obtain an effective *f*-electron Anderson Hamiltonian. The second step calculates the renormalized *f*-*f* ion interaction by the established procedure[3–6,25,26] of a SWT and perturbation theory. It is found that by modifying the conduction-electron spectral function through hybridization, the *d* electrons modify the *f*-*f* ion interactions and that correlations between the *d* electrons play a significant role in determining this effect.

While we believe that we have captured essential features of the effect of the *d* hybridization in the *f*-*f* ion interaction, to better represent the behavior of real systems of interest (such as the examples discussed in the Introduction) some further aspects of the physics are especially deserving of priority attention. Judging from our work in the one-species case,[2,37,38] introducing "real" electronic (band) structure information will probably significantly modify the anisotropy of the *f*-*f* ion interaction. Also it is desirable to treat realistic crystallographic structures, or at least key features of such structures such as the layer aspect of the CuO-type superconductors. At a more complicated level, effects of Coulomb exchange, as well as hybridization, should be included in the model Hamiltonian as has been done in Ref. 6 for a single hybridizing species. For orbitally driven magnetism and associated effects, in the single hybridizing species situation we have found[2,6,7,37,38] that while hybridization dominates for uranium systems, the orbital effects of Coulomb exchange dominate the behavior for the light rare earths.[6,7]

The present theory provides the framework of a methodology for treating the changes in *f*-electron species magnetic ordering in physical situations such as the motivating examples of $PrBa_2Cu_3O_7$ and (R or U)Mn_2X_2 discussed in the Introduction. For the magnetism/superconductivity competition in $PrBa_2Cu_3O_7$ this method is an essential ingredient in the development of a theory aimed to understand how and why magnetic ordering is destroyed in the Pr system as Y is substituted for Pr (i.e., decreasing the strength of the overall Pr *f*-electron hybridization with the oxygen *p* electrons compared to the overall strength of the Cu *d*-electron hybridization with the oxygen *p* electrons). Thus the present theory is directed toward understanding how superconductivity "kills" magnetism in $Pr_xY_{1-x}Ba_2Cu_3O_7$ as x decreases rather than vice versa as recently treated by Gao and Zhang.[20] Besides providing an understanding of the phenomenology of interest in itself, the full unraveling of this mechanism will provide valuable insight as to the nature of the coupling driving the superconductivity.[20]

ACKNOWLEDGMENTS

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APPENDIX: CALCULATION OF THE TWO ION INTERACTIONS FOR A LATTICE WITH MANY WEAKLY HYBRIDIZING LOCALIZED SPECIES

In this appendix we show how to construct an effective Hamiltonian to study magnetic order in a lattice that contains several species of partially delocalized electrons which weakly hybridize with the conduction bands. The system is described by an Anderson lattice Hamiltonian, Eq. (2.1), which for our purposes here we can divide as

$$H=H_0+H' , \tag{A1a}$$

where

$$H_0=\sum_{\mathbf{k}n\sigma}\epsilon_{\mathbf{k}n}c^\dagger_{\mathbf{k}n\sigma}c_{\mathbf{k}n\sigma}+\sum_{i\alpha m}\epsilon_\alpha l^\dagger_{i\alpha m}l_{i\alpha m}+\frac{1}{2}\sum_{\substack{i\alpha mm'\\ m\neq m'}}U_\alpha l^\dagger_{i\alpha m}l_{i\alpha m}l^\dagger_{i\alpha m'}l_{i\alpha m'} \tag{A1b}$$

is the bare Hamiltonian and the hybridization term

$$H'=\frac{1}{\sqrt{N_s}}\sum_{\substack{i\alpha m\\ \mathbf{k}n\sigma}}(V^{(\alpha)}_{\mathbf{k}n\sigma m}e^{-i\mathbf{k}\cdot\mathbf{R}_{i\alpha}}c^\dagger_{\mathbf{k}n\sigma}l_{i\alpha m}+\text{c.c.}) \tag{A1c}$$

is taken as a perturbation. Here the single-particle energies are taken with respect to the chemical potential of the interacting system.

The first step in the derivation consists in performing a canonical transformation defined by[5,25,26]

$$\bar{H}=e^{S}He^{-S} , \tag{A2}$$

where the generator S satisfies $S^\dagger=-S$ and obeys the equation

$$[S,H_0]=-H' \tag{A3}$$

chosen so as to eliminate the perturbation H' to linear order in $\bar{H}$. Expanding the transformed Hamiltonian $\bar{H}$ as a power series in H' and using Eq. (A3), we easily get

$$\bar{H}=H_0+\bar{H}' , \tag{A4a}$$

where

$$\bar{H}'=H_2+H_3+H_4+\cdots \tag{A4b}$$

and

$$H_2=\tfrac{1}{2}[S,H'] , \tag{A4c}$$

$$H_3=\tfrac{1}{3}[S,[S,H']] , \tag{A4d}$$

$$H_4=\tfrac{1}{8}[S,[S,[S,H']]] . \tag{A4e}$$

An explicit expression for the generator S can be obtained by noting that its equation of motion in the interaction representation is

$$\frac{dS_I}{dt}=\frac{1}{i\hbar}[S_I,H_0]=-\frac{1}{i\hbar}H'_I , \tag{A5}$$

where $O_I(t)=e^{iH_0t/\hbar}Oe^{-iH_0t/\hbar}$ for any operator O and we used Eq. (A3). Integrating this equation, we get[5,26]

$$S=S_I(t=0)=\frac{i}{\hbar}\int_{-\infty}^{0} dt' H_I'(t')e^{\epsilon t'} , \tag{A6}$$

where $\epsilon=0^+$ is an integrating factor. By explicit evaluation of this equation, we get

$$S=s-s^\dagger , \tag{A7a}$$

where

$$s=\frac{1}{\sqrt{N_s}}\sum_{i,\alpha,m,k}\sum_{p=0}^{p=2j_\alpha}\frac{V_{km}^{(\alpha)}e^{-i\mathbf{k}\cdot\mathbf{R}_{i\alpha}}}{\epsilon_k-\epsilon_\alpha-pU_\alpha}c_k^\dagger L_{i\alpha mp} , \tag{A7b}$$

where the superindex $k\equiv(\mathbf{k},n,\sigma)$ specifies the state of a conduction electron, and $L_{i\alpha mp}=l_{i\alpha m}A_{i\alpha p}(m)$. Here $A_{i\alpha p}(m)$ is a projection operator which projects all configurations at site $\mathbf{R}_{i\alpha}$ that have p electrons in states with $m'\neq m$, while the state m can be either occupied or unoccupied and is given by

$$A_{i\alpha p}(m)=\sum_{\{\delta\}}{}' N_{i\alpha j_\alpha}(\delta_{j_\alpha})\cdots N_{i\alpha m+1}(\delta_{m+1}) \times N_{i\alpha m-1}(\delta_{m-1})\cdots N_{i\alpha-j_\alpha}(\delta_{-j_\alpha}) , \tag{A8}$$

where δ_m can take values of zero or one,

$$N_{i\alpha m}(\delta_m)=\begin{cases} n_{i\alpha m}=l_{i\alpha m}^\dagger l_{i\alpha m} & \delta_m=1\\ 1-n_{i\alpha m} & \delta_m=0\end{cases}$$

and the primed summation indicates we should sum only over sets δ that satisfy $\delta_{j_\alpha}+\cdots+\delta_{m+1}+\delta_{m-1}+\cdots+\delta_{-j_\alpha}=p$, $0\leq p\leq 2j_\alpha$. From their definition, it is evident that the projection operators $A_{i\alpha p}(m)$ satisfy

$$\sum_{p=0}^{p=2j_\alpha} A_{i\alpha p}(m)|l_\alpha^{n_\alpha}>_i=|l_\alpha^{n_\alpha}\rangle_i . \tag{A9}$$

The properties of the operators $L_{i\alpha mp}$ are very important in this calculation. To study them it turns out to be convenient to define another projection operator $B_{i\alpha p}(m,m')$ by

$$A_{i\alpha p}(m)=(1-n_{i\alpha m'})B_{i\alpha p}(m,m') +n_{i\alpha m'}B_{i\alpha p-1}(m,m') , \tag{A10}$$

where $B_{i\alpha p}(m,m')=0$ for $p<0$ or $p\geq 2j_\alpha$. The projection operator $B_{i\alpha p}(m,m')$ projects all configurations in site $\mathbf{R}_{i\alpha}$ that have p electrons in states different from m,m'. The states m,m' can be occupied or unoccupied. In terms of these operators, we have

$$\{L_{i\alpha mp},L_{i'\alpha'm'p'}^\dagger\}=\delta_{i,i'}\delta_{\alpha,\alpha'}\delta_{p,p'}(\delta_{m,m'}A_{i\alpha p}(m)+(1-\delta_{m,m'})l_{i\alpha m'}^\dagger l_{i\alpha m}[B_{i\alpha p}(m,m')-B_{i\alpha p-1}(m,m')]) , \tag{A11}$$

$$L_{i\alpha m'p'}^\dagger L_{i\alpha mp}=l_{i\alpha m'}^\dagger l_{i\alpha m}\delta_{p,p'}[\delta_{m,m'}A_{i\alpha p}(m)+(1-\delta_{m,m'})B_{i\alpha p}(m,m')] \tag{A12}$$

and

$$\{L_{i\alpha mp},L_{i'\alpha'm'p'}\}=\delta_{i,i'}\delta_{\alpha,\alpha'}(1-\delta_{m,m'})l_{i\alpha m}l_{i\alpha m'}[B_{i\alpha p}(m,m')\delta_{p,p'-1}-B_{i\alpha p-1}(m,m')\delta_{p,p'+1}] . \tag{A13}$$

We now proceed to construct an effective Hamiltonian[39] which acts on a reduced Hilbert space starting from $\overline{H}$. Our reduced Hilbert space or model space (MS) consists of all states of the form

$$|\Phi\rangle=|G\rangle\Pi_{i,\alpha}|l_\alpha^{n_\alpha}\rangle_i \tag{A14}$$

where $|G\rangle$ denotes the conduction-electron ground state, and $|l_\alpha^n\rangle_i=l_{i\alpha m_1}^\dagger\cdots l_{i\alpha m_n}^\dagger|\phi_\alpha^c\rangle_i$ is a state of ion α consisting of n valence electrons in orbital l_α and core ground state $|\phi_\alpha^c\rangle_i$. If the dimensionality of the model space is d, there are d well defined eigenstates of the full Hamiltonian, which have their major part within the model space. Their projections into the model space or model functions correspond to the eigenvectors of the effective Hamiltonian, and their eigenvalues are the exact energies of the corresponding true states.

To construct the effective Hamiltonian, we first define a projection operator P which projects onto the model space by

$$P=\sum_{|\Phi\rangle\in\mathrm{MS}}|\Phi\rangle\langle\Phi| \tag{A15a}$$

and a projection operator Q which projects into the remaining space or orthogonal space by

$$Q=1-P , \tag{A15b}$$

where $\langle\Phi_a|\Phi_b\rangle=\delta_{a,b}$. For our degenerate open shell-model space with unperturbed energy E_0, the effective Hamiltonian can be written as a sum of closed diagrams (diagrams which operate within the model space) as

$$\begin{aligned}H_{\text{eff}}&=P\left[H_0+\overline{H}'+\overline{H}'\frac{Q}{E_0-H_0}\overline{H}'+\cdots\right]P\\&=P\left[E_0+H_2+H_2\frac{Q}{E_0-H_0}H_2+H_4+\cdots\right]P ,\end{aligned} \tag{A16}$$

where in the last line we used Eq. (A4) and the fact that H_3 has no closed diagrams to expand the Hamiltonian to fourth order in the hybridization.

Next, we proceed to evaluate the diagrams implicit in Eq. (A16). We start by explicitly calculating H_2 from Eq. (A4c). We get

$$H_2=H_2^{\text{ex}}+H_2^{l}+H_2^{ll} , \tag{A17a}$$

where

$$H_2^{\text{ex}}=\frac{1}{2N_s}\sum_{1,2}V_1V_2^*\left[\frac{1}{\Delta\epsilon_1}+\frac{1}{\Delta\epsilon_2}\right]c_{k_1}^\dagger c_{k_2}\{L_1,L_2^\dagger\} , \tag{A17b}$$

$$H_2^l=-\frac{1}{2N_s}\sum_{1,2}V_1V_2^*\left[\frac{1}{\Delta\epsilon_1}+\frac{1}{\Delta\epsilon_2}\right]\delta_{k_1,k_2}L_2^\dagger L_1\ , \tag{A17c}$$

$$H_2^{ll}=-\frac{1}{2N_s}\sum_{1,2}\left[\frac{V_1V_2}{\Delta\epsilon_1}c_{k_1}^\dagger c_{k_2}^\dagger\{L_1,L_2\}+\text{c.c.}\right]\ . \tag{A17d}$$

Here, $\Delta\epsilon_1=\epsilon_{k_1}-\epsilon_{\alpha_1p_1}$, $\epsilon_{\alpha_1p_1}=\epsilon_{\alpha_1}+p_1U_{\alpha_1}$, $V_1=V_{k_1m_1}^{(\alpha_1)}\exp(-i\mathbf{k}\cdot\mathbf{R}_{i_1\alpha_1})$, $L_1=L_{i_1\alpha_1m_1p_1}$, etc. For this derivation we expressed the hybridization term H', in Eq. (A1c), as

$$H=h+h^\dagger\ , \tag{A18}$$

where $h=\sum_1V_1c_{k_1}^\dagger L_1/\sqrt{N_s}$. The term H_2^{ex} contains the exchange interaction between the conduction and localized ions. The terms in H_2^l involving operators acting on different sites represent a hopping or banding Hamiltonian between the localized electrons, and the terms involving operators acting on the same site induce a renormalization of the crystal-field energy levels. Finally the term H_2^{ll} creates or destroys two localized electrons at the same site.

For our purposes of calculating a magnetic Hamiltonian, only certain terms of H_{eff} must be kept.[5] These terms which we denote by H^M have the form of Eq. (2.2a). It is evident from Eqs. (A16) and (A17) that

$$H^M=H_{\text{cs}}+H_{\text{se}}+H_4^M\ , \tag{A19a}$$

where

$$H_{\text{cs}}=PH_2^{\text{ex}}\frac{Q}{E_0-H_0}H_2^{\text{ex}}P\ , \tag{A19b}$$

$$H_{\text{se}}=PH_2^l\frac{Q}{E_0-H_0}H_2^lP\ , \tag{A19c}$$

and H_4^M stands for all contributions to H^M coming from PH_4P.

By explicit calculation, we get

$$\begin{aligned}H_{\text{cs}}=\frac{1}{4N_s^2}\sum_{\substack{1,2\\3,4}}V_1V_2^*V_3V_4^*&\left[\frac{1}{\Delta\epsilon_1}+\frac{1}{\Delta\epsilon_2}\right]\left[\frac{1}{\Delta\epsilon_3}+\frac{1}{\Delta\epsilon_4}\right]\\&\times\delta_{k_1,k_4}\delta_{k_2,k_3}\frac{(1-n_{k_1})n_{k_2}}{\epsilon_{k_2}-\epsilon_{k_1}}\\&\times P\{L_3,L_4^\dagger\}\{L_1,L_2^\dagger\}P\ ,\end{aligned} \tag{A20}$$

where $n_k\equiv n_F(\epsilon_k)$ evaluated at $T=0$ K. Clearly, for electrons located at different sites this term corresponds to a magnetic interaction mediated by the interchange of a particle-hole excitation of the conduction electrons. It represents a generalization of the Coqblin-Schrieffer interaction.[25]

A similar calculation for H_{se} gives

$$\begin{aligned}H_{\text{se}}=-\frac{1}{4N_s^2}\sum_{\substack{1,2\\3,4}}&\frac{V_1V_2^*V_3V_4^*}{\epsilon_{\alpha_2n_{\alpha_2}}-\epsilon_{\alpha_1n_{\alpha_1}-1}}\\&\times\left[\frac{1}{\Delta\epsilon_1}+\frac{1}{\Delta\epsilon_2}\right]\left[\frac{1}{\Delta\epsilon_3}+\frac{1}{\Delta\epsilon_4}\right]\\&\times\delta_{k_1,k_2}\delta_{k_3,k_4}\delta_{R_1,R_4}\delta_{R_2,R_3}\\&\times(1-\delta_{R_1,R_2})PL_4^\dagger L_3L_2^\dagger L_1P\ .\end{aligned} \tag{A21}$$

Here $R_1=\mathbf{R}_{i_1\alpha_1}$, etc. To derive this expression, we used the identity

$$\begin{aligned}L_{i'\alpha'm'p'}^\dagger L_{i\alpha mp}P=l_{i'\alpha'm'}^\dagger l_{i\alpha m}P\delta_{p,n_{\alpha-1}}&\\\times[\delta_{p',n_{\alpha-1}}\delta_{R_{i\alpha},R_{i'\alpha'}}&\\+\delta_{p',n_{\alpha'}}(1-\delta_{R_{i\alpha},R_{i'\alpha'}})]&\ .\end{aligned} \tag{A22}$$

The term H_{se} because of its origin in the virtual hopping of localized electrons corresponds to the kinetic superexchange described by Anderson.[5,40]

Finally, we consider the contributions of H_4^M to the magnetic Hamiltonian. A direct evaluation of H_4 is not practical since it contains many terms. Thus we exploit the fact that we only need the closed diagrams of H_4. We get

$$\begin{aligned}H_4^M=\tfrac{1}{8}P([s,[s^\dagger,[s^\dagger,h]]]&\\-[s,[s^\dagger,[s,h^\dagger]]]+\text{c.c.})P&\ .\end{aligned} \tag{A23}$$

To obtain this result we used the fact that the closed diagrams have no conduction electrons free lines and that although the term $P(-[s,[s,[s^\dagger,h^\dagger]]]+\text{c.c.})P$ does contribute to H_{eff}, it does not contribute to H_4^M because of Eq. (A13). After doing some algebra, we get

$$\begin{aligned}H_4^M=\frac{1}{8N_s^2}\sum_{\substack{1,2\\3,4}}V_1V_2^*V_3V_4^*\delta_{k_1,k_4}\delta_{k_2,k_3}[&(3\eta_{1,2,4,}+3\eta_{1,3,4}+\eta_{1,2,3}+\eta_{2,3,4})(1-n_{k_1})P\{L_1,L_2^\dagger\}\{L_3,L_4^\dagger\}P\\&-(3\eta_{1,2,3}+3\eta_{1,2,4}+\eta_{1,3,4}+\eta_{2,3,4})PL_1L_2^\dagger\{L_3,L_4^\dagger\}P]\ ,\end{aligned} \tag{A24}$$

where $n_{i,j,k}=(\Delta\epsilon_i\Delta\epsilon_j\Delta\epsilon_k)^{-1}$. The term H_4^M represents a direct magnetic interaction, i.e., a magnetic interaction that arises directly from the application of the canonical transformation to the Anderson Hamiltonian.

At this point, we can sum the different contributions to H^M namely Eqs. (A20), (A21), and (A24) and simplify them by using Eqs. (A11) and (A22). Then by collecting all terms involving two ions, we can write the interaction between ions located at $\mathbf{R}_{i\alpha}$ and $\mathbf{R}_{j\alpha'}$, as

$$h(\mathbf{R}_{i\alpha},\mathbf{R}_{j\alpha'})=-\sum_{\substack{m_1,m_1'\\ m_2,m_2'}} E^{\alpha\alpha'}_{m_1'm_1;m_2'm_2}(\mathbf{R}_{i\alpha}-\mathbf{R}_{j\alpha'})l^{\dagger}_{i\alpha m_1'}l_{i\alpha m_1}l^{\dagger}_{j\alpha' m_2'}l_{j\alpha' m_2}\ , \tag{A25a}$$

where the range function $E^{\alpha\alpha'}$ is given by

$$E^{\alpha\alpha'}_{m_1'm_1;m_2',m_2}(\mathbf{R})=-\frac{1}{N_s^2}\sum_{\substack{\mathbf{k}n\sigma\\ \mathbf{k}'n'\sigma'}} V^{(\alpha)}_{\mathbf{k}n\sigma m_1}V^{(\alpha)*}_{\mathbf{k}'n'\sigma' m_1'}V^{(\alpha')}_{\mathbf{k}'n'\sigma' m_2}V^{(\alpha')*}_{\mathbf{k}n\sigma m_2'}e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}F^{\alpha\alpha'}(\epsilon_{\mathbf{k}n},\epsilon_{\mathbf{k}'n'}) \tag{A25b}$$

and

$$\begin{aligned}F^{\alpha\alpha'}(\epsilon_k,\epsilon_{k'})=&\frac{1-n_k}{\epsilon_{k'}-\epsilon_k}\left[\frac{1}{\epsilon_k-\epsilon_{\alpha n_\alpha}}-\frac{1}{\epsilon_k-\epsilon_{\alpha n_\alpha-1}}\right]\left[\frac{1}{\epsilon_k-\epsilon_{\alpha' n_{\alpha'}}}-\frac{1}{\epsilon_k-\epsilon_{\alpha' n_{\alpha'}-1}}\right]\\ &+\frac{1-n_{k'}}{\epsilon_k-\epsilon_{k'}}\left[\frac{1}{\epsilon_{k'}-\epsilon_{\alpha n_\alpha}}-\frac{1}{\epsilon_{k'}-\epsilon_{\alpha n_\alpha-1}}\right]\left[\frac{1}{\epsilon_{k'}-\epsilon_{\alpha' n_{\alpha'}}}-\frac{1}{\epsilon_{k'}-\epsilon_{\alpha' n_{\alpha'}-1}}\right]\\ &+\frac{1}{(\epsilon_{\alpha n_\alpha}-\epsilon_{\alpha' n_{\alpha'}-1})(\epsilon_k-\epsilon_{\alpha n_\alpha})(\epsilon_{k'}-\epsilon_{\alpha n_\alpha})}+\frac{1}{(\epsilon_{\alpha' n_{\alpha'}}-\epsilon_{\alpha n_\alpha-1})(\epsilon_{k'}-\epsilon_{\alpha' n_{\alpha'}})(\epsilon_k-\epsilon_{\alpha' n_{\alpha'}})}\\ &-\frac{1}{2}\frac{1}{(\epsilon_k-\epsilon_{\alpha n_\alpha})(\epsilon_{k'}-\epsilon_{\alpha n_\alpha})}\left[\frac{1}{\epsilon_k-\epsilon_{\alpha' n_{\alpha'}}}+\frac{1}{\epsilon_{k'}-\epsilon_{\alpha' n_{\alpha'}}}\right]\\ &-\frac{1}{2}\frac{1}{(\epsilon_k-\epsilon_{\alpha' n_{\alpha'}})(\epsilon_{k'}-\epsilon_{\alpha' n_{\alpha'}})}\left[\frac{1}{\epsilon_k-\epsilon_{\alpha n_\alpha}}+\frac{1}{\epsilon_{k'}-\epsilon_{\alpha n_\alpha}}\right]\ .\end{aligned} \tag{A25c}$$

It is evident that this expression is symmetric in k and k' and by using Eq. (2.2) it is clear that the calculated two ion interaction is Hermitian. In the case where the two ions of interest belong to the same species, the above formula reduces to

$$\begin{aligned}F^{\alpha\alpha}(\epsilon_k,\epsilon_{k'})=&n_kn_{k'}\frac{1}{(\epsilon_k-\epsilon_{\alpha n_\alpha})(\epsilon_{k'}-\epsilon_{\alpha n_\alpha})}\left[\frac{2}{U_\alpha}-\frac{1}{\epsilon_k-\epsilon_{\alpha n_\alpha}}-\frac{1}{\epsilon_{k'}-\epsilon_{\alpha n_\alpha}}\right]\\ &+(1-n_k)(1-n_{k'})\frac{1}{(\epsilon_k-\epsilon_{\alpha n_\alpha-1})(\epsilon_{k'}-\epsilon_{\alpha n_\alpha-1})}\left[\frac{2}{U_\alpha}+\frac{1}{\epsilon_k-\epsilon_{\alpha n_\alpha-1}}+\frac{1}{\epsilon_{k'}-\epsilon_{\alpha n_\alpha-1}}\right]\\ &+n_k(1-n_{k'})\left[\frac{2}{U_\alpha(\epsilon_k-\epsilon_{\alpha n_\alpha})(\epsilon_{k'}-\epsilon_{\alpha n_\alpha-1})}+\frac{1}{\epsilon_k-\epsilon_{k'}}\left[\frac{1}{\epsilon_k-\epsilon_{\alpha n_\alpha}}-\frac{1}{\epsilon_{k'}-\epsilon_{\alpha n_\alpha-1}}\right]^2\right]\\ &+n_{k'}(1-n_k)\left[\frac{2}{U_\alpha(\epsilon_{k'}-\epsilon_{\alpha n_\alpha})(\epsilon_k-\epsilon_{\alpha n_\alpha-1})}+\frac{1}{\epsilon_{k'}-\epsilon_k}\left[\frac{1}{\epsilon_{k'}-\epsilon_{\alpha n_\alpha}}-\frac{1}{\epsilon_k-\epsilon_{\alpha n_\alpha-1}}\right]^2\right]\ .\end{aligned} \tag{A26}$$

This result was first obtained by Wills and Cooper[5] for a single-electron configuration *except* for a minor error,[37], i.e., the authors identified $F^{\alpha\alpha}(\epsilon,\epsilon')$ with the function $F_w(\epsilon,\epsilon')$, defined by Eq. (2.8) of Ref. 5, while the correct result is given by $F^{\alpha\alpha}(\epsilon,\epsilon')=F_w(\epsilon,\epsilon')+F_w(\epsilon',\epsilon)$. Physically, the term $\epsilon_{\alpha n_\alpha}=\epsilon_\alpha+n_\alpha U_\alpha$ represents the energy needed to add one more electron to an $|l_\alpha^{n_\alpha}\rangle$ configuration. Similarly the term $\epsilon_{\alpha n_\alpha-1}=\epsilon_\alpha+(n_\alpha-1)U_\alpha$ represents the energy difference between the $|l_\alpha^{n_\alpha}\rangle$ configuration and the configuration obtained by removing an electron from the above.

In practice, for multielectronic configurations the model space defined by Eq. (A14) contains too many states and one further projects this Hamiltonian into the preferred ionic multiplet $|l_\alpha^{n_\alpha},J,M\rangle$. Projecting into these orthonormal states, we get that the interaction between ions in their preferred multiplet is

$$h(\mathbf{R}_{i\alpha},\mathbf{R}_{j\alpha'})=-\sum_{\substack{M_1,M_1'\\ M_2,M_2'}} E^{\alpha\alpha'}_{M_1'M_1;M_2'M_2}(\mathbf{R}_{i\alpha}-\mathbf{R}_{j\alpha'})L^{i\alpha}_{M_1'M_1}L^{j\alpha'}_{M_2'M_2}\ , \tag{A27a}$$

where $L^{i\alpha}_{M'M}=|l_\alpha^{n_\alpha},J,M'\rangle_i\langle l_\alpha^{n_\alpha},J,M|_i$ is a basis operator, and the range function is given by[7]

$$E^{\alpha\alpha'}_{M_1'M_1;M_2',M_2}(\mathbf{R})=\sum_{\substack{m_1',m_1\\ m_2',m_2}} E^{\alpha\alpha'}_{m_1'm_1;m_2'm_2}(\mathbf{R})\times\langle l_\alpha^{n_\alpha},J_\alpha,M_1'|l^{\dagger}_{i\alpha m_1'}l_{i\alpha m_1}|l_\alpha^{n_\alpha},J_\alpha,M_1\rangle\langle l_{\alpha'}^{n_{\alpha'}},J_{\alpha'},M_2'|l^{\dagger}_{j\alpha' m_2'}l_{j\alpha' m_2}|l_{\alpha'}^{n_{\alpha'}},J_{\alpha'},M_2\rangle\ . \tag{A27b}$$

We note that for a single species $|l_\alpha^{n_\alpha}\rangle$ configuration, we usually have $\epsilon_{\alpha n_\alpha}>0$ and $\epsilon_{\alpha n_\alpha-1}<0$. From these inequalities and Eq. (A26), it is evident that the coefficients multiplying $(1-n_k)(1-n_{k'})$ (particle-particle contribution) and $n_k n_{k'}$ (hole-hole contribution) are both positive definite, i.e., they represent an antiferromagnetic contribution to the two ion interaction at short ranges. A similar analysis shows that the coefficients multiplying $n_k(1-n_{k'})$ and the term obtained by replacing $k\leftrightarrow k'$ are both negative definite, i.e., they represent ferromagnetic contributions to the two ion interaction at short ranges. Furthermore, we note that only the term involving $1/(\epsilon_k-\epsilon_{k'})$ is singular. Specializing to a very narrow parabolic conduction band, this singularity gives the usual $2k_FR$ characteristic oscillation that follows from

$$\frac{1}{N_s^2}\sum_{\mathbf{k},\mathbf{k}'} e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}\frac{(1-n_{\mathbf{k}})n_{\mathbf{k}}}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}}=\frac{9\pi}{4}\frac{n_c^2}{\epsilon_F}y(2k_FR)\,, \qquad \text{(A28)}$$

where $y(x)=[x\cos(x)-\sin(x)]/x^4$ and n_c is the number of conduction electrons per site. The other terms are not singular and oscillate with other wavelengths, and decay $1/R$ faster with distance. Thus, even though the singular term contribution dominates at short and large interparticle separations (with the exception of a magnetic insulator), the different contributions dephase with distance, and all contributions are significant at intermediate interparticle separations.

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