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Combined effect of hybridization and exchange Coulomb interaction on magnetic ordering in correlated-f-electron cerium systems

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The model Hamiltonian describing the partially delocalized f-electron system has been generalized to include both hybridization and band-f exchange Coulomb interaction. A method has been developed to calculate the parameters appearing in such a model Hamiltonian from first principles. This enables us to calculate f-electron-based electronic and magnetic phenomena of pertinent materials on a quantitative basis. Calculations have been done for cerium monopnictides and monochalcogenides. Results are in agreement with experiment on various unusual behaviors of these materials, such as anomalous crystal-field splitting and anisotropic magnetic ordering, all of which are caused by the interactions between f electrons and band electrons. In contrast to the earlier version of this theory that included only hybridization effects and produced range parameters (two-ion "exchange" coupling) that failed by an order of magnitude in matching the phenomenologically determined parameters which provide agreement with experiment, the present first-principles theory calculations which also include band-f Coulomb exchange provide excellent agreement with the phenomenologically required magnitude.

I. INTRODUCTION

There is much interest in the magnetic behavior of correlated f-electron cerium and light actinide materials. In cerium monopnictides, below the Néel temperature T_N, the materials have various phases with peculiar magnetic structures which are strongly anisotropic.[1] The paramagnetic crystal-field splitting of the $4f_{5/2}$ state in these compounds in much less than expected from extrapolation from heavier rare-earth monopnictides.[2] These unusual properties can be understood on the basis of the hybridization between the localized f electrons and the non-f band electrons, as well described by the lattice Anderson Hamiltonian. Studies have shown that the hybridization shifts the different crystal-field states by different amounts, and thus suppresses the crystal-field splitting. Studies also showed that the indirect two-ion interaction mediated by the hybridization is strongly anisotropic. By treating the parameters in the Anderson Hamiltonian as phenomenological input, Cooper *et al.*[3] successfully explained the diverse magnetic behavior of these materials. The theory is also available for broader classes of materials such as light actinide compounds.[3]

To elucidate the origins, in the electronic structure, of the observed behavior of different materials, and to make the theory materially predictive, techniques have been developed to calculate the parameters entering the theory from first principles. Wills and Cooper[4] calculated the hybridization strength using a resonance-width scheme based on a linearized muffin-tin orbital (LMTO) band structure using a warped muffin-tin potential with a true interstitial, and this enabled them to calculate the f-electron properties of cerium monopnictides on an *ab initio* absolute basis. Their calculation is in close agreement with experiment for the crystal-field splitting. For the two-ion interaction, which determines the magnetic structure, the calculation[4,5] successfully predicts range and angular dependence similar to those found by phenomenological theory,[3] which agrees with experiment, but the overall magnitude is about one order of magnitude smaller than that in the phenomenological theory. The situation is similar when applying the same sort of calculation to light actinide compounds.[6]

The success in predicting the suppression of crystal-field splitting and the anisotropic structure of the two-ion interaction, and the failure in predicting the overall magnitude of the two-ion interaction, suggest that the calculation has captured only part of the origins of these effects. In fact, the Anderson Hamiltonian focuses on hybridization but has left out other interactions, such as the band-f exchange Coulomb interaction. It is common for model Hamiltonians to attribute all effects that give qualitatively similar physical properties to a single parametrized interaction, regardless of the variety of the origins of those effects, and one can often make the theory satisfactory by adjusting the parameters in model Hamiltonians. However, when calculating those effects from first principles, it may lead to serious discrepancies if we include only part of the underlying effects but omit the others. Thus, to make the *ab initio* calculation of those effects realistic, one has to go back to the very beginning to check whether the model Hamiltonian reflects the real system completely, and what the origins of the interactions appearing in the model Hamiltonian are. For the two-ion interaction in the materials we are studying, there are contributions from both band-f hybridization and band-f exchange Coulomb interaction as we shall see below, and indeed it is necessary to include both these effects.

The undercalculation of the two-ion interaction in Refs. 4 and 5 may arise either from an undercalculation of the hybridization strength or from the neglect of band-f exchange or from both. The excellent agreement

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with experiment of the suppression of crystal-field splitting, which is a pure hybridization effect, suggests that the hybridization strength calculated is of the correct size. This is also supported by the calculation of the hybridization strength using the tight-binding fitting scheme.[7] In fact, anisotropic magnetic ordering and high T_N are the case not only for monopnictides of cerium, but also for monopnictides of other light rare-earth elements;[8] but crystal-field splitting data suggest that only cerium monopnictides have considerable hybridization effect. Therefore, there must be contributions to the two-ion interaction other than hybridization, namely, the band-f exchange Coulomb interaction.

In the attempt to perform *ab initio* calculations of the parameters appearing in the model Hamiltonian from a realistic band structure, one has to be careful about the following question. The model Hamiltonian describing the f-electron systems is a many-body Hamiltonian which reflects the many-body nature of the f-electron problem. However, the band calculation is based on an effective one-electron theory—the effects of two-body interactions are approximated by an effective crystal potential and its output gives one-electron quantities with two-body effects effectively included therein. Because of this difference between the many-body model Hamiltonian and one-body band calculation, one must make clear which two-body effects have been effectively included in the one-electron quantities by the method used in the band calculation; and their corresponding terms in the many-body model Hamiltonian must be excluded to avoid double counting. On the other hand, for those two-body effects which are not effectively included by the band calculation, such as band-f exchange Coulomb interaction, their corresponding terms must be kept in the many-body model Hamiltonian, and one must develop schemes to calculate these terms using the output or intermediate results of the band calculation. Only when this is taken care of can the model Hamiltonian so synthesized with the band calculation reflect the real systems completely, and quantitative comparison of calculated results with experiments be trusted.

Commonly, the RKKY (Ruderman-Kittel-Kasuya-Yosida) type of two-ion interaction is regarded as an interaction between spin parts of the local moments only, and, as a consequence of the spin-only interaction, is isotropic. This is a good approximation only for d electrons whose orbital angular moments are quenched by the crystal field. For f electrons, which are much more localized than d electrons, the orbital angular moments are well retained and coupled to these spins. Therefore, it is the total angular moment instead of the spin which is the good quantum number for f-electron systems. The two-ion interaction in f-electron systems occurs between the total moments and is no longer isotropic. For magnetic properties, the contributions from band-f hybridization and band-f exchange are complementary: both lead to anisotropic magnetic ordering due to the orbital-motion-driven interactions.

In Sec. II, we start from the fundamental origins in the interelectronic Coulomb interaction and derive a model Hamiltonian which reflects the real system completely. This is done with particular concern paid to which quantities are available from the band-structure calculation and what two-body effects have been included in these quantities. In Sec. III, we derive the expression for the two-ion interaction from this model Hamiltonian. In Sec. IV, we describe a scheme to calculate the band-f exchange interaction based on a LMTO (linearized combination of muffin-tin orbitals) band calculation. (The techniques used to calculate the other parameters entering the model Hamiltonian, and the two-ion interaction, have been discussed previously.[4,5]) Finally, in Sec. V we will present the results of the calculation of the two-ion interaction and consequent ordering temperature and ordered moments for cerium compounds and compare the results with experiments; and in Sec. VI we provide a summary and discussion.

II. THE MODEL HAMILTONIAN

In this section, we will derive a model Hamiltonian describing f electrons interacting with non-f band electrons, where all the quantities in it can either be matched to the output of a LMTO (linearized muffin-tin orbital) band calculation or be calculated separately using the information given by a LMTO band calculation.

We first classify the electric charge in the crystal into two types with regard to atomic origin: (1) the charge of the nuclei and filled-shell electrons, and (2) that of the f (partially filled transition-shell) electrons and of the outermost s, p, and d valence electrons which form the non-f conduction bands in the solid. We are interested in the solid-state behavior of the electrons giving the type-(2) charge, with that of type (1) being viewed as an essentially rigid background on which the f and non-f valence electrons move and interact. We write the Hamiltonian for this f-electron plus conduction-electron "active" part of the solid-state electronic system as

$$H=\sum_i \nabla_i^2+V_0(r_i)+\frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} \; ; \tag{2.1}$$

here r_{ij} stands for $|r_i-r_j|$, and we have set the electric charge unit $e^2=1$. $V_0(r)$ is the periodic potential from the fixed background of type-(1) charges. $1/r_{ij}$ is the Coulomb interaction between type (2) (f and conduction) electrons and is a two-body interaction. Hamiltonian (2.1) can be regarded as the "true Hamiltonian" and is our starting point.

We then compare Hamiltonian (2.1) with the Hamiltonian in the band theory. Band theory approximates the real system by use of an effective one-body Hamiltonian

$$H=\nabla^2+V(r) \; , \tag{2.2}$$

where $V(r)$ is the effective potential in which a single electron moves. In the band calculation, this potential is obtained by a self-consistent iterative procedure. The effects of the two-body interaction in (2.1) are partly included in $V(r)$ in the sense of the local-density approximations (LDA). We can write $V(r)$ as

$$V(r)=V_0(r)+V_1(r) \; , \tag{2.3}$$

where $V_0(r)$ is from the fixed background charge, and $V_1(r)$ represents the effect of the two-body interaction with the other active electrons as included by use of the LDA. $V_0(r)$ in (2.3) is identical with $V_0(r)$ in (2.1). By comparing the matrix elements of Hamiltonians (2.1) and (2.2), we can see how the matrix elements of the many-body "true Hamiltonian" and the matrix elements of the one-body band-theory Hamiltonian should be matched to each other. Below we give a detailed term-by-term analysis of the matrix elements of the "true Hamiltonian" (2.1) into those parts included in the (LDA) band theory and those parts not included in the band-theory treatment and thereby requiring separate explicit representation in the model Hamiltonian. Besides allowing us to recognize explicitly the terms not already included by the (LDA) band theory, among such terms we can recognize which terms are qualitatively the same and thereby quantitatively additive. This procedure allows us to be confident in the absolute scale of our final calculated results and the significance of absolute comparison between calculated and experimentally measured quantities such as magnetic ordering temperature.

To obtain the model Hamiltonian, we now second-quantize the "true Hamiltonian" (2.1):

$$H=\langle \Phi(r)|\nabla^2+V_0(r)|\Phi(r)\rangle + \frac{1}{2}\left\langle \Phi(r_1)\Phi(r_2)\left|\frac{1}{r_{12}}\right|\Phi(r_2)\Phi(r_1)\right\rangle , \qquad (2.4)$$

where $|\Phi(r)\rangle$ is the field operator of electronic states. To treat the band states and nonband f states as distinct states as the Anderson Hamiltonian does, we separate the field $|\Phi(r)\rangle$ into a band field $|\Phi_B(r)\rangle$ and a nonband f field $|\Phi_F(r)\rangle$:

$$\Phi(r)=\Phi_B(r)+\Phi_F(r) , \qquad (2.5a)$$

$$\Phi_B(r)=\sum_k \phi_k(r)b_k , \qquad (2.5b)$$

$$\Phi_F(r)=\sum_{Rm} \psi_m(r-R)c_m(R) , \qquad (2.5c)$$

where b_k is the annihilation operator of band state $\phi_k(r)$, and k signifies both momentum and band index; c_m is the annihilation operator of the local f state $\psi_m(r)$; R stands for an atomic site; and m is the index of a local state. We can further restrict the local f states to a subspace of a spin-orbital multiplet of total angular moment j. Since most of the physics happens in the subspace of the partially filled spin-orbital multiplet, it is proper to do this. In this subspace, m is the magnetic quantum number of the f states.

We expand the right-hand side of (2.4). The first term on the right-hand side of (2.4) is of one-body type and is simple in nature. It is expanded into three terms.

(i) $\langle \Phi_B(r)|\nabla^2+V_0(r)|\Phi_B(r)\rangle=\sum_k \epsilon_k^0 b_k^\dagger b_k$.

This is the bare band-state energy (i.e., not containing LDA corrections from interactions with other non-f band electrons or with f electrons).

(ii) $\langle \Phi_F(r)|\nabla^2+V_0(r)|\Phi_F(r)\rangle=\sum_{Rm} \epsilon_m^0 c_m^\dagger(R)c_m(R)$.

This is the bare f-state energy (i.e., not containing LDA corrections from interactions with other f electrons or non-f band electrons). In writing this, we have neglected the direct overlap between f states centered on different sites, i.e., the $R\neq R'$ terms. In other words, we have neglected the self-banding effect of the f states. For a system in which f states are well localized (e.g., typical cerium systems), it is proper to do so; but in some more itinerant f-electron systems (e.g., typical uranium systems), the self-banding effects should not be neglected. We further approximate that all the f states with different quantum number m have the same energy E_f, i.e., neglect the effects of the crystal-field splitting and magnetic polarization for the f states at this stage.

(iii)

$$\langle \Phi_B(r)|\nabla^2+V_0(r)|\Phi_F(r)\rangle+\text{H.c.} = \sum_{kmR} V_{km}^0 e^{i\mathbf{k}\cdot\mathbf{R}} b_k^\dagger c_m(R)+\text{H.c.}$$

This is the bare hybridization between band states and f states (i.e., not containing the LDA correction due to the changes of the f electrons and non-f band electrons).

The second term on the right-hand side of (2.4) is of two-body type. To make it more comprehensible, we write it in the form of an integral, and the summation over spins is implicit in the integral operation:

$$\frac{1}{2}\left\langle \Phi(r_1)\Phi(r_2)\left|\frac{1}{r_{12}}\right|\Phi(r_2)\Phi(r_1)\right\rangle=\frac{1}{2}\int\int [\Phi_B^\dagger(r_1)+\Phi_F^\dagger(r_1)][\Phi_B(r_1)+\Phi_F(r_1)] \times\frac{1}{r_{12}}[\Phi_B^\dagger(r_2)+\Phi_F^\dagger(r_2)][\Phi_B(r_2)+\Phi_F(r_2)]dr_1^3dr_2^3 .$$

When it is expanded, we have terms (iv) through (xi).

(iv) $\frac{1}{2}\int\int \Phi_B^\dagger(r_1)\Phi_B(r_1)\frac{1}{r_{12}}\Phi_B^\dagger(r_2)\Phi_B(r_2)dr_1^3dr_2^3$.

This is the Coulomb interaction between non-f band electrons. When $\Phi_B(r)$ is expanded in k space as in (2.5b), this integral contains the direct Coulomb parts and exchange-correlation parts, both of which are included in the band-state energy ϵ_k given by LDA. Therefore we merge this term into term (i) and replace the bare band energy ϵ_k^0 by a LDA band energy ϵ_k.

$$\text{(v)}\ \frac{1}{2}\int\int \Phi_F^\dagger(r_1)\Phi_F(r_1)\frac{1}{r_{12}}\Phi_F^\dagger(r_2)\Phi_F(r_2)dr_1^3dr_2^3 \ .$$

This is the Coulomb interaction between local f electrons. By neglecting the interatomic part ($R \neq R'$) which is very small and keeping only the intra-atomic part, this term can be regarded as a correction to the f-state energy E_f in term (ii). Generally, it contains a direct Coulomb part, which can be written as

$$\frac{U}{2}\sum_{R,m\neq m'} n_m(R)n_{m'}(R) \ , \tag{2.6}$$

and an exchange Coulomb part. If the exchange Coulomb part is included, there will be energy splitting between different multiplets when there is more than one f electron in one atom. If we neglect this effect, then we can neglect the exchange Coulomb part and keep only the direct Coulomb part U in (2.6).

Here we do not merge the U effect into the f-state energy E_f as LDA does, since this approximation would eliminate the effects of the interconfigurational fluctuations of the f states, such as $f^n \leftrightarrow f^{n\pm1}$, which are important for f-electron phenomena. Because U is not included in E_f, E_f is different from the f-state energy given by the LDA band calculation. However, one can relate the non-LDA energy E_f and U to the LDA energies of different f^n configurations, which can be evaluated by a supercell calculation.[5]

$$\text{(vi)}\ \int\int \Phi_B^\dagger(r_1)\Phi_B(r_1)\frac{1}{r_{12}}\Phi_F^\dagger(r_2)\Phi_F(r_2)dr_1^3dr_2^3 \ .$$

$$\text{(vii)}\ \int\int \Phi_B^\dagger(r_1)\Phi_F(r_1)\frac{1}{r_{12}}\Phi_F^\dagger(r_2)\Phi_B(r_2)dr_1^3dr_2^3 \ .$$

These are Coulomb interactions between band and nonband f electrons. (vi) is the direct Coulomb interaction and (vii) is the exchange Coulomb interaction. Written in explicit form, they are

$$\sum_{kk'}\sum_{mm'R}[U_{mm'}(\mathbf{k},\mathbf{k}')-J_{mm'}(\mathbf{k},\mathbf{k}')] \times e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} b_k^\dagger b_{k'} c_m^\dagger(R) c_{m'}(R) \ , \tag{2.7}$$

where $U_{mm'}(\mathbf{k},\mathbf{k}')$ is the direct Coulomb term

$$U_{mm'}(\mathbf{k},\mathbf{k}') = \int\int \phi_k^*(r_1)\phi_{k'}(r_1)\frac{1}{r_{12}}\psi_m^*(r_2)\psi_{m'}(r_2)dr_1^3dr_2^3 \tag{2.8}$$

and $J_{mm'}(\mathbf{k},\mathbf{k}')$ is the exchange Coulomb term

$$J_{mm'}(\mathbf{k},\mathbf{k}') = \int\int \phi_k^*(r_1)\psi_{m'}(r_1)\frac{1}{r_{12}}\psi_m^*(r_2)\phi_{k'}(r_2)dr_1^3dr_2^3 \ . \tag{2.9}$$

In (2.8) and (2.9), we have neglected the terms with $R \neq R'$, since $\psi_m(r)$ is very localized and $1/r_{12}$ decays with distance so that the integrals (2.8) and (2.9) are very small when $\psi_m(r_1)$ and $\psi_{m'}(r_2)$ are centered on different sites. In the band energy ϵ_k given directly by the LDA and the f-state energy E_f indirectly by LDA (i.e., using the supercell calculation and taking pertinent energy differences[5]), (vi) and (vii) make their contributions within the LDA approximation. However, when we go to the higher orders of $U_{mm'}(\mathbf{k},\mathbf{k}')$ and $J_{mm'}(\mathbf{k},\mathbf{k}')$, there are terms connecting different atomic sites, e.g., the two-ion interaction terms. For such two-ion interactions, the energy of an f electron at one location is determined by the state of an f electron at another location, and vice versa. This is quite different from what is presumed in the LDA, that the energy of an electron depends only on the charge densities at its own location. Thus, the two-ion interactions are not contained in the LDA energies. For the purpose of calculating the two-ion interactions, $U_{mm'}(\mathbf{k},\mathbf{k}')$ and $J_{mm'}(\mathbf{k},\mathbf{k}')$ should be retained, while keeping in mind that their lowest-order effects are already included in ϵ_k directly by the LDA, and in E_f indirectly by the LDA,[5] as are their higher-order effects involving only one atom. However, when the random-phase approximation (RPA) is applied, the contribution of $U_{mm'}(\mathbf{k},\mathbf{k}')$ to the two-ion interaction is in effect the screened Coulomb interaction between two f electrons at different sites. Such interaction is very small even before the screening effect is included, and screening only makes it smaller. Thus we neglect $U_{mm'}(\mathbf{k},\mathbf{k}')$, recognizing that its contributions to the LDA energies are already counted in and that its contributions to the two-ion interaction are small. (Traditionally, $U_{mm'}(\mathbf{k},\mathbf{k}')$ is dismissed from the two-ion interaction for a simpler reason: it causes no magnetization. This is true only when spin is counted as the only source of magnetization and orbital moment is neglected.) We retain $J_{mm'}(\mathbf{k},\mathbf{k}')$ since the two-ion interaction due to this term, by its nature, cannot be viewed as an effectively screened Coulomb interaction between two f electrons at different sites, and thus is not negligibly small. We can also take into account the screening effect for $J_{mm'}(\mathbf{k},\mathbf{k}')$. This will be discussed in Sec. IV.

$$\text{(viii)}\ \int\int \Phi_B^\dagger(r_1)\Phi_F(r_1)\frac{1}{r_{12}}\Phi_B^\dagger(r_2)\Phi_B(r_2)dr_1^3dr_2^3 + \text{H.c.}$$

$$\text{(ix)}\ \int\int \Phi_B^\dagger(r_1)\Phi_F(r_1)\frac{1}{r_{12}}\Phi_F^\dagger(r_2)\Phi_F(r_2)dr_1^3dr_2^3 + \text{H.c.}$$

The net effects of these two terms are hybridization between band and local f electrons. As an approximation, we replace $\Phi_B^\dagger(r_2)\Phi_B(r_2)$ by $\langle\rho_B(r_2)\rangle$ in (viii) and $\Phi_F^\dagger(r_2)\Phi_F(r_2)$ by $\langle\rho_F(r_2)\rangle$ in (ix). Thus (viii) and (ix) can be written together as

$$\int\int \Phi_B^\dagger(r_1)\frac{\langle\rho_B(r_2)+\rho_F(r_2)\rangle}{r_{12}}\Phi_F(r_1)dr_1^3dr_2^3 + \text{H.c.}$$

Since $\langle\rho_B(r_2)+\rho_F(r_2)\rangle/r_{12}$ is included in the effective potential $V_1(r)$ in (2.3), the effect of this term is to dress the bare hybridization V_{km}^0 of term (iii) by replacing $V_0(r)$ by the LDA potential $V(r)$ of (2.3). Thus, we merge the effects of (viii) and (ix) into term (iii) and replace the bare hybridization V_{km}^0 with a LDA hybridization V_{km}.

$$\text{(x)}\ \frac{1}{2}\int\int \Phi_B^\dagger(r_1)\Phi_F(r_1)\frac{1}{r_{12}}\Phi_B^\dagger(r_2)\Phi_F(r_2)dr_1^3dr_2^3 \ .$$

$$\text{(xi)}\ \frac{1}{2}\int\int \Phi_F^\dagger(r_1)\Phi_B(r_1)\frac{1}{r_{12}}\Phi_F^\dagger(r_2)\Phi_B(r_2)dr_1^3dr_2^3 \ .$$

These two terms create or annihilate two local f electrons. We neglect them since such processes incur very high energy costs.

We finally obtain the following model Hamiltonian:

$$H=H_0+H_1 \ , \tag{2.10a}$$

$$H_0=\sum_k \epsilon_k b_k^\dagger b_k+\sum_{Rm} E_f c_m^\dagger(R)c_m(R) + \frac{U}{2}\sum_{R,m\neq m'} n_m(R)n_{m'}(R) \ , \tag{2.10b}$$

$$H_1=\sum_{kmR}[V_{km}e^{-i\mathbf{k}\cdot\mathbf{R}}b_k^\dagger c_m(R)+\text{H.c.}] - \sum_{kk'}\sum_{mm',R} J_{mm'}(\mathbf{k},\mathbf{k}')e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} \times b_k^\dagger b_{k'} c_m^\dagger(R)c_{m'}(R) \ . \tag{2.10c}$$

The sources of the parameters in this Hamiltonian are summarized as follows: term (i) is incorporated in the LDA band energy ϵ_k; term (ii) in the f-state energy E_f, which is not a LDA energy but can be calculated indirectly from the LDA (as in Ref. 5); term (iii) in the LDA hybridization V_{km}; term (iv) in ϵ_k; term (v) in the intra-atomic f-f correlation U, which can be calculated indirectly from the LDA (as in Ref. 5); term (vi) in ϵ_k and E_f; term (vii) partly in ϵ_k and E_f but with its effects on the two-ion interaction represented separately by the band-f exchange Coulomb interaction $J_{mm'}(\mathbf{k},\mathbf{k}')$; and terms (viii) and (ix) in V_{km}. This model Hamiltonian can be read either as the Anderson Hamiltonian plus a band-f exchange term or as the Kondo Hamiltonian plus a hybridization term.

The Schrieffer-Wolff transformation[9] on the Anderson Hamiltonian gives an effective indirect exchange term arising from the hybridization, and makes the Anderson and Kondo Hamiltonians equivalent in some phenomenological sense. Although phenomenological theories based on these model Hamiltonians do not distinguish the true band-f Coulomb exchange and the hybridization-induced effective exchange, these two are from different physical origins and their contributions to the properties of materials are additive. For a first-principles calculation, these two should be evaluated separately and regarded as simultaneously existing effects.

III. TWO-ION INTERACTION

In this section, we will derive the expression for the two-ion interaction from the model Hamiltonian (2.10). Wills and Cooper[4] derived the expression for the two-ion interaction from the Anderson lattice Hamiltonian by making a Schrieffer-Wolff transformation (SW)[9] and keeping terms up to fourth order. The band-f exchange term in Hamiltonian (2.10) will make the SW transformation extremely tedious. Here we use a perturbation approach.

The general form of a two-ion interaction is

$$H(1,2)=-\sum_{n_1n_1'}\sum_{n_2n_2'} E_{n_1n_1'}^{n_2n_2'}(\mathbf{R}_2-\mathbf{R}_1)\times c_{n_2}^\dagger(2) \times c_{n_2'}(2)c_{n_1}^\dagger(1)c_{n_1'}(1) \tag{3.1}$$

and $E_{n_1n_1'}^{n_2n_2'}$ is the perturbation energy

$$E_{n_1n_1'}^{n_2n_2'}(\mathbf{R}_2-\mathbf{R}_1)=\sum_i \left\langle n_1,n_2 \left| H_1\frac{1}{E_0-H_0}H_1\frac{1}{E_0-H_0}H_1\cdots H_1\right| n_1',n_2'\right\rangle \ , \tag{3.2}$$

where $|n_1,n_2\rangle$ and E_0 are the ground state and its energy. In the ground state, the band electrons form a closed Fermi sea, and all the ions are in the f^1 (i.e., Ce^{3+}) configuration with n_1 (n_2) being the magnetic quantum number of the f electron located at $\mathbf{R}_1$ ($\mathbf{R}_2$). For the intermediate states, the ions can either be in f^1,f^2, or f^0 configuration. $\sum_i$ means summing over the ith-order perturbation, and, for each order of perturbation, taking into account all the possible virtual excitation processes which involve electron (hole) exchange between the two ions.

Within the fourth order, all the virtual excitation processes can be classified into three categories. (i) The J^2 effect, which arises from second-order perturbation, and is a pure band-f Coulomb exchange effect. (ii) The V^2J effect, which arises from third-order perturbation. In this type of process, hybridization occurs on one ion while band-f exchange Coulomb interaction occurs on the other ion. We call these cross-effect processes. (iii) The V^4 effect, which arises from fourth-order perturbation, and is a pure hybridization effect. In the following formalism, we set the zero of energy at the Fermi level. For convenience, we call the hybridization term in H_1 the V interaction, and the band-f exchange term in H_1 the J interaction.

J^2 effect. What happens in this process is that the two ions exchange an electron-hole pair through two consecutive J interactions, one on each of them. Its expression is

$$E_{n_1n_1'}^{n_2n_2'}(\mathbf{R}_2-\mathbf{R}_1)_{J^2}=\sum_{kk'} J_{n_2n_2'}(\mathbf{k},\mathbf{k}')J_{n_1n_1'}(\mathbf{k}',\mathbf{k}) \times e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_2-\mathbf{R}_1)} \times F_1(\epsilon_k,\epsilon_{k'})+(1\leftrightarrow 2) \ , \tag{3.3a}$$

where $(1\leftrightarrow 2)$ stands for the term which is the same as the first term with 1 and 2 interchanged, and

$$F_1(\epsilon_k,\epsilon_{k'})=\frac{1}{\epsilon_k-\epsilon_{k'}}(1-f_{k'})f_k \tag{3.3b}$$

with f_k being the Fermi function.

V^2J effect. There are four possible V^2J processes.

(1) First, a J interaction occurs on ion 1, creating an electron-hole pair $(\epsilon_k<0,\epsilon_{k'}>0)$ in the band. Then a V interaction occurs on ion 2, filling the hole $(\epsilon_k<0)$ and leaving ion 2 in an f^0 configuration. Then another V interaction occurs on ion 2, absorbing the electron $(\epsilon_{k'}>0)$ and returning ion 2 back to the f^1 configuration.

(2) First, a J interaction occurs on ion 1, creating an electron-hole pair $(\epsilon_k<0,\epsilon_{k'}>0)$ in the band. Then a V interaction occurs on ion 2, absorbing the electron $(\epsilon_{k'}>0)$ and leaving ion 2 in the f^2 configuration. Then another V interaction occurs on ion 2, filling the hole $(\epsilon_k<0)$ and returning ion 2 back to the f^1 configuration.

(3) First, a V interaction occurs on ion 1, creating an electron $(\epsilon_k>0)$ in the band and leaving ion 1 in the f^0 configuration. Then the electron $(\epsilon_k>0)$ scatters to an $(\epsilon_{k'}>0)$ state through a J interaction occurring on ion 2. Then another V interaction occurs on ion 1, absorbing the electron $(\epsilon_{k'}>0)$ and returning ion 1 back to the f^1 configuration.

(4) First, a V interaction occurs on ion 1, creating a hole $(\epsilon_{k'}<0)$ in the band and leaving ion 1 in the f^2 configuration. Then the hole $(\epsilon_{k'}<0)$ scatters to an $(\epsilon_k<0)$ state through a J interaction occurring on ion 2. Then another V interaction occurs on ion 1, absorbing the hole $(\epsilon_k<0)$ and returning ion 1 back to the f^1 configuration.

Adding (1)–(4) together, we obtain the V^2J effect in the two-ion interaction:

$$E^{n_2n_2'}_{n_1n_1'}(\mathbf{R}_2-\mathbf{R}_1)_{V^2J}=\sum_{kk'}V^*_{k'n_2}V_{kn_2'}J_{n_1n_1'}(\mathbf{k}',\mathbf{k})\times e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_2-\mathbf{R}_1)}\times F_2(\epsilon_k,\epsilon_{k'})+(1\leftrightarrow 2)\ , \tag{3.4a}$$

where

$$F_2(\epsilon_k,\epsilon_{k'})=\left[\frac{-1}{\epsilon_{k'}-E_f}+\frac{1}{\epsilon_k-E_f-U}\right]\frac{1}{\epsilon_k-\epsilon_{k'}}(1-f_{k'})f_k-\frac{1}{\epsilon_{k'}-E_f}\frac{1}{\epsilon_k-E_f}(1-f_{k'})(1-f_k)-\frac{1}{\epsilon_{k'}-E_f-U}\frac{1}{\epsilon_k-E_f-U}f_{k'}f_k\ . \tag{3.4b}$$

The meaning of E_f and U has been discussed in Sec. I, and they can be calculated from a supercell calculation.[5]

V^4 effect. There are 12 possible V^4 processes which can be classified into four categories.

(1) First, two consecutive V interactions occur on ion 1, either through the $(f^1\rightarrow f^0\rightarrow f^1)$ or the $(f^1\rightarrow f^2\rightarrow f^1)$ channel, creating an electron-hole pair in the band and leaving ion 1 still in the f^1 configuration. Then another two consecutive V interactions occur on ion 2, either through the $(f^1\rightarrow f^0\rightarrow f^1)$ or the $(f^1\rightarrow f^2\rightarrow f^1)$ channel, annihilating the electron-hole pair and leaving ion 2 still in the f^1 configuration. There are four processes in this category.

(2) First, ion 1 ejects an electron (or hole) to the band through a V interaction; that same electron (or hole) is absorbed by ion 2 through a second V interaction. These interactions move one electron (or hole) from ion 1 to ion 2, but the band is left as a closed Fermi sea. By another two consecutive V interactions which are similar to the first two, the excess electron (or hole) on ion 1 is moved back to ion 2. There are four processes in this category.

(3) First, through two consecutive V interactions, both ions eject one electron each, leaving two electrons in the band and both ions in the f^0 configuration. Through another two consecutive V interactions, the electron ejected by ion 1 is absorbed by ion 2, and the electron ejected by ion 2 is absorbed by ion 1; and both ions go back to the f^1 configuration. There are two processes in this category.

(4) Similar to (3), but both ions absorb one electron initially through two consecutive V interactions, leaving two holes in the band and both ions in the f^2 configuration. Through the next two consecutive V interactions, both ions go back to the f^1 configuration. There are two processes in this category.

Adding (1)–(4) together, we obtain the V^4 effect in the two-ion interaction. Its expression is the same as that obtained from the Anderson Hamiltonian by the SW transformation:[10]

$$E^{n_2n_2'}_{n_1n_1'}(\mathbf{R}_2-\mathbf{R}_1)_{V^4}=\sum_{kk'}V^*_{k'n_2}V_{kn_2'}V^*_{kn_1}V_{k',n_1'}\times e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_2-\mathbf{R}_1)}\times F_3(\epsilon_k,\epsilon_{k'})+(1\leftrightarrow 2)\ , \tag{3.5a}$$

where

$$F_3(\epsilon_k,\epsilon_{k'})=\left[\left[\frac{-1}{\epsilon_{k'}-E_f}+\frac{1}{\epsilon_k-E_f-U}\right]^2\frac{1}{\epsilon_k-\epsilon_{k'}}+\frac{2}{U}\frac{1}{\epsilon_{k'}-E_f}\frac{1}{\epsilon_k-E_f-U}\right](1-f_{k'})f_k$$
$$+\frac{1}{2}\left[\frac{1}{\epsilon_{k'}-E_f}\right]\left[\frac{1}{\epsilon_k-E_f}\right]\left[\frac{2}{U}+\frac{1}{\epsilon_k-E_f}+\frac{1}{\epsilon_{k'}-E_f}\right](1-f_{k'})(1-f_k)$$
$$+\frac{1}{2}\left[\frac{1}{\epsilon_{k'}-E_f-U}\right]\left[\frac{1}{\epsilon_k-E_f-U}\right]\left[\frac{2}{U}-\frac{1}{\epsilon_{k'}-E_f-U}-\frac{1}{\epsilon_k-E_f-U}\right]f_{k'}f_k\ . \tag{3.5b}$$

The total two-ion interaction is the sum of the J^2, V^2J, and V^4 effects.

$$E_{n_1n_1'}^{n_2n_2'}(\mathbf{R}_2-\mathbf{R}_1)=\sum_{kk'}[J_{n_2n_2'}(\mathbf{k},\mathbf{k}')J_{n_1n_1'}(\mathbf{k}',\mathbf{k})F_1(\epsilon_k,\epsilon_{k'})+V_{k'n_2}^{*}V_{kn_2'}J_{n_1n_1'}(\mathbf{k}',\mathbf{k})F_2(\epsilon_k,\epsilon_{k'})$$
$$+V_{k'n_2}^{*}V_{k,n_2'}V_{kn_1}^{*}V_{k',n_1'}F_3(\epsilon_k,\epsilon_{k'})]e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_2-\mathbf{R}_1)}+(1\leftrightarrow 2)\ , \tag{3.6}$$

where $F_1(\epsilon_k,\epsilon_{k'})$, $F_2(\epsilon_k,\epsilon_{k'})$, and $F_3(\epsilon_k,\epsilon_{k'})$ are given by Eqs. (3.3b), (3.4b), and (3.5b), respectively.

This two-ion interaction is anisotropic. It can be reduced to the simple isotropic form of $\mathbf{S}_1\cdot\mathbf{S}_2$ only when we neglect the orbital-transfer terms, in which the two f electrons interchange orbital states. But such neglect is inappropriate for f-electron systems.

IV. CALCULATION OF THE BAND-f EXCHANGE COULOMB INTERACTION

There are five parameters in the two-ion interaction (3.6) to be evaluated from *ab initio* calculations: $\epsilon_k, E_f, U, V_{km}$, and $J_{nn'}(\mathbf{k},\mathbf{k}')$. The values of ϵ_k, E_f, and U can be extracted from band-structure and supercell calculations, as described by Wills and Cooper[4] and Kioussis and co-workers.[5] Wills and Cooper have developed the resonance-width scheme[4] to calculate V_{km} from a linearized combination of muffin-tin orbitals (LMTO) band-structure calculation. Here we describe a scheme to calculate $J_{nn'}(\mathbf{k},\mathbf{k}')$, the band-$f$ exchange Coulomb interaction, based on a LMTO band-structure calculation. The form of the band-f exchange interaction is defined in Eq. (2.7) as

$$J_{nn'}(\mathbf{k},\mathbf{k}')=\left\langle\phi_k^*(r_1)\psi_n^*(r_2)\left|\frac{1}{r_{12}}\right|\psi_{n'}(r_1)\phi_{k'}(r_2)\right\rangle\ . \tag{4.1}$$

Since $J_{nn'}(\mathbf{k},\mathbf{k}')$ depends on k, there are too many elements of $J_{nn'}(\mathbf{k},\mathbf{k}')$ to be calculated directly. However, taking advantage of the LMTO scheme, $J_{nn'}(\mathbf{k},\mathbf{k}')$ can be expanded in elements which are independent of k and limited in number. This is done in the following way. The band wave function $\phi_k(r)$ is a linear combination of Bloch basis functions $\varphi_{lms}^k(r)$,

$$\phi_k(r)=\sum_{lms}a_{lms}^k\varphi_{lms}^k(r)\ , \tag{4.2}$$

where lms stand for angular momentum, magnetic quantum number, and spin, respectively. In the LMTO method, $\varphi_{lms}^k(r)$ is represented as a Bloch sum of muffin-tin orbitals $\chi_{lms}(r)$, with $\chi_{lms}(r)$ evaluated for specified energy parameters E_l and κ,[4,11] so that

$$\phi_k(r)=\sum_{lms}\alpha_{lms}^k\sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\chi_{lms}(r-R)\ , \tag{4.3}$$

where R is summed over the lattice sites. As discussed above, the integral giving $J_{nn'}(k,k')$ in (2.7) is very small when the f-state functions $\psi_m(r)$ are centered on different sites. We make use of this in evaluating the integral, and therefore adopt the single-site expansion for the Bloch sum of augmented muffin-tin orbitals;[12] so that (4.3) becomes

$$\phi_k(r)=\sum_{lms}[X_{lms}^1(\mathbf{k})\chi_{lms}^1(r)+X_{lms}^2(\mathbf{k})\chi_{lms}^2(r)]\ , \tag{4.4a}$$

where $\chi_{lms}^1(r)$ is just the muffin-tin orbital centered at the site in question, and the second term in (4.4a) represents the LMTO tails from all other sites when expanded about the site in question, so that

$$X_{lms}^1(\mathbf{k})=a_{lms}^k\ , \tag{4.4b}$$

$$X_{lms}^2(\mathbf{k})=\sum_{l'm's'}a_{l'm's'}^kS_{lmsl'm's'}^k\ , \tag{4.4c}$$

where $S_{lmsl'm's'}^k$ is the Korringa-Kohn-Rostoker (KKR) structure function.[12] Having (4.4), we can express $J_{nn'}(\mathbf{k},\mathbf{k}')$ in terms of coefficients $X_{lms}^t(\mathbf{k})$ and the B tensor given below:

$$J_{nn'}(\mathbf{k},\mathbf{k}')=\sum_{tt'}\sum_{\substack{lms\\l'm's'}}X_{lms}^{t*}(\mathbf{k})B_{n\ \ n'}^{lmstl'm's't'}X_{l'm's'}^{t'}(\mathbf{k}')\ , \tag{4.5}$$

where $B_{n\ \ n'}^{lmstl'm's't'}$ is the matrix element between the f states $\psi_n(r)$ and muffin-tin orbitals or reexpanded MTO tail functions, and is independent of k and k',

$$B_{n\ \ n'}^{lmstl'm's't'}=\left\langle\chi_{lms}^{t*}(r_1)\psi_n^*(r_2)\left|\frac{1}{r_{12}}\right|\psi_n(r_1)\chi_{l'm's'}^{t'}(r_2)\right\rangle\ . \tag{4.6}$$

At this point, we only need to calculate the B tensor. Since the LMTO method expresses all wave functions in terms of a limited number of muffin-tin orbitals, the number of the B tensor elements is limited, and the calculation becomes practical.

To calculate the B tensor, we write down $\chi_{lms}(r)$ and ψ_n explicitly in terms of their radial part, angular part, and spin part:

$$\chi_{lms}(r)=R_l(r)Y_{lm}(\theta,\phi)\eta_s \ , \tag{4.7a}$$

$$\psi_n(r)=F_3(r)[C_1Y_{3,n-1/2}(\theta,\phi)\eta_{+1/2} +C_2Y_{3,n+1/2}(\theta,\phi)\eta_{-1/2}] \ , \tag{4.7b}$$

where Y_{lm} is a spherical harmonic, η_s is a spinor, R_l is the radial part of the muffin-tin orbital or reexpanded MTO tail function, F_3 is the radial part of the f-wave function, and C_1, C_2 are Clebsch-Gordan coefficients. R_l and F_3 can be extracted from the LMTO band calculation. Let

$$\xi_{lms}(r)=U_l(r)Y_{lm}(\theta,\phi)\eta_s \ , \tag{4.8}$$

where U_l can be either R_l or F_3 of (4.7). Then the Coulomb integral between $\xi_{lms}(r)$ can be expanded in terms which are practical for numerical calculation:[13]

$$\begin{aligned}\left\langle \xi^*_{l'''m'''s'''}(r_1)\xi^*_{l''m''s''}(r_2)\left|\frac{1}{r_{12}}\right|\xi_{l'm's'}(r_1)\xi_{lms}(r_2)\right\rangle &= \sum_{pq}(-1)^{l''-l'}[(2l'''+1)(2l''+1)(2l'+1)(2l+1)]^{1/2}\begin{bmatrix} l'' & p & l \\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l' & p & l''' \\ 0 & 0 & 0\end{bmatrix} \\ &\quad\times(-1)^{l''-m''}\begin{bmatrix} l'' & p & l \\ -m'' & q & m\end{bmatrix}(-1)^{l'-m'}\begin{bmatrix} l' & p & l''' \\ -m' & q & m'''\end{bmatrix}\delta_{s,s''}\delta_{s',s'''} \\ &\quad\times\int\int U_{l'''}(r_2)^*U_{l''}(r_1)^*\frac{r^p_<}{r^{p+1}_>}U_{l'}(r_2)U_l(r_1)r_1^2r_2^2dr_1dr_2 \ ,\end{aligned} \tag{4.9}$$

where, in the usual notation, $r_<$ ($r_>$) means the smaller (larger) of r_1 and r_2. Since the angular part of the integral has been expressed in terms of $3j$ symbols in (4.9), only the radial part of the integral needs to be done numerically. In our calculation, it is done by a Simpson integral on a 331×331 logarithmic mesh. The radial part of the f-state wave function F_3 is highly concentrated within the muffin-tin sphere. In the case of CeBi, 98.6% of the f electron charge is within the muffin-tin sphere. Therefore, the integral outside the muffin-tin sphere can be neglected. This is the only approximation involved.

Having evaluated (4.9), we project $\chi_{lms}(r)$ and $\psi_n(r)$ onto $\xi_{lms}(r)$ according to (4.7) and obtain the B tensor. With the B tensor so calculated, all the elements of $J_{nn'}(\mathbf{k},\mathbf{k}')$ can be obtained according to (4.5).

All the above discussions are based on a bare Coulomb interaction. In real systems, the Coulomb interaction is shielded. Thomas-Fermi theory gives the shielded Coulomb interaction,

$$V(r)=\frac{e^{-r/\lambda}}{r} \ , \tag{4.10}$$

$$\frac{1}{\lambda^2}=\frac{6\pi e^2 n_0}{E_{\text{Fermi}}} \ , \tag{4.11}$$

where n_0 is the density of conduction electrons. The addition theorem for the shielded Coulomb interaction is

$$\frac{e^{-r_{12}/\lambda}}{r_{12}}=\frac{4\pi}{\lambda}\sum_{lm}\kappa_l\left(\frac{r_>}{\lambda}\right)i_l\left(\frac{r_<}{\lambda}\right)Y^*_{lm}(\theta_1,\phi_1) \times Y_{lm}(\theta_2,\phi_2) \ , \tag{4.12}$$

where $i(x)$ and $\kappa(x)$ are the first- and second-type modified spherical Bessel functions. The derivation of this formula is in the Appendix. To include the shielding effects, we replace $r^p_< / r^{p+1}_>$ by

$$\frac{2p+1}{\lambda}\kappa_p\left(\frac{r_>}{\lambda}\right)i_p\left(\frac{r_<}{\lambda}\right)$$

in the integral in (4.9). All other treatments remain the same.

In the case of CeBi and CeSb, λ is $0.89a_0$ and $0.85a_0$, respectively. Comparing with the unshielded Coulomb interaction, the shielding effect scales down the B tensor elements by a factor between 1 and 0.5, depending on the tensor element.

One could raise the question if it is possible to calculate the screened exchange Coulomb interaction from the LDA. We consider this in two steps. (1) Is it possible to calculate this interaction from the LDA in principle? (2) If it is possible in principle, is it feasible to carry out such a calculation in practice? In principle, it is possible to formulate the screened exchange Coulomb interaction in a manner which can be calculated directly from the output of the LDA band-structure calculation. To do this, the bare Coulomb interaction $1/r$ in Eq. (4.1) should be replaced by the screened Coulomb interaction $V(r)$; and $V(r)$ should be calculated from

$$V(r)=\sum_q\frac{1}{\varepsilon(q)q^2}e^{-i\mathbf{q}\cdot\mathbf{r}} \ , \tag{4.13}$$

where $\varepsilon(q)$ is the static dielectric constant, and $1/q^2$ is the bare Coulomb interaction in q space. $\varepsilon(q)$ can be written in a form which can be evaluated directly from the LDA band energies,

$$\varepsilon(q)=1+\frac{1}{q^2}\sum_k \frac{f(k)-f(k+q)}{\epsilon_{k+q}-\epsilon_k}\ , \tag{4.14}$$

where ϵ_k is the LDA band energy and $f(k)$ is the Fermi function. In fact, when $q\rightarrow 0$, under some approximations, $\varepsilon(q)$ reduces to $1+\lambda^2/q^2$, and the screened Coulomb interaction $V(r)$ reduces to the Thomas-Fermi form, as we used in this paper. But if we require that the screened Coulomb interaction be calculated from the LDA, we have to avoid these approximations and evaluate $\varepsilon(q)$ directly from Eq. (4.14) and the LDA band energies.

In practice, to synthesize Eqs. (4.13) and (4.14) with a realistic band-structure calculation would require a huge amount of numerical computation. First, to do a reliable Fourier transformation, as Eq. (4.13) requires, would call for the values of $\varepsilon(q)$ for a large number of q points. All the wave functions used in the exchange integral (4.1) are calculated on a real-space mesh which has 331 points for the radial dimension, and $V(r)$ in (4.13) needs to be calculated on the same real-space mesh. To make the calculation reliable, the q-space mesh used to calculate $\varepsilon(q)$ should not be less precise. To estimate how many q points are needed, we use the most conservative estimate for the radial dimension of q space, which is about 331 points; for the angular dimension of q space, we believe several hundred points are needed [bearing in mind that $\varepsilon(q)$ is anisotropic due to the anisotropic distribution of the screening charges]. Thus, the number of q points needed is on the order of 10^4-10^5. Second, to calculate $\varepsilon(q)$ for each q point according to Eq. (4.14), one has to take the summation over many k points. To do this, one has to calculate the value of ε_{k+q} for each k point first; and this coverage over k points must be repeated for each of the 10^4-10^5 q points. Therefore, to calculate the screened exchange Coulomb interaction from the LDA, the amount of numerical computation is too large, and thus not feasible.

One may ask why not approximate Eq. (4.14) by some simpler form which is feasible for numerical calculation? Actually, any approximation will not make a significant reduction in the amount of numerical computation, unless it makes some assumptions to simplify the structure of the energy surface ϵ_k in Eq. (4.14). But this will wipe out the ϵ_k structure given by the LDA. Thus, any practically useful approximation will disqualify the calculation as being "from the LDA," and has no reason to be believed as a significant improvement of the Thomas-Fermi theory.

V. RESULTS AND COMPARISON WITH EXPERIMENTS

The calculations in this work are for cerium monopnictides and monochalcogenides. This group of materials is of interest because of their anomalous crystal-field behavior and unusual anisotropic magnetic behavior, both thought to have their origins in relatively weakly correlated f-electron behavior.[3,4] One can find a summary of the experimental properties in the literature.[14] For these materials, phenomenological theory has treated many of the most striking aspects of the experimental behaviors thoroughly and successfully.[3] First-principles calculation of band-f hybridization has predicted hybridization-induced suppression of crystal-field splitting which is in excellent agreement with experiment.[4] It also predicts two-ion coupling constants giving correct magnetic structures, but seriously underestimates the ordering temperature.[5] Here we present the description and results of a complete first-principles calculation including both the hybridization and band-f exchange Coulomb interaction.

The following is a brief outline of the calculation. The band-structure calculation, upon which the evaluation of parameters in the model Hamiltonian (2.10) is based is a true interstitial warped-muffin-tin orbital calculation. The potential within the muffin-tin spheres is spherically averaged; the potential in the interstitial region is expanded in Fourier series. Exchange and correlation are treated in the Hedin-Lundqvist version of the local-density approximation. Spin-orbit coupling is included perturbatively and self-consistently.[4] The bands located in the vicinity of the Fermi level are the cerium $5d$ and the pnictogen p bands. The cerium $4f$ states are treated as local states confined within the core. When calculating their interaction with the band states, they are further restricted to the spin-orbit coupled states of $j=\frac{5}{2}$, since the $j=\frac{7}{2}$ states are 0.3 eV higher in energy and can be neglected. We use the resonance-width scheme[4] to calculate the hybridization strength. The band-f exchange interaction is calculated using the scheme given in Sec. IV. Both hybridization and the exchange interaction are calculated for an 89-k-point mesh in the irreducible wedge of the Brillouin zone. When calculating the two-ion interaction, the summation over $\mathbf{k},\mathbf{k}'$ is done by projecting the quantities to be summed into energy space using the tetrahedral technique[15] and then integrating over energy space.

We first compare the results with the phenomenological theory.[3] In the phenomenological theory, with the quantization axis lying along the bonding direction, the $E_{1/2\,1/2}^{1/2\,1/2}$ component is regarded as the dominant element in the two-ion interaction and taken as a fitting parameter. By fitting $E_{1/2\,1/2}^{1/2\,1/2}$ for several nearest neighbors, this procedure gives the correct magnetic structure and Néel temperature T_N. We calculated the two-ion interaction for first, second, and third nearest neighbors, with quantization axis along the bonding direction from first principles; and we can see how the interaction so obtained compares to that in the phenomenological theory.

The general form of the two-ion interaction is given in Eq. (3.6) where $E_{n_1 n_1'}^{n_2 n_2'}(\mathbf{R}_2-\mathbf{R}_1)$ is the interaction between the two ions, with n_1,n_2,n_1',n_2', each taking the six values $\frac{5}{2},\frac{3}{2},\frac{1}{2},-\frac{1}{2},-\frac{3}{2},-\frac{5}{2}$. Generally, therefore, the two-ion interaction tensor has 6^4 elements. However, if there is approximate axial symmetry about the two-ion axis, one approximately conserves the component of angular momentum along the interionic axis in transitions; and if one further selects those such elements corresponding to exchange scattering,[3,16] this approximation reduces[16] the number of independent two-ion interaction parameters for a Ce^{3+} lattice to $6^2=36$ at each neighbor distance. (In fact, there is a further reduction because of hermiticity and because of time-reversal symmetry since the parameters are calculated in the paramagnetic state.)

To calculate the equilibrium magnetic behavior, we use a mean-field approximation. Within that approximation, we choose an ion as a central ion. The neighbors of the central ion provide an average mean field acting on the central ion. (This mean field is of a complicated multipolar form.[3]) This can be done by using the average to replace the interaction operator. Thus, the mean-field Hamiltonian for the central ion is written as

$$H_{\mathrm{MF}}=-\sum_{j}\sum_{\alpha,\beta}E(\alpha,\beta,R_j)\times\langle c_\alpha^\dagger(j)c_\beta(j)\rangle c_\beta^\dagger(0)c_\alpha(0)\ , \tag{5.1}$$

where $\langle\cdots\rangle$ means thermal average, j stands for neighbors, and 0 stands for the central ion.

The expressions (3.6) and (5.1) are written in a coordinate system in which the bonding axis between two ions is the quantization axis of angular momentum. This causes a problem because the bonding axes of different pairs of ions are not parallel. Therefore, it is necessary to write all two-ion interactions in a common crystal-lattice coordinate system. This can be done by transforming the wave function from many "bonding axis" coordinate systems to the common coordinate system.[3] From experiment, we know that CeSb and CeBi have easy magnetic axes along a [001] direction. So for convenience we choose the [001] direction as the z axis of our common coordinate system for those materials. After the transformation, the mean-field Hamiltonian for the central ion becomes

$$H_{\mathrm{MF}}=-\sum_{\mu\nu}\sum_{\varepsilon\sigma}\sum_{j}B_{\varepsilon\sigma}^{\mu\nu}(\theta_j)e^{-i(\mu-\nu+\varepsilon-\sigma)\varphi_j}\times\langle c_\varepsilon^\dagger(j)c_\sigma(j)\rangle c_\mu^\dagger(0)c_\nu(0)\ , \tag{5.2}$$

where θ_j and φ_j are the polar and azimuthal angles of the bonding axis between the central and jth sites with respect to the common coordinate system, respectively; and the coefficient is given by[3]

$$B_{\varepsilon\sigma}^{\mu\nu}(\theta_j)=\sum_{\alpha\beta}E(\alpha,\beta,R_j)d_{\varepsilon\alpha}(\theta_j)d_{\sigma\beta}(\theta_j)d_{\mu\beta}(\theta_j)d_{\nu\alpha}(\theta_j)\ . \tag{5.3}$$

Here the function $d_{\alpha\beta}(\theta_j)$ is the matrix element for the $\frac{5}{2}$th (six-dimensional) irreducible representation of the full rotation group. For CeBi, the 6×6 $E(\alpha,\beta)$ tensors used in Eq. (5.3) are listed in Table I.

The symmetry about the diagonal is expected from hermiticity. Thus for Ce^{3+} lattices, at each neighbor distance, we have 21 independent components. Time-reversal symmetry reduces this[17] to 12; and if we further take the large-separation limit, this is further reduced to two components for each neighbor shell,[17] namely, those involving $\alpha,\beta=\pm\frac{1}{2}$ with respect to the two-ion axis, thereby yielding the form of the phenomenological theory.[3] These dominant $\pm\frac{1}{2}$ components involve $m_l=0$ components for the two ions, i.e., the cooperative hybridization effect tends to "suck out" ionic charge into a flattened disk with axis along the interionic axis. This then gives the picture of orbitally driven anisotropic two-ion exchange interactions.[17] This interaction is anisotropic because the ionic orbital moments tend to align perpendicular to the plane of the hybridized disklike ionic charge cloud which contains the interionic axis. The experimentally observed sensitivity to chemical environment can be easily understood when the close relationship between f-electron charge shaping and magnetic behavior is recognized.

TABLE I. Two-ion interaction tensor for CeBi (in K). Here the quantization axis is along the bonding axis.

$\hat{E}_1$ (first nearest neighbors)					
−0.4	1.3	0.4	1.3	1.2	0.7
1.3	3.2	4.2	7.7	1.9	1.2
0.4	4.2	18	27	7.7	1.3
1.3	7.7	27	18	4.2	0.4
1.2	1.9	7.7	4.2	3.2	1.3
0.7	1.2	1.3	0.4	1.3	−0.4
$\hat{E}_2$ (second nearest neighbors)					
5.9	3.6	4.9	7.4	5.3	2.5
3.6	2.6	3.0	11	4.0	5.3
4.9	3.0	14	22	11	7.4
7.4	11	22	14	3.0	4.9
5.3	4.0	11	3.0	2.6	3.6
2.5	5.3	7.4	4.9	3.6	5.9
$\hat{E}_3$ (third nearest neighbors)					
−0.05	0.02	−0.25	−0.09	−0.02	−0.19
0.02	−0.02	−0.49	−0.40	−0.18	−0.02
−0.25	−0.49	−0.81	−0.85	−0.40	−0.09
−0.09	−0.40	−0.85	−0.81	−0.49	−0.25
−0.02	−0.18	−0.40	−0.49	−0.02	0.02
−0.19	0.02	−0.09	−0.25	0.02	−0.05

For CeBi and CeSb, we find the $E_{\pm1/2\,\pm1/2}^{\pm1/2\,\pm1/2}$ components to be substantially larger than other components, as can be seen from Table I for CeBi. This structural behavior of the two-ion interaction is in agreement with the phenomenological theory. In Table II, we compare the size and range dependence of the two-ion interaction calculated from first principles with their values in the phenomenological theory.[3] If the exchange Coulomb interaction is neglected, as was done in the earlier calculations,[4,5] the two-ion interaction is of the order of magnitude of 1 K. Thus it is clear that the contribution from the exchange Coulomb interaction is dominant in determining the two-ion interaction in the cerium compounds treated here.

Next we compare the calculated Néel temperature T_N and low- (i.e., zero-) temperature ordered moment m_o with experiment. The calculation is a mean-field calcula-

TABLE II. Comparison of the size and range dependence of the two-ion interaction calculated from first principles with their values in the phenomenological theory. E_n stands for $E^{1/2\,1/2}_{1/2\,1/2}$ of the nth nearest neighbor. The results for the phenomenological theory are from Ref. 3.

		E_1 (K)	E_2 (K)	E_3 (K)
First principles	CeBi	18	14	−0.8
	CeSb	29	27	−0.6
Phenomenological	CeBi	36	39	neglected
	CeSb	22	24	neglected

TABLE III. The calculated results of Néel temperature T_N and low-temperature ordered moment m_o and their experimental values. The experimental data are from Refs. 3 and 14.

	CeBi	CeSb	CeTe[a]
T_N (K) (calculated)	26	38	3.9
m_o (μ_B) (calculated)	2.1	2.1	0.30
T_N (K) (experiment)	26	18	2.2
m_o (μ_B) (experiment)	2.1	2.1	0.3

[a] Reference 20.

tion using the first-principles results of the two-ion interaction for the first, second, and third nearest neighbors. (The technique used is essentially that of Refs. 3 and 5.)

(i) CeBi. This material is ordered at $T_N=26$ K in a AF-I structure.[14] The structure is an alternating stacking of ordered-moment-up and ordered-moment-down layers with moment being in the [001] direction and perpendicular to the ferromagnetically ordered layers. At low temperature, the ordered moment m_o is nearly saturated: $m_0=2.1\mu_B$. The calculation gives $T_N=26$ K and $m_o=2.1\mu_B$.

(ii) CeSb. This material is ordered at $T_N=18$ K in an unusual structure.[14] The structure is a stacking of layers in a repeating sequence of $(m_o=2.1\mu_B\rightarrow m_o=-2.1\mu_B\rightarrow m_o=0)$, i.e., every third layer has a zero ordered moment. The moment is in the [001] direction and perpendicular to the layers. By treating the crystal with three sublattices, the calculation gives $T_N=38$ K and $m_o=2.1\mu_B$ for the two ordered layers and $m_o=0$ for the other. The entropy behavior is interesting: for the $m_o=2.1\mu_B$ layers; the entropy per atom has a sharp drop from $k\ln 6$ to $k\ln 1.5$ when the temperature decreases across T_N, which indicates a disorder-order phase transition; for the $m_o=0$ layer, the entropy per atom decreases to about $k\ln 4$ in the region below T_N, which indicates that this layer is still in a disordered, or in other words, a paramagnetic state below T_N. This is contrary to the theory which explains the $m_o=0$ layer as being in a "Kondo state." Our results are consistent with our previous understanding of this behavior on the basis of the phenomenological theory.[18]

(iii) CeTe. In contrast with cerium monopnictides, this material has a low Néel temperature $T_N=2.2$ K and a diminished low-temperature ordered moment $m_o=0.3\mu_B$.[19] It has antiferromagnetic ordering of the second type. The calculation gives $T_N=3.9$ K and $m_o=0.30\mu_B$. Here a small moment does not indicate that there is disorder at low temperature. The entropy per atom is $k\ln 1$ at zero temperature, and therefore the atoms are in a perfectly ordered state. It is the anisotropy of the two-ion interaction which forces the atomic ground state to have a small expectation value of m.

We have seen that the orbital-motion-driven anisotropic two-ion interaction[17] is behind the diverse magnetic behavior of the cerium compounds we have studied. In Table III, we list the calculated results for Néel temperature T_N and low-temperature ordered moment m_o and compare them with the experimental values.

VI. SUMMARY AND DISCUSSION

We have developed a model Hamiltonian describing f electrons interacting with non-f band electrons. In this model Hamiltonian, the f-with-non-f interactions include both band-f hybridization and band-f exchange Coulomb interaction. We have developed schemes to calculate the quantities in the model Hamiltonian on the basis of band-structure calculations. For cerium monopnictides and monochalcogenides, we perform a LMTO band-structure calculation to calculate these quantities, and from these quantities calculate the two-ion interaction. The two-ion interaction so calculated contains contributions from the orbital motion of the f electron. This causes the two-ion interaction to be highly anisotropic, and accordingly causes the peculiar magnetic behavior in these materials. The first-principles results are in excellent agreement with phenomenology on structural and range behavior of the two-ion interaction and with experiment on ordered moment. They slightly overestimate the ordering temperatures, being within a factor of 2 or less of experiment. The results for CeTe are in excellent agreement with the strongly reduced experimental T_N and ordered moment.

There are several aspects of the physics which are neglected in our theory. (1) Our band calculation neglects the influence of the local moments on band states, i.e., the reciprocal effect to that of the bands on the local moments, which we treat. Such an influence can make the magnetic structure and band structure sensitively correlated, and could be important toward understanding such correlated behavior in the bands as gives rise to heavy-fermion behavior. (2) The local moment is calculated in the mean field of neighboring moments, and moment fluctuations are neglected. Moment fluctuations can be destructive to the mean-field ordering, and including such effects could improve the T_N calculation. (3) The extended (delocalized) states are viewed as Bloch (band) states which extend throughout the whole crystal. In this view, an interaction with the f-electron charge (and associated moment) in the $4f$ shell for a given atomic site will affect the band electrons throughout the whole crystal equally. In reality, a band-f interaction affects the band electrons only within a region surrounding the local moment. Thus the charge fluctuations (driven by hybridization in the presence of the on-site Coulomb repulsion and as modified by Coulomb exchange) which transmit the two-ion exchange presumably involve charge pulsating only between a given f shell and some "extended shell" rather than total delocalization. This may alter the formalism of the two-ion interaction and the consequent description of the way in which the ordered moment may disappear in such systems.

While these aspects merit future consideration, we have achieved at present significant understanding of the magnetic interactions and ordering in correlated $4f$-electron systems through this first-principles study. First, we have seen that exchange Coulomb interaction as well as hybridization plays an important role in the magnetic behavior of such f-electron systems. Which of the two interactions is stronger depends on the material. Sometimes neglecting one of them may only cause quantitative discrepancies because, as demonstrated by the Schrieffer-Wolff transformation, there is some equivalence between some of their effects. The fact that keeping only the hybridization and neglecting the exchange interaction still predicts the correct magnetic structure while underestimating the ordering temperature[5] supports this viewpoint. However, it is clear that sometimes neglect of one of the interactions may cause qualitative differences. (For example, the crystal-field dressing is totally a hybridization effect.[4]) Second, we have seen that localization and orbital motion (and associated orbital moment) are two inseparable characteristics of these f-electron systems. Orbital motion is due to the spherical symmetry of the field the electron stays in. But the ionic field is close to spherical only in a small core region, and outside of it the crystal-field dominates. So only when an electron is confined within the small core region will it have a strong orbital motion, and it must have a strong orbital motion once it is confined within the core region. From the orbital-motion-driven anisotropic magnetism, we can conjecture that a higher degree of anisotropy indicates stronger orbital motion, which further indicates higher degree of localization. In fact, anisotropic magnetism is seen more frequently in f-electron systems than in d- and p-electron systems. Here the relationship of localization—orbital motion—anisotropy is evident. (We caution, however, that this does not mean that a band, rather than a highly localized, point of view may not be a better starting point for important aspects of the f-electron behavior of higly anisotropic uranium materials.[21] However, even in a relatively bandlike material, such as UTe, the great marjority of f electrons are localized in space and energy.) Third, we have seen that a diminished local moment does not always indicate "Kondo compensation." It is also possibly a consequence of the structure of the magnetic interaction. The concept of "Kondo compensation," which is transplanted from the single-impurity problem, should be used only with very special care and justification in a magnetically ordered system.

The materials we have studied here can be regarded as "almost localized" f-electron systems. Toward the other extreme, there are "almost itinerant" f-electron systems, such as some light actinide compounds, and we will subsequently present our treatment[21] of such systems. Note, however, that as stated above, even in such an "almost itinerant" f-electron material as UTe, the great majority of f electrons are localized. A small change in the fraction of delocalized f electrons has a large qualitative effect. (Lim and Cooper[22] have developed a spin and orbitally polarized band-calculation technique based on the work of Brooks and Kelly[23] to treat the limit of fully itinerant f-electron systems.) Between the two extremes, there is a wide range of f-electron systems exhibiting phenomena such as heavy-fermion behavior. The understanding of heavy-fermion systems is still lacking. Our study of the "almost localized" and "almost itinerant" f-electron systems is an exploration on the outskirts of the heavy-fermion region. Though it does not address the heavy-fermion problem directly, it provides a framework of reference for exploring this problem, and it may contribute in seeking for a comprehensive understanding of the heavy-fermion problem.

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APPENDIX: ADDITION THEOREM FOR SHIELDED COULOMB POTENTIAL

The shielded Coulomb potential satisfies the modified Helmholtz equation

$$\nabla^2\Phi - k^2\Phi = 0 \ . \tag{A1}$$

Accordingly, it can be expanded in terms of the general solutions of Eq. (A1). Suppose there is a source at point $\mathbf{r}'$ and an observer at point $\mathbf{r}$. Let γ be the angle between $\mathbf{r}$ and $\mathbf{r}'$. Rotate the coordinate so that $\mathbf{r}'$ lies on the z axis. Then the expansion is

$$\frac{e^{-|\mathbf{r}-\mathbf{r}'|/\lambda}}{|\mathbf{r}-\mathbf{r}'|} = \sum_l [A_l i_l(kr) + B_l \kappa_l(kr)] P_l(\cos\gamma) \ , \tag{A2}$$

where $k^2 = 1/\lambda^2$, $P_l(x)$ is the Legendre function, and $i_l(x)$ and $\kappa_l(x)$ are the first- and second-type modified spherical Bessel functions. Switching source and observer, we have the same expansion in terms of r'. Since the potential remains finite at $r, r' = 0$ and $r, r' \to \infty$, the nonzero terms in the expansion are

$$\frac{e^{-|\mathbf{r}-\mathbf{r}'|/\lambda}}{|\mathbf{r}-\mathbf{r}'|} = \sum_l C_l \kappa_l(kr_>) i_l(kr_<) P_l(\cos\gamma) \ . \tag{A3}$$

To determine C_l, consider when $\lambda \to \infty$. Then this equation should reduce to the well-known equation

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_l \frac{r_<^l}{r_>^{l+1}} P_l(\cos\gamma) \ . \tag{A4}$$

Knowing the asymptotic behavior of $i_l(x)$ and $\kappa_l(x)$,

$$\begin{aligned} i_l(x) &\sim \frac{x^l}{(2l+1)!!} \quad (x \ll 1) \\ \kappa_l(x) &\sim \frac{(2l-1)!!}{x^{l+1}} \quad (x \ll 1) \end{aligned} \tag{A5}$$

we have

$$C_l = \frac{2l+1}{\lambda} . \tag{A6}$$

Using the well-known addition theorem for spherical harmonics, we arrive at (4.12).

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