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First-principle study of hybridization effects and magnetic ordering in correlated-electron uranium systems

Q. G. Sheng, Bernard R. Cooper, and S. P. Lim
Department of Physics, West Virginia University, Morgantown, West Virginia 26506-6315

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Correlated-f-electron systems have a wide range of f-electron delocalization varying from "almost localized" to "almost itinerant." Previously, techniques to calculate hybridization and exchange Coulomb interaction in the f-electron systems have been developed from the "core point of view." Such a procedure is appropriate for "almost localized" systems, i.e., typically cerium systems where the electrons of interest are $4f$. Here techniques for the same purposes are discussed, and that to calculate hybridization is developed in detail, from a "band point of view" in order to treat "almost itinerant" systems, i.e., typically light actinide systems where the electrons of interest are $5f$ such as uranium systems. Calculations have been done for uranium monopnictides and monochalcogenides. Results on magnetic ordering are in good agreement with experiment. Validity and limitations of the two points of view are discussed in regard to their application to realistic systems.

I. INTRODUCTION

Correlated-f-electron phenomena in cerium and light actinide materials have a wide range of behavior.[1] Presumably this behavior depends in a sensitive way on the interrelated matters of degree of f-electron delocalization and the solid-state chemical environment for a specific system. With regard to the degree of the f-electron delocalization, cerium monopnictides, and monochalcogenides (where the cerium f-electron configuration is close to $4f^1$) belong to the "almost localized" systems; and the isostructural (NaCl structure) uranium compounds belong to the "almost itinerant" systems. Various aspects and consequences of the f-electron behaviors in these systems have been studied phenomenologically and from first-principles by us previously.[1–10] The first-principles studies calculate materially determined parameters which are then incorporated into phenomenological (many-body model Hamiltonian) theory, and the results are compared with the phenomenology; hence the theories are materially predictive.

In the previous work, the first-principles techniques have been in the main designed for the "almost localized" systems, such as cerium monopnticides and monochalcogenides.[3] They are successful in predicting properties, such as suppressed crystal-field splitting[2,11] and anisotropic magnetic ordering.[1,3,12] In the present work, we proceed to develop first-principles techniques for the "almost itinerant" systems, such as uranium monopnictides and monochalcogenides. (A preliminary discussion appeared in Ref. 9.)

As an introduction, we briefly outline here the theoretical framework laid down in previous publications.[3] The f-electron system is described by a lattice model Hamiltonian. This Hamiltonian contains the following elements: non-f conduction bands; local f states; an intra-atomic f-f Coulomb interaction; a hybridization between the f states and the non-f band states; and an exchange Coulomb interaction between the f and non-f states as well:

$$H=H_0+H_1\ , \tag{1.1a}$$

$$H_0=\sum_k \epsilon_k b_k^+ b_k+\sum_{Rm}\epsilon_m c_m^+(R)c_m(R)+\frac{U}{2}\sum_{R,m\neq m'} n_m(R)n_{m'}(R)\ , \tag{1.1b}$$

$$H_1=\sum_{kmR}[V_{km}e^{-i\mathbf{k}\cdot\mathbf{R}}b_k^+c_m(R)+\text{H.c.}]+\sum_{kk'}\sum_{mm',R}J_{mm'}(\mathbf{k},\mathbf{k}')e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}b_k^+c_m^+(R)\times b_{k'}c_{m'}(R)\ , \tag{1.1c}$$

where ϵ_k, ϵ_m, U, V_{km}, and $J_{nn'}(\mathbf{k},\mathbf{k}')$ are the conduction-band energy, f energy, intra-atomic f-f Coulomb repulsion interaction, band-f hybridization, and band-f exchange Coulomb interaction, respectively. m is the magnetic quantum number of the f states. R stands for an atomic site. Hybridization and exchange interaction, both consequences of Coulomb interaction, enter Hamiltonian (1.1) on an equal footing, and (1.1) is a hybrid combination of the Anderson and Kondo Hamiltonians developed to reflect realistic systems more completely. Derivation of this Hamiltonian is given in Ref. 3.

On the basis of this model Hamiltonian, perturbation theory is used to give the interaction tensor between two f electrons located at neighboring atomic sites:

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$$
\begin{aligned}
E^{m_b m_b'}_{m_a m_a'}(\mathbf{R}_\mathrm{b}-\mathbf{R}_\mathrm{n}) = {} & \sum_{kk'} J_{m_b m_b'}(\mathbf{k},\mathbf{k}')J_{m_a m_a'}(\mathbf{k}',\mathbf{k})e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_\mathrm{b}-\mathbf{R}_\mathrm{a})}F_1(\epsilon_k,\epsilon_{k'})+(a\leftrightarrow b) \\
& +\sum_{kk'} V^*_{k'm_b}V_{km_b'}J_{m_a m_a'}(\mathbf{k}',\mathbf{k})e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_\mathrm{b}-\mathbf{R}_\mathrm{a})}F_2(\epsilon_k,\epsilon_{k'})+(a\leftrightarrow b) \\
& +\sum_{k,k'} V^*_{k'm_b'}V_{k,m_b}V^*_{km_a}V_{k',m_a'}e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_\mathrm{b}-\mathbf{R}_\mathrm{a})}F_3(\epsilon_k,\epsilon_{k'})+(a\leftrightarrow b)\ ,
\end{aligned}
\tag{1.2}
$$

where $F_1(\epsilon_k,\epsilon_{k'})$, $F_2(\epsilon_k,\epsilon_{k'})$, and $F_3(\epsilon_k,\epsilon_{k'})$ are long and complicated expressions. They are given in Ref. 3. $m_a(m_b)$ is the magnetic quantum number of the f electron located at atom $a(b)$. $\mathbf{R}_a(\mathbf{R}_b)$ is the location of atom $a(b)$. $(a\leftrightarrow b)$ means a term which is the same as the preceding one except the subscripts of m_a and m_b are interchanged.

A two-ion interaction $H(a,b)$, which is the source of magnetic ordering, arises from $E^{m_b m_b'}_{m_a m_a'}$ when atom a and b contain f electrons. When there is only one f electron per atom, as in the case of cerium compounds, the relation between $H(a,b)$ and $E^{m_b m_b'}_{m_a m_a'}$ is simple:

$$
H(a,b) = -\sum_{\substack{m_a m_a' \\ m_b m_b'}} E^{m_b m_b'}_{m_a m_a'}(\mathbf{R}_\mathrm{b}-\mathbf{R}_\mathrm{a}) \times c^+_{m_b}(b)c_{m_b'}(b)c^+_{m_a}(a)c_{m_a'}(a)\ ,
\tag{1.3}
$$

where $c^+_{m_a}(a)$ $[c_{m_a}(a)]$ creates (annihilates) an f electron with quantum number m_a at atom a. When there are more than one f electrons per atom, as in the case of uranium compounds, $H(a,b)$ is the interaction between two f multiplets located at atom a and b, and the relation between $H(a,b)$ and $E^{m_b m_b'}_{m_a m_a'}$ is more complicated. This relation has not been given in our previous publications, and we will derive it in Sec II.

The task of first-principles calculation then consists of two stages.[13] For a specified material, the first stage is to calculate all the parameters appearing in Eq. (1.1) and (1.2): ϵ_k, ϵ_m, U, and V_{km}, and $J_{mm'}(\mathbf{k},\mathbf{k}')$; and the second stage is then to treat the phenomena using the Hamiltonian of (1.1)–(1.3). Over a period of time, techniques have been developed to fulfill both these tasks, where initially the hybridization-parameter-calculating technique of the first stage was developed with "almost localized" cerium compounds in mind: ϵ_k is a natural outcome of band-structure calculation;[2] ϵ_m and U are calculated by performing a super-cell calculation[4] and taking total-energy differences (bearing in mind some simple linearized transition theory); for the "almost localized" systems, V_{km} is calculated using a resonance width scheme;[2] and $J_{mm'}(\mathbf{k},\mathbf{k}')$ is calculated by a scheme described in Ref. 3. All of these schemes are based on a warped muffin-tin linearized combination of muffin-tin orbitals (LMTO) band-structure calculation. The calculations of the second stage for magnetic ordering phenomenology then treat the f electrons from the "core point" of view.

As stated, in the schemes to calculate V_{km} and $J_{mm'}(\mathbf{k},\mathbf{k})$ referred to above, approximations have been made[2,3] that the f electrons in the systems are "almost localized." Take the resonance width scheme[2] which calculates the hybridization between the f and non-f states. Roughly its procedures are (i) the f states are confined within the core and the f self-banding is neglected; (ii) the f and non-f states are first calculated from a LMTO band-structure calculation without hybridization between them; (iii) the hybridization between them is then calculated; (iv) the calculation ends here without further seeking the reciprocal effects of hybridization on either f or non-f states. Clearly this procedure looks at the f electrons in the system for a "core point of view." Calculations for cerium compounds from this point of view have been successful.[2,3] However, will the techniques so established for almost localized systems be fully suitable for "almost itinerant" uranium compounds? To answer this question, we first compare the degree of f-electron delocalization in rare earths and light actinide-based materials. Figure 1 shows the squared magnitude of the wave function $|\psi(r)|^2$ versus radial distance r for $4f$ states in rare-earth monopnictides and $5f$ states in USb and UTe. It is evident that the $5f$-electron states in the uranium compounds are much more delocalized than the $4f$-electron states in the rare-earth compounds. If we regard the amount of the f wave outside of the muffin-tin sphere as "f charge leakage," we have the following charge leakage in terms of percentage:

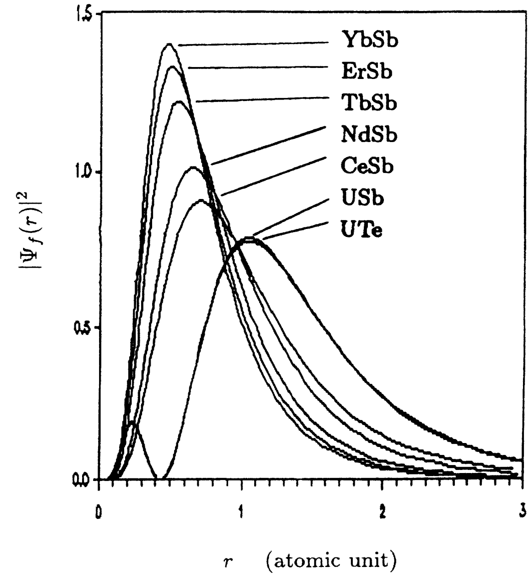

FIG. 1. Square of f-state wave functions $|\psi_f(r)|^2$ versus radial distance r.

YbSb	ErSb	TbSb	NdSb	CeSb	USb	UTe
0.18%	0.25%	0.21%	0.60%	1.6%	4.0%	3.1%
	localized		→	weakly delocalized	→	almost itinerant

The charge leakage of uranium $5f$ states is more than an order of magnitude larger than that of heavy rare-earth $4f$ states and a factor of 2 or 3 larger than for the cerium materials. This provides a warning that, with regard to the question of whether the f self-banding can be neglecting, there is a serious difference between light rare earths and light actinides.

To see whether it is justified to use the core point of view for uranium compounds, we compare three spectra obtained from the density of states of USb (shown in Fig. 2): the spectrum of pure f bands with non-f states removed from the system; the spectrum of non-f bands with f states removed; and the full spectrum of hybridized f and non-f bands. It is clear that the hybridized spectrum is drastically different from a simple addition of the f and non-f spectra with each other, i.e., the hybridization alters the shapes of unhybridized spectrums significantly. This indicates that the influence of hybridization upon the f banding is profound and *vice versa.* This situation can be contrasted with the case of cerium monopnictides. In the paper presenting the resonance width scheme, Wills and Cooper[2] show the hybridized and unhybridized spectrum of CeSb, in which the hybridized spectrum is basically a simple addition of the f and non-f spectrums with each other without altering their shape significantly. This indicates that the mutual influence between hybridization and f self-banding is weak in cerium monopnictides, and thus the use of the resonance width scheme for them is justified. In contrast, the mutual influence between hybridization and f self-banding is strong in uranium compounds; thus the core point of view fails to reflect much of the reality which contributes significantly to the hybridization in these materials.

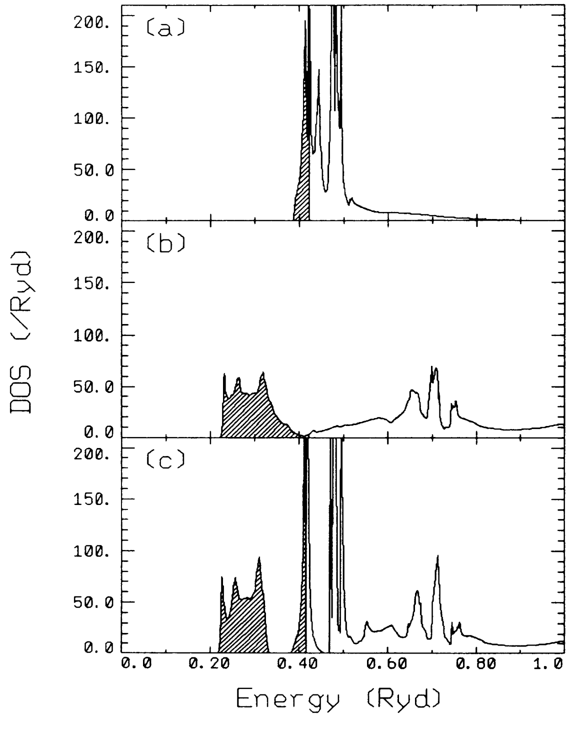

FIG. 2. Density of states of USb. (a) is of the pure f bands; (b) the non-f bands; (c) the fully hybridized f and non-f bands. The states below the Fermi level are indicated by hatching. In (a) and (b), we assume that three electrons belong to the f band and the rest belong to the non-f bands.

In Sec. III, we will develop a scheme to calculate the hybridization from a "band point of view," in which the f self-banding effect is preserved. We have not yet developed a scheme to calculate the exchange Coulomb interaction from a band point of view, and in the Appendix we will briefly discuss pertinent problems.

Basically, the core point of view and band point of view start from different bases: the former from a set of core basis states $\psi(R)$, and the later from a set of band basis states $\phi(k)$, where R and k are lattice site and wave-vector, respectively. Generally the two sets of bases are related by a Fourier transformation:

$$\psi(R)=\frac{1}{\sqrt{N}}\sum_{R} e^{ik\cdot R}\phi(k) , \qquad (1.3a)$$

$$\phi(k)=\frac{1}{\sqrt{N}}\sum_{k} e^{-ik\cdot R}\psi(R) . \qquad (1.3b)$$

Though seeming equivalent in Eq. (1.3), use of the core or of the band bases leads to very different results in practical calculations. This is because approximations in such calculations are inevitable. The core point of view and band point of view are different not only in respect to their choice of the basis states, but also in respect to their adoption of different approximations in the practical calculations. The approximations involved in the resonance width scheme provide an example.

With regard to reflecting the reality in particular materials, neither view is fully adequate or fully inadequate; rather, both views reflect reality to a limited extent. Answering the question of which point of view is closer to the reality, and therefore which viewpoint gives the better results, depends on the material to be studied, and, for a given material, also on the quantities to be calculated. Therefore the choice between the two points of view should not be absolute and rigid. In some cases, a hybrid of the two points of view will reflect the reality more closely and completely. In our treatment of uranium compounds, we will calculate the hybridization from the band point of view, based on the reasons given in the foregoing sections. But we will return to the core point of view to calculate the two-ion interaction and magnetic ordering. The reason is that the band point of view neglects the on-site Coulomb correlation and such neglect is inadequate for treating the magnetic properties of these materials. Although they show self-banding, f states in uranium compounds are still highly concentrated within the core region; and the intra-atomic Coulomb correlation, represented by U in the model Hamiltonian (1.1), still plays an important role on the magnetic behavior of the system. Thus in this paper, we direct our attention primarily to fulfilling the task of the first stage of our two-stage procedure, the evaluation of parameters for input into the theory of magnetic ordering phenomenology for light-actinide (e.g., uranium)-based materials.

In Sec. II, we derive the two-ion interaction $H(a,b)$ when atom a and b contain f multiplets. In Sec. III, we present a scheme to calculate the hybridization from the band point of view based on a LMTO band-structure calculation. In Sec. IV, we present the results of applying this scheme to magnetic ordering in USb and UTe.

II. THE TWO-ION INTERACTION BETWEEN f^3 MULTIPLETS

When an atom contains more than one electron in the same f shell, these f electrons form multiplets. The wave function of a multiplet is not unique, depending on the coupling mechanism. In general, regardless of what type of coupling mechanism, the wave function of a f^3 multiplet has the following form:

$$\Psi_{J,M}(1,2,3)=\sum_{\mu\mu'\mu''}\Gamma^{JM}_{\mu\mu'\mu''}\varphi_{\mu}(1)\varphi_{\mu'}(2)\varphi_{\mu''}(3)\ , \tag{2.1}$$

where J is the total angular momentum quantum number of the multiplet, M is the total magnetic quantum number of the multiplet, $\varphi_\mu(i)$ is the single-electron wave function with quantum number μ occupied by the ith f electron of the multiplet, and 1,2,3 indicate the first, second, and the third f electron composing the multiplet. The notation μ includes the orbital magnetic quantum number m_l and spin m_s of the single-electron state $\varphi_\mu(i)$; or, in the spin-orbit coupled representation, includes the quantum number j and m_j of that state. The coefficient $\Gamma^{JM}_{\mu\mu'\mu''}$ is determined by the way $\Psi_{J,M}(1,2,3)$ is constructed which will be described later.

The two-ion interaction occurs between the ground-state multiplets located at two neighboring atoms. Generally, it has the following form:

$$H(a,b)=-\sum_{\substack{M_aM'_a\\ M_bM'_b}}\mathcal{E}^{M_bM'_b}_{M_aM'_a}(\mathbf{R_b}-\mathbf{R_a})\times C^{+}_{M_b}(b)C_{M'_b}(b)C^{+}_{M_a}(a)C_{M'_a}(a)\ , \tag{2.2}$$

where a and b indicate neighboring atom a and b, $C^{+}_{M_a}(a)$ $[C_{M_a}(a)]$ creates (annihilates) multiplet state $\Psi_{J,M_a}(1_a,2_a,3_a)$ at atom a, and $C^{+}_{M_b}(b)$ $[C_{M_b}(b)]$ has the similar meaning for atom b. $\mathcal{E}^{M_bM'_b}_{M_aM'_a}$ is determined by the perturbation expression:

$$\mathcal{E}^{M_bM'_b}_{M_aM'_a}(\mathbf{R_b}-\mathbf{R_a})=\sum_i\left\langle M_a,M_b\left|H_1\frac{1}{E_0-H_0}H_1\frac{1}{E_0-H_0}H_1\cdots H_1\right|M'_a,M'_b\right\rangle\ , \tag{2.3}$$

where $|M_a,M_b\rangle$ and E_0 are the ground state and its energy. In the ground state, the band electrons form a closed Fermi sea, and atom a and b are in the f^3 multiplet states $\Psi_{J,M_a}(1_a,2_a,3_a)$ and $\Psi_{J,M_b}(1_b,2_b,3_b)$, respectively. For the intermediate states, the atoms are assumed to be in either f^2, f^3, or f^4 configurations; all other intermediate f^n configurations being omitted because of their high-energy costs. $\sum_i$ 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 atoms. The Hamiltonian H_0 and H_1 are defined by Eq. (1.1).

To determine $\mathcal{E}^{M_bM'_b}_{M_aM'_a}$ according to Eq. (2.3), we make the further approximation that in the summation $\sum_i$, we keep only terms corresponding to the lowest order perturbation. This in effect keeps only those virtual excitation processes in which an f electron is annihilated only once and created only once in each atom,[1] or, in other words, a pair of f electron operators $[c^{+}_{m_a}(R_a)c_{m'_a}(R_a)]$ act only once on atom a, and the same happens for atom b.

There are three f electrons in each atom, and the three are equivalent. This equivalence is implemented in the form of the wave function $\Psi_{J,M}(1,2,3)$ of the f^3 multiplet shown in Eq. (2.1). Therefore, when $c^{+}_{m}(R)$ or $c_{m'}(R)$ in H_1 acts on an atom, it has an equal chance to pick the first, second or third f electron. Define a transition rate caused by $[c^{+}_{m}(R)c_{m'}(R)]$:

$$P^{JM'\to JM}_{m'\to m}\equiv\langle\Psi^{*}_{JM}(1,2,3)|c^{+}_{m}c_{m'}|\Psi_{JM'}(1,2,3)\rangle\ . \tag{2.4}$$

We have omitted the atomic site indicator R since all quantities in Eq. (2.4) are for the same atom. Then, according to Eq. (2.1), we have

$$\begin{aligned}P^{JM'\to JM}_{m'\to m}=\sum_{\mu\mu'}[&\Gamma^{JM}_{m\mu\mu'}\Gamma^{JM'}_{m'\mu\mu'}\langle\varphi^{*}_{m}(1)\varphi^{*}_{\mu}(2)\varphi^{*}_{\mu'}(3)|c^{+}_{m}c_{m'}|\varphi_{m'}(1)\varphi_{\mu}(2)\varphi_{\mu'}(3)\rangle\\&+\Gamma^{JM}_{\mu m\mu'}\Gamma^{JM'}_{\mu m'\mu'}\langle\varphi^{*}_{\mu}(1)\varphi^{*}_{m}(2)\varphi^{*}_{\mu'}(3)|c^{+}_{m}c_{m'}|\varphi_{\mu}(1)\varphi_{m'}(2)\varphi_{\mu'}(3)\rangle\\&+\Gamma^{JM}_{\mu\mu'm}\Gamma^{JM'}_{\mu\mu'm'}\langle\varphi^{*}_{\mu}(1)\varphi^{*}_{\mu'}(2)\varphi^{*}_{m}(3)|c^{+}_{m}c_{m'}|\varphi_{\mu}(1)\varphi_{\mu'}(2)\varphi_{m'}(3)\rangle]\ ,\end{aligned} \tag{2.5}$$

where the coefficients $\Gamma^{JM}_{\mu\mu'\mu''}$ are the same as what appeared in Eq. (2.1). In fact, all the brackets $\langle \cdots | c^{+}_{m} c_{m'} | \cdots \rangle$ in (2.5) are unity and the zero brackets are already excluded from (2.5). Thus, (2.5) reduces to

$$P^{JM'\to JM}_{m'\to m}=\sum_{\mu\mu'}(\Gamma^{JM}_{m\mu\mu'}\Gamma^{JM'}_{m'\mu\mu'}+\Gamma^{JM}_{\mu m\mu'}\Gamma^{JM'}_{\mu m'\mu'}+\Gamma^{JM}_{\mu\mu' m}\Gamma^{JM'}_{\mu\mu' m'}) \; . \qquad (2.6)$$

$P^{JM'\to JM}_{m'\to m}$ has the following meaning: when an f^3 multiplets changes from the $\Psi_{J,M'}(1,2,3)$ state to the $\Psi_{J,M}(1,2,3)$ state under the restriction that an f electron can be annihilated and created only once, $P^{JM'\to JM}_{m'\to m}$ is the rate that that single-electron transition is from the single-electron f state φ'_m to φ_m. The perturbation energy corresponding to transitions between single-electron f states is $E^{m_b m'_b}_{m_a m'_a}(\mathbf{R_b}-\mathbf{R_a})$ given by Eq. (1.2). This $E^{m_b m'_b}_{m_a m'_a}$, derived in Ref. 3, is also based on the approximation that an f electron is annihilated and created only once in each atom. In Eq. (2.3), counting in all possible transitions between single-electron f states and their rates, we get

$$\mathcal{E}^{M_b M'_b}_{M_a M'_a}(\mathbf{R_b}-\mathbf{R_a})=\sum_{\substack{m_a m'_a\\ m_b m'_b}} P^{JM'_a\to JM_a}_{m'_a\to m_a} P^{JM'_b\to JM_b}_{m'_b\to m_b} \times E^{m_b m'_b}_{m_a m'_a}(\mathbf{R_b}-\mathbf{R_a}) \; . \qquad (2.7)$$

Once $\Psi_{J,M}(1,2,3)$ and $E^{m_b m'_b}_{m_a m'_a}$ are known, we can find the two-ion interaction according to Eqs. (2.6) and (2.7). In the case of the f^1 configuration, $\mathcal{E}^{M_b M'_b}_{M_a M'_a}$ reduces to $E^{m_b m'_b}_{m_a m'_a}$.

In the actual computation, according to the approximation discussed in Ref. 3, the fourth-rank tensors $E^{m_b m'_b}_{m_a m'_a}$ and $\mathcal{E}^{M_b M'_b}_{M_a M'_a}$ are approximated by matrices E^{mn}_{nm} and $\mathcal{E}^{MN}_{NM}$, and Eq. (2.7) reduces to

$$\mathcal{E}^{MN}_{NM}(\mathbf{R_b}-\mathbf{R_a})=\sum_{mn} P^{JM\to JN}_{m\to n} P^{JN\to JM}_{n\to m} E^{mn}_{nm}(\mathbf{R_b}-\mathbf{R_a}) \; . \qquad (2.8)$$

Next, we construct the wave function $\Psi_{J,M}(1,2,3)$. We use the LS coupling. According to Hund's rule, the ground-state f^3 multiplet has a total spin $S=\frac{3}{2}$, a total orbital angular momentum $L=6$, and a total angular moment $J=\frac{9}{2}$. Thus, we write $\Psi_{J=9/2,M}(1,2,3)$ in terms of the total orbital part and total spin part:

$$\Psi_{J=9/2,M}(1,2,3)=\sum_{M_L+M_S=M} C^{6,3/2,9/2}_{M_L,M_S,M} O^{L=6}_{M_L}(1,2,3) \times \Xi^{S=3/2}_{M_S}(1,2,3) \; , \qquad (2.9)$$

where $O^{L=6}_{M_L}(1,2,3)$ is the coupled orbital wave function with $L=6$, $\Xi^{S=3/2}_{M_S}(1,2,3)$ is the coupled spin function with $S=\frac{3}{2}$, and $C^{j_1,j_2,j_3}_{m_1,m_2,m_3}$ is the Clebsh-Gordan coefficient:

$$C^{j_1,j_2,j_3}_{m_1,m_2,m_3}=\langle j_1,m_1,j_2,m_2 | j_1,j_2,j_3,m_3\rangle =(-1)^{-j_1+j_2-m_3}(2j_3+1)^{1/2} \times \begin{bmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{bmatrix} . \qquad (2.10)$$

Since we restrict the discussion to the ground state, from now on we omit the superscripts and simply write O_{M_L} implying $L=6$ and Ξ_{M_S} implying $S=\frac{3}{2}$. The way of constructing $\Xi_{M_S}(1,2,3)$ is unique:

$$\Xi_{\pm 3/2}(1,2,3)=\eta_{\pm}(1)\eta_{\pm}(2)\eta_{\pm}(3) \; , \qquad (2.11a)$$

$$\Xi_{\pm 1/2}(1,2,3)=\frac{1}{\sqrt{3}}[\eta_{\mp}(1)\eta_{\pm}(2)\eta_{\pm}(3)+\eta_{\pm}(1)\eta_{\mp}(2)\eta_{\pm}(3)+\eta_{\pm}(1)\eta_{\pm}(2)\eta_{\mp}(3)] \; , \qquad (2.11b)$$

where η_{+} (η_{-}) is the single-electron spinor of spin-up (down). $\Xi_{M_S}(1,2,3)$ is symmetric between any two of the three electrons.

The way of constructing $O_{M_L}(1,2,3)$ is not unique.

First, two f electrons, say electron 1 and 2, are coupled into an intermediate two-electron wave function $O^{l_{12}}_{m_{l_{12}}}(1,2)$ with total angular moment l_{12}, and there are seven possible values for l_{12}: $l_{12}=0,1,2,3,4,5,6$. Then, electron 3 is coupled with $O^{l_{12}}_{m_{l_{12}}}$ to give $O_{M_L}(1,2,3)$. The seven possible values of intermediate l_{12} provide seven possible channels of coupling. Among them, $l_{12}=0,1$ are too small to give $L=\frac{9}{2}$, and are thus excluded. Among the rest of the channels, when $l_{12}=2,4,6$, $O^{l_{12}}_{m_{l_{12}}}(1,2)$ is symmetric between electron 1 and 2; when $l_{12}=3,5$, $O^{l_{12}}_{m_{l_{12}}}(1,2)$ is antisymmetric between electron 1 and 2. Since $\Psi_{J,M}(1,2,3)$ is antisymmetric and $\Xi_{M_S}(1,2,3)$ is symmetric, $O_{M_L}(1,2,3)$ should be antisymmetric. Thus, the channels of $l_{12}=2,4,6$ are excluded. We are left with two coupling channels: $l_{12}=3,5$. They will result in two different orbital wave functions: $O_{M_L}(1,2,3)|_{l_{12}=3}$ and $O_{M_L}(1,2,3)|_{l_{12}=5}$. Experiment cannot distinguish between them, so we take the average of them. The constructions of $O^{l_{12}}_{m_{l_{12}}}(1,2)$ and $O_{M_L}(1,2,3)$ result in the following:

$$O^{l_{12}}_{m_{l_{12}}}(1,2)=\sum_{m_{l_1}+m_{l_2}=m_{l_{12}}} C^{3,3,l_{12}}_{m_{l_1},m_{l_2},m_{l_{12}}} \times \psi_{m_{l_1}}(1)\psi_{m_{l_2}}(2) \qquad (2.12)$$

and

$$O_{M_L}(1,2,3)=\sum_{\substack{l_{12}=3,5\\ m_{l_{12}}+m_{l_3}=M_L}} C^{l_{12},3,9/2}_{m_{l_{12}},m_{l_3},M_L} \times O^{l_{12}}_{m_{l_{12}}}(1,2)\psi_{m_3}(3) \; , \qquad (2.13)$$

where $\psi_{m_l}(i)$ is the orbital part of the single-electron wave function $\varphi_\mu(i)$, supposing $\varphi_\mu(i)\equiv\psi_{m_l}(i)\eta_{m_s}(i)$. $O_{M_L}(1,2,3)$ so constructed is antisymmetric only between electron 1 and 2, but not between electron 1 and 3, or 2 and 3. To achieve the full antisymmetry, we have to treat all the three possible intermediate two-electron wave functions $O^{l_{12}}_{m_{l_{12}}}(1,2)$, $O^{l_{23}}_{m_{l_{23}}}(2,3)$, and $O^{l_{31}}_{m_{l_{31}}}(3,1)$ symmetrically. This is in effect cycling electrons 1, 2, and 3 in Eq. (2.14) and then adding them together:

$$\frac{1}{\sqrt{3}}[O_{M_L}(1,2,3)+O_{M_L}(3,1,2)+O_{M_L}(2,3,1)] \rightarrow O_{M_L}(1,2,3) \ . \qquad (2.14)$$

The procedures described in the foregoing for constructing $O_{M_L}(1,2,3)$ also apply to the spin function $\Xi_{M_S}(1,2,3)$, except that in the case of $\Xi_{M_S}(1,2,3)$ there is only one coupling channel of intermediate $s_{12}=1$ and the resulting function is symmetric instead of antisymmetric. In fact, $\Xi_{M_S}(1,2,3)$ appearing in Eq. (2.11) can be reexpressed in a similar form to that of the orbital functions appearing in Eq. (2.12) and (2.13) by using the coefficients $C^{1/2,1/2,1}_{m_{s_1},m_{s_2},m_{s_{12}}}$ and $C^{1,1/2,3/2}_{m_{s_{12}},m_{s_3},M_S}$.

From Eqs. (2.9) through (2.14), we obtain the wave function $\Psi_{J=9/2,M}(1,2,3)$ in the form of Eq. (2.1). The coefficients $\Gamma^{JM}_{\mu\mu'\mu''}$, if we let μ indicate the orbital magnetic quantum number m_l and spin m_s of a single-electron wave function, are given below:

$$\Gamma^{(9/2)M}_{\mu\mu'\mu''}=\frac{1}{\sqrt{N}}(\Upsilon_{\mu\mu'\mu''}+\Upsilon_{\mu''\mu\mu'}+\Upsilon_{\mu'\mu''\mu}) \ , \qquad (2.15)$$

where

$$\begin{aligned}\Upsilon_{m_lm_sm_l'm_s'm_l''m_s''}=&(C^{3,3,3}_{m_l,m_l',m_l+m_l'}C^{3,3,6}_{m_l+m_l',m_l'',m_l+m_l'+m_l''}+C^{3,3,5}_{m_l,m_l',m_l+m_l'}C^{5,3,6}_{m_l+m_l',m_l'',m_l+m_l'+m_l''})\\&\times C^{1/2,1/2,1}_{m_s,m_s',m_s+m_s'}C^{1,1/2,3/2}_{m_s+m_s',m_s'',m_s+m_s'+m_s''}C^{6,3/2,9/2}_{m_l+m_l'+m_l'',m_s+m_s'+m_s'',M}\end{aligned} \qquad (2.16)$$

and N is the normalization factor. If we let μ indicate the j and m_j quantum numbers of the spin-orbital coupled single-electron wave function, $\Upsilon_{m_lm_sm_l'm_s'm_l''m_s''}$ should be replaced by $\Upsilon_{jm_jj'm_j'j''m_j''}$ in Eq. (2.15), and we have the following transformation:

$$\Upsilon_{jm_jj'm_j'j''m_j''}=\sum_{\substack{m_lm_l'm_l''\\m_sm_s'm_s''}}C^{3,1/2,j}_{m_l,m_s,m_j}C^{3,1/2,j'}_{m_1',m_s',m_j'}\times C^{3,1/2,j''}_{m_1'',m_s'',m_j''}\Upsilon_{m_1m_sm_l'm_s'm_l''m_s''} \ . \qquad (2.17)$$

This completes the information needed to obtain the wave function $\Psi_{J=9/2,M}(1,2,3)$; and, as stated above, this allows us to find the two-ion interaction according to Eqs. (2.6) and (2.7).

III. CALCULATING THE HYBRIDIZATION

The LMTO band-structure calculation provides us with a self-consistent lattice potential. This potential includes, within the local-density approximation, the complete effects of the core charges and valence charges of f and non-f electrons. This potential is regarded as an accurate first-principles potential and is taken as the background of the rest of the calculation.

The lattice potential is divided into the muffin-tin sphere regions (spheres centered at each atomic site) and interstitial regions. It is spherically averaged within the muffin-tin spheres, and appears in terms of Fourier components in the interstitials. The part of the potential within a muffin-tin sphere can also be separated out to be taken as the atomic potential of that atomic site. With this atomic potential, we construct the atomic f state as the first step.

To preserve its f characteristic, we stipulate that the atomic f state is in the form

$$\psi_m(\mathbf{r})=P_l(r)Y_{lm}(\Omega) \ , \qquad (3.1)$$

where $P_l(r)$ is the radial part of the wave function, and $Y_{lm}(\Omega)$ is the angular part with Ω being the solid angle. The f characteristic of the wave function is specified by the form of $Y_{lm}(\Omega)$—a spherical harmonic of $l=3$. m is the magnetic quantum number. Here we have taken the atomic site at $R=0$.

$\psi_m(\mathbf{r})$ is to be obtained from the Schrödinger equation:

$$[-\nabla^2+V(r)-E]\psi_m(\mathbf{r})=0 \ , \qquad (3.2)$$

where $V(r)$ is the atomic potential (taken as the spherically averaged self-consistent lattice potential inside the muffin-tin sphere). Thus, within the muffin-tin sphere $(r<r_m)$, $V(r)$ is spherical; outside the muffin-tin sphere $(r>r_m)$, $V(r)$ is taken to be a constant potential with the value V_M obtained by volume averaging the lattice potential in the interstitial region. Knowing that $Y_{lm}(\Omega)$ is a spherical harmonic, Eq. (3.2) is reduced to its radial part:

$$\left[-\frac{d^2}{dr^2}+V(r)+\frac{l(l+1)}{r^2}-E\right]rP_l(r)=0, \quad \text{if } r<r_m \ , \qquad (3.3a)$$

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}-\kappa^2\right]rP_l(r)=0, \quad \text{if } r>r_m \ , \qquad (3.3b)$$

where $\kappa^2=E-V_M$. Equation (3.3a) has a solution $\chi(E,r)$, where E is to be determined; Eq. (3.3b) has a solution in the form of a linear combination of the spherical Bessel $j_l(\kappa r)$ and Neumann function $n_l(\kappa r)$, where κ^2 is to be determined. So the solution of Eq. (3.3) is

$$P_l(r)=\begin{cases}\chi(E,r), & \text{if } r<r_m\\ \kappa[n_l(\kappa r)+C(E)j_l(\kappa r)] & \text{if } r>r_m\ ,\end{cases} \tag{3.4}$$

where the coefficient $C(E)$ is to ensure that $P_l(r)$ is a continuous and smooth function at the muffin-tin sphere boundary $r=r_m$. In fact, when taking the Bloch sum of $\psi_m(r)$ in the later procedure, summing over the spherical Bessel function $j_l(\kappa r)$ gives zero; therefore the term $C(E)j_l(\kappa r)$ has no net effect and can be omitted from Eq. (3.4).

To determine E, we notice the fact that for the potential used in obtaining the USb and UTe $5f$ states, Eq. (3.3) has no solution belonging to the discrete spectrum, so E has to be chosen from the continuous spectrum. This continuous spectrum has a resonance behavior: the density of states has a peak at a resonance level E_r, and the solution with $E=E_r$ has the sharpest spatial concentration around the center of the muffin-tin sphere, compared to the other solutions. The f states have a marked resonance behavior because of the large centrifugal potential $l(l+1)/r$ in Eq. (3.3). We choose the solution at the resonance level $E=E_r$ as the atomic f state. κ^2 is chosen at the center of the occupied valence band, since, being the extended tail of the f state, $n_l(\kappa r)$ merges with the non-f valence band.

The atomic f states $\psi_m(\mathbf{r})$ so constructed are highly concentrated within the core regions. They can be used in either of two ways: taking them directly as the core-f bases so that the f electrons are treated from the core point of view; or, Fourier transforming them into the band-f bases so that the f electrons are treated from the band point of view. The two sets of bases are related by

$$\psi_{km}(r)=\frac{1}{\sqrt{N}}\sum_R e^{ik\cdot R}\psi_m(r-R)\ , \tag{3.5a}$$

$$\psi_m(r-R)=\frac{1}{\sqrt{N}}\sum_k e^{-ik\cdot R}\psi_{km}(r)\ , \tag{3.5b}$$

where $\psi_{mk}(r)$ is the band f basis state of wave vector $\mathbf{k}$, R is a lattice site, and N the number of lattice sites.

We then implement the band point of view. To do this, we introduce two sets of band bases into the system: the f-band basis ψ_{km} defined in Eq. (3.5a) and the non-f-band basis ϕ_{kn}. ϕ_{kn} is constructed according to the standard LMTO method,[14] where $\mathbf{k}$ is the wave vector and n is the basis index abbreviating the following: the type of atom if the material is a compound, the principal quantum number, the orbital quantum number, the orbital magnetic quantum number, and the spin.

Comparing the method of constructing ψ_{km} to that of constructing ϕ_{kn} by the LMTO scheme, we see that they are the same except that special choices, of orbital quantum number l and ways of determining E and κ, have been made for ψ_{km}. Therefore ψ_{km} can be regarded as precisely a special case of ϕ_{kn}, special because of its quantum number $l=3$ and because its wave is highly concentrated within the core regions. Accordingly, ψ_{km} can be incorporated into the LMTO scheme and treated with the non-f ϕ_{kn} on an equal footing and using the same computational procedures.

We calculate the elements of the Hamiltonian matrix according to the standard LMTO method. There are elements among f bases $(H_f^k)_{mm'}$, among non-f bases $(H_c^k)_{nn'}$, and between f and non-f bases $(V^k)_{mn}$, where k is the wave vector:

$$(H_f^k)_{mm'}=\langle\psi_{km}(r)|H|\psi_{km'}(r)\rangle\ , \tag{3.6a}$$

$$(H_c^k)_{nn'}=\langle\phi_{kn}(r)|H|\phi_{kn'}(r)\rangle\ , \tag{3.6b}$$

$$(V^k)_{mn}=\langle\psi_{km}(r)|H|\phi_{kn}(r)\rangle\ . \tag{3.6c}$$

The fully hybridized Hamiltonian is

$$H^k=\begin{bmatrix}H_f^k & V^k\\ V^{k+} & H_c^k\end{bmatrix}\ , \tag{3.7}$$

where H_f^k, H_c^k, and V^k are subblocks whose elements are defined in Eq. (3.6).

Since our object is to calculate the hybridization between the *unhybridized* f and non-f states, we have to find these *unhybridized* states first. To do this, we suppress the f-non-f hybridization. This is equivalent to setting V^k to be zero:

$$H^k_{\text{unhybridized}}=\begin{bmatrix}H_f^k & 0\\ 0 & H_c^k\end{bmatrix}\ . \tag{3.8}$$

Diagonalizing this Hamiltonian gives the eigenvalues and eigenstates of the *unhybridized* f and non-f bands. They are

$$H_f^k:\ \text{eigenvalue: } \epsilon_k^m;\ \text{eigenstate: } |a_k^m\rangle=\sum_{m'}\alpha^k_{mm'}\psi_{km'}(r), \tag{3.9a}$$

$$H_c^k:\ \text{eigenvalue: } \epsilon_k^n;\ \text{eigenstate: } |b_k^n\rangle=\sum_{n'}\beta^k_{nn'}\phi_{kn'}(r)\ , \tag{3.9b}$$

where $\alpha^k_{mm'}$ and $\beta^k_{nn'}$ are eigenvectors; m and n are band indices; m' and n' are basis indices. $\alpha^k_{mm'}$ and $\beta^k_{nn'}$ together form a transformation matrix:

$$T^k=\begin{bmatrix}\alpha^k & 0\\ 0 & \beta^k\end{bmatrix} \tag{3.10}$$

which transforms $\psi_{km}(r)$ to $a_k^m\rangle$ and $\phi_{kn}(r)$ to $|b_k^n\rangle$ as in Eq. (3.9). The same T^k also transforms the unhybridized Hamiltonian (3.8) into a diagonalized one, which can be written in the second quantized form:

$$\begin{aligned}\mathcal{H}_{\text{unhybridized}}&=\sum_k T^{k+}H^k_{\text{unhybridized}}T^k\\ &=\sum_k \epsilon_k^m a_k^{m+}a_k^m+\epsilon_k^n b_k^{n+}b_k^n\ ,\end{aligned} \tag{3.11}$$

where operators a_k^{m+} and b_k^{n+} create an f state $|a_k^m\rangle$ and non-f state $|b_k^n\rangle$, respectively.

We now consider the hybridization between the *unhybridized* f and non-f states:

$$V_k^{mn}=\langle a_k^m|H|b_k^n\rangle\ . \tag{3.12}$$

Including V_k^{mn} into the unhybridized Hamiltonian (3.11), it becomes a hybridized Hamiltonian:

$$\mathcal{H}=\sum_k \epsilon_k^m a_k^{m+} a_k^m+\epsilon_k^n b_k^{n+} b_k^n+(V_k^{mn} a_k^{m+} b_k^n+\mathrm{H.c.}) . \tag{3.13}$$

Notice that the same T^k transforming the unhybridized Hamiltonian from (3.8) to (3.11) should also transform the full Hamiltonian from (3.7) to (3.13):

$$\mathcal{H}=\sum_k T^{k+} H^k T^k . \tag{3.14}$$

The relation between V_k^{mn} (hybridization matrix between f and non-f eigenstates) and $(V^k)_{mn}$ (hybridization matrix between f and non-f bases) is implicit in Eq. (3.14). Writing this explicitly, it is

$$V_k^{mn}=\sum_{m'n'} \alpha_{mm'}^k \beta_{nn'}^k (V^k)_{m'n'} , \tag{3.15}$$

where the value of $(V^k)_{mn}$, as defined in Eq. (3.6c), is computed according to the LMTO procedure.

To put it simply, what this scheme does is to divide the complete basis set of a system into two sets: an f set and a non-f set. Thus the full Hamiltonian (3.7) is also correspondingly divided into four elements: one of f self-energy, one of non-f self-energy, and the other two of f-non-f hybridization. But such division has a degree of artificiality, since, although the distinction between the f and non-f states is assumed to be well defined, it is not yet clear whether there is a clear-cut border line between the two in a realistic system. Almost all of the models for the f-electron systems presume a clear-cut border line between the two. For a first-principles calculation tending to project its output onto a model Hamiltonian, this brings in a question of how and where to draw such a line in a realistic system. In fact, this is a ubiquitous question for the correlated f-electron problems, despite which, it has not yet been investigated.

We maintain that a reasonable physically defined division between "f" and "non-f" should met two criteria: (i) those waves belonging to the f have a distinct $l=3$ orbital motion near the core regions; (ii) all the remaining waves have no overlap (being orthogonalized) with the f, and belong to the non-f. In the scheme described above, clearly condition (i) is met, but not (ii). Generally, the f and non-f bases are not orthogonalized with each other:

$$\langle \psi_{km}(r) | \phi_{kn}(r) \rangle \neq 0 . \tag{3.16}$$

To meet condition (ii), we subtract the f components from the non-f basis states:

$$\phi'_{kn}(r)=\phi_{kn}(r)-\sum_m \psi_{km}(r) \langle \psi_{km}(r) | \phi_{kn}(r) \rangle . \tag{3.17}$$

What we really need to introduce into the system is a set of f-basis functions $\psi_{km}(r)$ and a set of non-f basis functions $\phi'_{kn}(r)$ which is orthogonalized to the former. To implement this, we replace $\phi_{kn}(r)$ by $\phi'_{kn}(r)$ in Eq. (3.6) and the following equations.

As we mentioned in Sec. I, we will return to the core point of view[3] to calculate the two-ion interaction and magnetic ordering. Therefore what we need is what appears in the model Hamiltonian (1.1) and in the two-ion interaction (1.2): namely, the hybridization matrix between non-f-band eigenstates and local f-basis states:

$$V_{km}^n=\langle \psi_m(r) | H | b_k^n \rangle . \tag{3.18}$$

To obtain its value, we use the Fourier transformation (3.5). This gives

$$\begin{aligned} V_{km}^n &= \frac{1}{\sqrt{N}} \sum_{k'} \langle \psi_{k'm}(r) | H | \sum_{n'} \beta_{nn'}^k \phi_{kn'}(r) \rangle e^{ik'\cdot R} \\ &= \frac{1}{\sqrt{N}} \sum_{k'n'} \beta_{nn'}^k (V^k)_{mn'} \delta_{kk'} e^{ik'\cdot R} \\ &= \frac{1}{\sqrt{N}} \sum_{n'} \beta_{nn'}^k (V^k)_{mn'} , \end{aligned} \tag{3.19}$$

where Eqs. (3.5b) and (3.9b) have been used in the first equality; (3.6c) in the second; and $R=0$ in the last.

IV. RESULTS AND DISCUSSION

We have applied the scheme described in Secs. II and III to USb and UTe. USb is antiferromagnetic with a 3-k magnetic structure when the temperature is below 213 K.[15] UTe is ferromagnetic with the easy axis along the [111] direction when the temperature is below 104 K. Phenomenological theory[1] has treated the magnetism in these materials with great success.

The ordering temperature, T_N or T_C, and low-temperature ordered moment m_o are calculated by mean-field theory using the two-ion interaction calculated by the method described in the text. A detailed description of the mean-field treatment can be found in Ref. 3. The results are listed in Table I, together with the results for the cerium compounds for comparison. Hybridizations in uranium compounds are calculated from the

TABLE I. Ordering temperature T_N or T_C and low-temperature ordered moment m_o of cerium and uranium compounds. The experimental data is from Refs. 15 and 16.

	US	USb	UTe	CeTe	CeBi	CeSb
T_N (K) (calculated)*		240	220	3.9	26	38
T_N (K) (experiment)*	178	213	104	2.2	26	18
m_o (μ_B) (calculated)		3.3	3.3	0.30	2.1	2.1
m_o (μ_B) (experiment)	1.55	2.85	2.25	0.3	2.1	2.1
m_o (μ_B) (band theory)	1.52	1.99	1.65	1.71		1.52

*T_C (K) for US and UTe

band point of view; hybridizations in cerium compounds are calculated from the core point of view. Exchange interactions are calculated from the core point of view for both uranium and cerium compounds (reasons are discussed in the Appendix). As discussed in the Appendix, this should be a good approximation for UTe and USb. The two-ion interaction and magnetic ordering are calculated from the core point of view for both uranium and cerium compounds. Thus, the cerium compounds are treated from the core point of view throughout the whole calculation; and uranium compounds are treated with a combination of the core and band points of view. In Table I, for comparison, we also list the results of the spin and orbitally polarized band theory,[10] which are fully from the band point of view.

The calculated T_N is of the same order of magnitude as experiment, within a factor of 2 or less. Two scales of ordering temperature, hundreds of Kelvin for uranium compounds, and tens of Kelvin for cerium compounds, are captured. The calculated m_0 is accurate for the almost-saturated-moment (CeBi and CeSb) cerium compounds, but is larger than the experimental value by about 15% for USb, and by about 50% for UTe. For CeTe, the ordered moment is strongly reduced from the saturated moment of a localized $\mathrm{Ce}^{3+}(f^1)$ system, so the result matching experiment closely is a demanding success for the theory. One can see that the core point of view works very well for the cerium compounds; the combination of the two points of view works fairly well for the uranium compounds, with discrepancies that make the magnetic ordering appear too strong; the band point of view works very well for US but poorly for the other materials. One expects US to be the most bandlike of the materials shown in Table I since the uranium sites are significantly closer together than in UTe and USb. As the uranium materials start to develop "correlated-electron" effects (coming from the fully itinerant f-electron direction) as in UTe, we expect the band theory moment to be in error on the low side compared to experiment. This happens because in the band theory, hybridization broadens the f bands. This lowers the f-band density of states near the Fermi energy, and in consequence the ordered moment is lowered artificially. (We have not yet performed the present correlated-electron theory calculations for US.) For CeTe, where one is entering the correlated-electron region from the localized f-electron direction, in the band theory hybridization artificially creates a density of f states at the Fermi energy giving an artificially strong magnetic ordering. In general, band theory will fail to capture the rapid change from almost saturated to almost vanishing ordered moment for the cerium compounds because of the neglect of on-site correlation effects as witness the underestimate of ordered moment for CeSb and the marked overestimate for CeTe.

If we use the "core point of view" for the uranium compounds throughout the whole calculation, (i.e., use the resonance width scheme to calculate the hybridization,) the results for T_N or T_C will be one order of magnitude smaller than experiment. Clearly such a point of view is not valid for the uranium compounds.

The cause of the discrepancies between calculation and experiment for the uranium compounds is related to how the calculation compromises between the two extremes of localization and itinerancy. It is worthwhile to analyze this more closely. The systems we studied are in the middle ground between the two extremes of core and band-f behavior. In which region of this middle ground a system lies depends on, (i) the hybridization strength of the system, and (ii) the on-site f-f correlation of the system. Both (i) and (ii) are, conversely, dependent on where the system lies between the two extremes.

Point (i) can be clearly understood from the density of states behavior of USb shown in Fig. 2: Without the hybridization, the pure f bands form a clearly peaklike spectrum. With the hybridization, the "f peak" loses some of its weight [to see this, compare Fig. 2 (a) to Fig. 2(c)], while the extended band spectrum gains weight. [To see this, compare Fig. 2(b) to Fig. 2(c).] The amount of weight gained by the extended spectrum is of f-wave character. This can be viewed as giving an "f extension" that is formed with the amount of spectrum weight which is stripped off from the f peak as a result of the hybridization. Figure 3 shows both the density of states and the $l=3$ projected density of states of USb. The f spectrum is indicated by hatching. It is clear that part of the f waves is in the extended region of the spectrum, thus forming an f extension. The larger the amount of spectral weight is in the f extension, the more itinerant is the system. Thus, a stronger hybridization causes the system to be more itinerant.

To see point (ii), we consider the interconfigurational fluctuation of $f^n \leftrightarrow f^{n+1}$ on an atomic site. Without such fluctuations, hybridization could not occur, since hybridization moves an f electron to the conduction band or the reverse. But such fluctuations cost energy because of the on-site f-f correlation. Therefore, the on-site f-f corre-

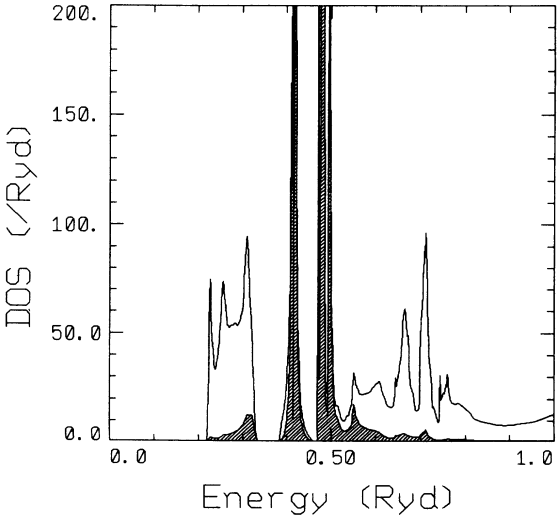

FIG. 3. Density of states of USb. The solid line is the total density of states. The hatched area is that of the f wave. It is clear that part of the f wave is in the extended region of the spectrum, thus forming the "f extension."

lation energy (Coulomb repulsion energy) is a restraint on the hybridization. Furthermore, the f-f correlation is stronger when the f wave gathers more closely around the atomic site, which means that the f electrons are more localized. Thus, a more localized system has a stronger f-f correlation; which means a stronger restraint on the hybridization; which is clearly a resistance to the tendency caused by (i) and prevents the system from being more itinerant. As a result, the balance between the two tendencies caused by (i) and (ii) determines where between localization and itinerancy the system lies. This balancing point can be represented by the proportion between the spectral weights in the f peak and in the f extension.

Considering the f peak and f extension, if one is negligible in comparison to the other, the problem becomes simple: we have either a fully localized or fully itinerant f-electron system. But in the uranium compounds, we face the reality that both the f peak and the f extension are significant, so treating the system has a degree of elusiveness in trying to deal with the dual spectral character. Because of the f extension, the f electrons are itinerant, so the f self-banding causes effects. But because the f peak is also distinct, the f electrons have a sharp local concentration. As a result, the on-site f-f correlation and interconfigurational fluctuations also cause effects. In order to reflect reality as closely as possible, one has to select an optimized compromise between the two extremes. As a price of the compromise, one loses some accuracy in the calculation.

When calculating the two-ion interaction and magnetic ordering for uranium materials from the core point of view, we in effect put all the f waves into the f peak. But the correlation effects are small for the f electrons belonging to the f extension. Thus, the core point of view exaggerates the correlation effects. It also allows an excessive amount of f waves to participate in the magnetic ordering, since the waves in the f extension presumably do not always follow the magnetic polarization of the waves in the f peak. Thus, it is not surprising that the core point of view overestimates the magnetic ordering in the uranium compounds; while as already pointed out above, the band point of view underestimates the ordering moment in the correlated-electron uranium compounds.

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APPENDIX: EXCHANGE COULOMB INTERACTION

The exchange Coulomb interactions between f bands and non-f bands are integrals over the Coulomb repulsion $1/|r_1-r_2|$:

$$J_{mm'}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4) = \left\langle \phi_{k_1}(r_1)\psi_{mk_2}(r_2)\frac{1}{r_{12}}\phi_{k_3}(r_2)\psi_{m'k_4}(r_1)\right\rangle , \tag{A1}$$

where $1/r_{12}$ stands for $1/|r_1-r_2|$; $\psi_{mk}(r)$ is the band-f bases as defined in (3.5a); $\phi_{nk}(r)$ is the non-f-band bases as stated in Sec. III; $\mathbf{k}$ is the wave vector and m is the magnetic quantum number of the band f bases. The condition must be satisfied that $k_1+k_2=k_3+k_4$.

According to (3.5a), $\psi_{mk}(r)$ can be expanded in terms of the atomic f states $\psi_m(r-R)$ centered at different lattice sites R:

$$\psi_{km}(r)=\frac{1}{\sqrt{N}}\sum_R e^{ik\cdot R}\psi_m(r-R) . \tag{A2}$$

Thus, Eq. (A1) can be written as

$$J_{mm'}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)=J_{R=R'}+J_{R\neq R'} , \tag{A3a}$$

$$J_{R=R'}=\frac{1}{N}\sum_R\left\langle \phi_{k_1}(r_1)\psi_m(r_2-R)\frac{1}{r_{12}}\phi_{k_3}(r_2) \times\psi_{m'}(r_1-R)\right\rangle e^{-i(k_2-k_4)R} , \tag{A3b}$$

$$J_{R\neq R'}=\frac{1}{N}\sum_{R\neq R'}\left\langle \phi_{k_1}(r_1)\psi_m(r_2-R)\frac{1}{r_{12}}\phi_{k_3}(r_2) \times\psi_{m'}(r_1-R')\right\rangle e^{-i(k_2R-k_4R')} , \tag{A3c}$$

where $J_{R=R'}$ is the one-site term involving one center integrals; $J_{R\neq R'}$ is the two-site term involving two center integrals.

In the scheme calculating exchange Coulomb interaction from the core point of view,[3] the $J_{R\neq R'}$ term is neglected. This is based on the reasoning that since $\psi_m(r)$ is assumed to be highly concentrated on one lattice site, the presence of $1/|r_1-r_2|$ causes the one-center integrals to be dominant over the two-center integrals (which decay, roughly, according to $1/|R-R'|$).

From the band point of view, $J_{R\neq R'}$ makes contributions. However, it is very complicated to calculate these since they involve two-center integrals. Moreover, the two-center integrals are different for different neighbor distances between R and R', thus bringing in additional technical complication.

However, without actually carrying out these integrals, one can estimate the influence of delocalization on them. It is clear from (A3) that when $\psi_m(r)$ becomes more spatially extended (delocalized), the one-center integrals in $J_{R=R'}$ are reduced, while the two-center integrals in $J_{R\neq R'}$ are increased. The reduction of $J_{R=R'}$ is more significant than the increase of $J_{R\neq R'}$ if these changes occur when $\psi_m(r)$ is still essentially concentrated on one lattice site. The increase of $J_{R\neq R'}$ is more significant than the reduction of $J_{R=R'}$ if these changes occur when $\psi_m(r)$ is already very delocalized so that it spreads its weight among several lattice sites.

For UTe and USb, $\psi_m(r)$ is essentially concentrated on one lattice site. Therefore, the reduction of $J_{R=R'}$ is more important than the increase of $J_{R\neq R'}$. Thus, since the correction due to the $J_{R\neq R'}$ contributions is small, using the scheme for calculating the exchange Coulomb interaction from the core point of view (which in effect includes all the $J_{R=R'}$ contributions) as we have done, should be a good approximation.

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