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ELUSIVE s-f INTRASITE INTERACTIONS AND DOUBLE EXCHANGE IN SOLIDS: FERROMAGNETIC VERSUS NONMAGNETIC GROUND STATE

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From the theory of many-electron states in atoms, we know that there exists a strong Coulomb repulsion, which results in the electronic term structure of atoms and is responsible for Hund's rules. By expanding the Coulomb on-site repulsion into a multipolar series, we derive this interaction and show that it is also present in solids as a correlation effect, which means that the interaction requires a multideterminant version of the Hartree–Fock method. Of particular interest is the case where this interaction couples states of localized (f) and delocalized (s) electrons. We show that the interaction is bilinear in the creation/annihilation operators for localized electrons and bilinear in the operators for conduction electrons. To study the coupling, we consider a simple model in the framework of an effective limited configuration interaction method with one localized f-electron and one itinerant s-electron per crystal site. The on-site multipole interaction between the f- and s-electrons is explicitly taken into account. It is shown that depending on the low-lying excitation spectrum imposed by the crystal electric field, the model can lead not only to ferromagnetism but also to a nonmagnetic state. The model is relevant for solids with localized and itinerant electron states.

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1. INTRODUCTION

Presently, *ab initio* calculations of the electronic band structure for solids have become a routine procedure. But it is known that even the most sophisticated methods lack some very important correlation effects (for a review, see [1]). One example is the famous Hubbard repulsion, which has to be included explicitly into an effective Hamiltonian [1]. The Hubbard repulsion is not the only correlation effect. In this paper, we discuss another important class of on-site correlations that can be described in general as mulipole Coulomb intrasite interactions [2–4]. These many-electron correlations are well known in the theory of atoms [5], but are often ignored in the band structure calculations of solids. Zener first realized the importance of these correlations and proposed a mechanism called "double exchange" to explain the origin of ferromagnetism and antiferromagnetism in solids [6]. He considered the coupling of an incomplete d-shell to the conduction electrons and concluded that in accordance with Hund's rules, it tends to align the spins in a ferromagnetic manner. (This is the third principle of his double-exchange concept [6].) Because the multipole Coulomb interactions offer a microscopic basis for Hund's rules and can even describe the exceptions to them for a number of elements (like atomic cerium with the $^1G_4$ ground-state configuration; see [7] and the references therein), we can apply the technique to derive effective magnetic correlations from first principles.

The problem was also addressed in a number of recent publications [8–10], where many-electron f-states

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are embedded into a bath of conduction electrons, and several parameters of the model (Kondon–Shortley–Slater radial integrals for the f-shell) are calculated from first principles in the local density approximation (LDA). It is called the "Hubbard-I" approximation (HIA) and we compare it with our model in Sec. 3.

We start by explaining why multipole interactions are not fully taken into account. The limitations of band structure calculations become apparent in the limit of large distance between the constituent atoms. In this case, the energy spectrum of a solid becomes atomic. Therefore, one should find discrete multiplet spectra (the ground-state level and excited terms) of atoms, which are well documented in the literature (see Ref. [7] for lanthanides). Instead, the full potential LAPW and LMTO methods [11] give a ground-state energy calculated with a spherically symmetric effective potential. One-electron energies of the corresponding s-, p-, d-, and f-states are obtained in the spherical approximation. Atomic calculations of that sort are inadequate in the sense that they do not reproduce the atomic terms observed in atomic spectra [5] and cannot give the correct value of the atomic ground-state energy.

We further illustrate the main idea by considering a simple example of an atom with only two electrons: one of the f type and the other of the s type. This model is very useful for lanthanides and actinides, where the ground states have a few $4f$ ($5f$) electrons and one or two $6s$ ($7s$) electrons. In the limit of large lattice constants, the band structure calculations give energy spectra containing two energy levels, $\epsilon(s)$ and $\epsilon(f)$. (The influence of the rest of the crystal in the limit is negligible.) The energy $\epsilon(s)$ is independent of the spin projection of an s electron. The energy $\epsilon(f)$ of an f electron is also independent of its spin (s_z) and orbital (m_z) projections. The resultant 28-fold degeneracy of the two-electron states is a consequence of the effective field with the spherical symmetry. As a result, the localized states of an f electron are uncorrelated with the states of the s electron. From the theory of atomic spectra [5], we know that this picture is incorrect. There exist important observations known as Hund's rules, which prescribe the effective couplings between the valence electrons. In the case of two electrons, the first Hund's rule requires that the two electrons have the total spin quantum number $\mathbf{S} = \mathbf{s}(s) + \mathbf{s}(f)$ equal to one, $S = 1$ in the ground state, and $S = 0$ for the exited state. However, Hund's rules are just empirical observations. The real driving force behind the term splitting is the Coulomb intrasite repulsion between the valence electrons. In what follows, we demonstrate this by using the technique of multipolar expansion, which was formulated in a number of publications [2–4]. It is worth noting that all interactions are derived from the Coulomb repulsion, which distinguishes our approach from others based on model Hamiltonians constructed from symmetry arguments [12] or some other considerations.

2. INTRASITE COULOMB CORRELATIONS

2.1. Interactions in atoms

We first introduce two-electron basis ket-vectors

$$|I\rangle = |i^s, i^f\rangle. \tag{1}$$

Here, the index $i^f = (m^f, s_z^f)$ stands for the orbital projection ($m^f = 1$–7) and spin projection ($s_z = \pm 1/2$) quantum numbers of one f electron. Therefore, there are 14 states, to be labeled by $i^f = 1$–14. The two states of an s electron are labeled by $i^s = 1, 2$. The cumulative index I therefore ranges from 1 to 28. The two-electron wave functions are

$$\langle \mathbf{r}_1, \mathbf{r}_2 | I\rangle = \frac{1}{\sqrt{2}} \sum_{a=1,2} (-1)^{P(a)} \langle \mathbf{r}_{a1} | i^s\rangle \cdot \langle \mathbf{r}_{a2} | i^f\rangle, \tag{2}$$

where a stands for a permutation of two electrons sending the first electron to $a1 = 1, 2$ and the second to $a2 = 2, 1$, correspondingly. The factor $(-1)^P$ accounts for the parity of a permutation. We note that each wave function corresponds to a 2×2 determinant, and there are 28 such determinants in total. Finally,

$$\langle \mathbf{r} | i^f\rangle = \mathcal{R}_f(r) \langle \hat{r} | i^f\rangle, \tag{3a}$$

$$\langle \mathbf{r}' | i^s\rangle = \mathcal{R}_s(r') \langle \hat{r}' | i^s\rangle, \tag{3b}$$

where $\mathcal{R}_f$ and $\mathcal{R}_s$ are the radial components of the f and s electrons and $\hat{r}$ denotes the polar angles $\Omega = (\Theta, \phi)$. The f spin orbitals can be written as

$$\langle \hat{r} | i^f\rangle = \langle \hat{r} | m_f\rangle \, u_s(s_z(f)), \tag{4}$$

where u_s is the spin function ($s = \pm$). The f-orbital parts $\langle \hat{r} | m_f\rangle$ are expressed in terms of spherical harmonics $Y_l^m(\Omega) = \langle \hat{r} | l, m\rangle$. We find it convenient to work with real spherical harmonics Y_l^τ [13], where $\tau = 0$, (m, c), or (m, s).

The order of indices in (1) is important. For example, as follows from the dynamical equivalence of electrons, the state $|i^s, i^f\rangle$ can be reduced to $|i^f, i^s\rangle$ by interchanging two electrons, i.e.,

$$|i^f, i^s\rangle = -|i^s, i^f\rangle. \tag{5}$$

In what follows, we study the intraatomic correlations of electrons within a formalism based on a multipole expansion of the Coulomb potential $V(\mathbf{r},\mathbf{r}') = 1/|\mathbf{r}-\mathbf{r}'|$ between two electrons (charge $e=-1$). The multipole expansion in terms of real spherical harmonics Y_l^0, $Y_l^{m,c}$, and $Y_l^{m,s}$ (we use the phase convention and definitions in Ref. [13]) is given by

$$V(\mathbf{r},\mathbf{r}') = \sum_{l,\tau} v_l(r,r')\, Y_l^{\tau}(\hat{r})\, Y_l^{\tau}(\hat{r}'), \tag{6}$$

where τ denotes $m=0$, (m,c), or (m,s) of the real spherical harmonics and

$$v_l(r,r') = \frac{r_<^l}{r_>^{(l+1)}}\,\frac{4\pi}{2l+1} \tag{7}$$

with $r_> = \max(r,r')$ and $r_< = \min(r,r')$.

The direct matrix elements for the intrasite Coulomb interactions are obtained if we consider the $i^f \to j^f$ transitions for the first electron and the $i^s \to j^s$ transitions for the second. We start from Eq. (6) and obtain

$$\langle I|V(\mathbf{r},\mathbf{r}')|J\rangle^{Coul} = \\ = \sum_{l,\tau} v_l^{ff-ss} c_{l,\tau}(i^f,j^f)\, c_{l,\tau}(i^s,j^s), \tag{8}$$

where

$$v_l^{ff-ss} = \int dr\, r^2 \int dr'\, r'^2\, \mathcal{R}_f^2(r)\, \mathcal{R}_s^2(r')\, v_l(r,r') \tag{9}$$

accounts for the average radial dependence. The transition matrix elements $c_{l,\tau}(i^t,j^{t'})$ $(t=t'=f,s)$ are defined by

$$c_{l,\tau}(i,j) = \int d\Omega\, \langle i^t|\hat{r}\rangle\, Y_l^{\tau}(\hat{r})\, \langle \hat{r}|j^{t'}\rangle. \tag{10}$$

We note that in the basis with real orbitals and with real spherical harmonics Y_l^{τ}, the coefficients $c_{l,\tau}$ are real.

The other possibility is to consider the transitions $i^f \to j^s$ for the first electron and the transitions $i^s \to j^f$ for the second. This gives the exchange interaction; we then use (5) to return to the standard order of the spin orbitals. We find

$$\langle I|V(\mathbf{r},\mathbf{r}')|J\rangle^{exch} = \\ = -\sum_{l,\tau} v_l^{fs-sf}\, c_{l,\tau}(i^f,j^s)\, c_{l,\tau}(i^s,j^f), \tag{11}$$

where the coefficients $c_{l,\tau}$ are again given by Eq. (10) with $t=f$, $t'=s$ or $t=s$, $t'=f$, and

$$v_l^{fs-sf} = \int dr\, r^2 \mathcal{R}_f(r)\mathcal{R}_s(r)\, \times \\ \times \int dr'\, r'^2\, \mathcal{R}_s(r')\mathcal{R}_f(r')\, v_l(r,r'). \tag{12}$$

The typical value of v_l^{fs-sf} is 0.7–0.8 eV for lanthanides and 1.0–1.1 eV for actinides.

For the sf configuration, there are only three types of these coefficients. For the s–s transition, only one integral $\langle s|Y_0^0|s\rangle = 1/\sqrt{4\pi}$ is nonzero. For the f–f transitions and real spherical harmonics [13], the coefficients $c_{l,\tau}(i^f,j^f)$ were tabulated in Ref. [2]. Although some coefficients $c_{l,\tau}(i^f,j^f)$ are not zero for $l=0,2,4$, and 6, we conclude from Eq. (8) that because of the s–s transition, only the spherically symmetric repulsion ($l=0$) is relevant. In that case, the coefficient $c_{l=0}(i^f,j^f)$ becomes diagonal,

$$c_{l=0}(i_f,j_f) = \frac{1}{\sqrt{4\pi}}\,\delta(i^f,j^f), \tag{13}$$

and we rewrite Eq. (8) as

$$\langle I|V(\mathbf{r},\mathbf{r}')|J\rangle^{Coul} = \frac{v_0^{ff-ss}}{4\pi}\,\delta(i^f,j^f)\,\delta(i^s,j^s). \tag{14}$$

We note that this expression is exactly the one obtained in the approximation of a spherically symmetric repulsion. The contribution of Eq. (14) is further combined with the attraction from the nucleus and the repulsion and exchange from the core electrons. The core electrons form only closed electron shells; in accordance with the Unsöld theorem, this results in a spherically symmetric electron density ($l=0$). Neither the field of the nucleus not the closed shells give any contribution with $l \neq 0$.

Finally, there are f–s and s–f transitions, which require the evaluation of $c_{l,\tau}(i^f,j^s)$. From the orthogonality of spherical harmonics, we find that

$$\langle 0,0|Y_3^{\tau}|3,\tau\rangle = \frac{1}{\sqrt{4\pi}}, \tag{15}$$

where $\tau=0$, (m,c), (m,s) for $m=1$–3 and zero otherwise. We observe that the exchange term, Eq. (11), results in the repulsion component with a nontrivial octupolar component of the electron density ($l=3$). We rewrite Eq. (11) as

$$\langle I|V(\mathbf{r},\mathbf{r}')|J\rangle^{exch} = \\ = -\frac{v_3^{fs-sf}}{4\pi}\,\delta(\tau_{i^f},\tau'_{j^f})\,\delta(u_{i^f},u_{j^s})\,\delta(u_{i^s},u_{j^f}). \tag{16}$$

The first Kronecker symbol in the right-hand side of Eq. (16) states that the exchange coupling is possible only between the basis states I and J that have the same f-orbital part (Y_3^τ). The second and the third Kronecker symbol impose conditions on the spin components.

We now consider the matrix of the Hamiltonian in our basis $|I\rangle$. There are only seven different orbital parts for our basis vectors, which are characterized by the orbital part of the f-electron ($\tau = 0$, (m, c), (m, s), where $m = 1, 2, 3$). We rearrange our 28 vectors into groups of seven as follows: for $I = 1$–7, we define $u_f = +1/2$ and $u_s = +1/2$; for $I = 8$–14, $u_f = -1/2$ and $u_s = +1/2$; for $I = 15$–21, $u_f = +1/2$ and $u_s = -1/2$; and for $I = 22$–28, $u_f = -1/2$ and $u_s = -1/2$. Then the 28×28 matrix of the Hamiltonian is given by

$$\langle I|H|J\rangle = \\ = \left|\begin{array}{cccc} (E-A)\hat{1} & \hat{0} & \hat{0} & \hat{0} \\ \hat{0} & E\hat{1} & -A\hat{1} & \hat{0} \\ \hat{0} & -A\hat{1} & E\hat{1} & \hat{0} \\ \hat{0} & \hat{0} & \hat{0} & (E-A)\hat{1} \end{array}\right|, \qquad (17)$$

where $\hat{1}$ is the 7×7 identity matrix, $\hat{0}$ is the 7×7 zero matrix, and

$$A = \frac{v_3^{fs-sf}}{4\pi} > 0. \qquad (18)$$

E is the energy of the atom in the spherical approximation, $l = 0$. It is easy to show that matrix (17) has the $(3 \times 7 = 21)$-fold degenerate eigenvalue $E - A$ (spin triplets) and the 7-fold degenerate eigenvalue $E + A$ (spin singlets). The result is in agreement with the first Hund's rule.

The important conclusion is that the energy of the sf configuration is lower than in the spherically symmetric model by the value of A, Eq. (18). This value is always larger than zero, because according to Eq. (12) it can be regarded as the self-interaction energy of a classical octupole with the radial density $\mathcal{R}_f(r)\mathcal{R}_s(r)$. We computed this energy for the lanthanides and the actinides (see the Table). The radial dependences for f- and s-electrons were taken from the density functional theory (LDA) relativistic atomic calculations. (These computations are of course based on a spherically symmetric model for the effective potential.) We note that this energy decrease is visible for all lanthanides and actinides, and cannot be neglected.

Table. Calculated values of $A = v_3^{fs-sf}/4\pi$, in meV, for the indicated atomic ground-state configurations of lanthanides and actinides

Lanthanides			Actinides		
La	$5d6s^2$	60.0	Ac	$6d7s^2$	139.8
Ce	$4f5d6s^2$	57.8	Th	$6d^27s^2$	101.6
Pr	$4f^36s^2$	64.7	Pa	$5f^26d7s^2$	102.7
Nd	$4f^46s^2$	61.5	U	$5f^36d7s^2$	94.1
Pm	$4f^56s^2$	59.5	Np	$5f^46d7s^2$	88.2
Sm	$4f^66s^2$	58.1	Pu	$5f^67s^2$	89.2
Eu	$4f^76s^2$	58.9	Am	$5f^77s^2$	92.7
Gd	$4f^75d6s^2$	56.3	Cm	$5f^76d7s^2$	84.2
Tb	$4f^96s^2$	56.9	Bk	$5f^97s^2$	84.8
Dy	$4f^{10}6s^2$	55.9	Cf	$5f^{10}7s^2$	82.5
Ho	$4f^{11}6s^2$	55.0	Es	$5f^{11}7s^2$	80.9
Er	$4f^{12}6s^2$	54.0	Fm	$5f^{12}7s^2$	80.0
Tm	$4f^{13}6s^2$	52.9	Md	$5f^{13}7s^2$	79.5
Yb	$4f^{14}6s^2$	51.9	No	$5f^{14}7s^2$	79.3
Lu	$4f^{14}5d6s^2$	50.8	Lr	$5f^{14}7s^27p$	91.1

2.2. Interactions in solids

So far, we have considered an atom with the fs configuration. The question is what happens to this octupole interaction when we construct a crystal consisting of such atoms? Intuitively, it is clear that the interaction cannot disappear in the assembled solid. Indeed, any band state is just a linear combination of the local states, and vice versa. The effective on-site interaction in the basis of local states, Eq. (17), persists in the basis of delocalized states [14]. In what follows, we demonstrate this explicitly in the tight-binding approximation for the s-electrons [15]. We consider a hypothetical crystal of N atoms with the fs valence electron configuration. We assume that the s-electrons are delocalized and the f-electrons are localized. This is the case for all lanthanides (except cerium) and for the actinides of the second half of the series. We label the local s and f states at a site n ($n = 1 - N$) as $|i_s\rangle_n$ and $|i_f\rangle_n$. Starting with the N local $|s\rangle_n$ states (where we focus only on the orbital part of the s states), we can construct N independent delocalized states

$$|\mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\mathbf{k}\cdot\mathbf{x}(n)} |s\rangle_n, \qquad (19)$$

where the radius vector $\mathbf{x}$ gives the position of the nucleus of atom n. In addition, each state $|\mathbf{k}\rangle$ can have two different spin polarizations, $s_z = \pm 1/2$. Although it is not always mentioned explicitly, band structure calculations involve a single determinant trial wave function,

$$\langle \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N | B \rangle = \\ = \sum_a (-1)^{P(a)} \langle r_{a1} | \mathbf{k} = 0, u_+ \rangle \cdot \ldots \times \\ \times \ldots \langle r_{an} | \mathbf{k}, u \rangle \cdot \ldots \cdot \langle r_{aN} | \mathbf{k}_F, u_- \rangle, \quad (20)$$

where all one-electron wave functions with the wave vectors from $\mathbf{k} = 0$ to the Fermi level $\mathbf{k}_F$ are present, and $|B\rangle$ stands for the metallic state of N electrons. In the absence of the localized $|f\rangle_n$ states, the energy spectrum of the s-electrons is

$$E(\mathbf{k}) = E_0 - \gamma \sum_\kappa \cos(\mathbf{k} \cdot \mathbf{R}_\kappa), \quad (21)$$

where $\gamma > 0$ (attractive metallic bond), and the summation is taken over the nearest neighbors indicated by the index κ [15]. Each metallic state accommodates two itinerant electrons with two spin components $s_z = \pm 1/2$. Therefore, without the localized f-electrons, we have a conventional metallic ground state and no magnetic effects.

We now consider the intrasite interaction with the localized states. We start with one conduction electron in the $\mathbf{k}$ state and N localized f-electrons. The conduction electron is also specified by its spin polarization index $i^s = 1, 2$. As we have seen, the localized f states cannot be characterized by a single determinant. We use the index i^f_g (g = 1–14) to describe the 14 f states at a site n, $|i^f_g\rangle_n$. For a crystal with N sites, we therefore obtain 2×14^N different determinants of the type $|i^s; i^f_1, i^f_2, \ldots, i^f_n, \ldots, i^f_N\rangle$. Because it is not possible to deal with such a large number, we simplify the problem by considering only 28 of the determinants, $|i^s; (i^f)^N\rangle$, namely, those where all N localized f-electrons are in the same state characterized by the index $i^f = i^f_1 = \ldots = i^f_n = i^f_N$. The problem can then be solved in the reduced basis. We consider the band electron ($\mathbf{k} = 0$) interacting with the localized electron at a site n. Again, we find the octupole interaction there, which now has the form

$$\langle I_{red} | V(\mathbf{r}, \mathbf{r}') | J_{red} \rangle_n^{exch} = \\ = -\frac{A}{N} \delta(\tau_{i^f}, \tau'_{j^f})\, \delta(u_{i^f}, u_{j^s})\, \delta(u_{i^s}, u_{j^f}). \quad (22)$$

However, by summing over the N crystal sites, we obtain the same result as before (cf. Eq. (16)):

$$\langle I_{red} | V(\mathbf{r}, \mathbf{r}') | J_{red} \rangle^{exch} = \\ = -A \delta(\tau_{i^f}, \tau'_{j^f})\, \delta(u_{i^f}, u_{j^s})\, \delta(u_{i^s}, u_{j^f}). \quad (23)$$

The last expression describes the interaction of one s-electron with N localized electrons in the same quantum state i_f. As is clear from the approximation, there is a one-to-one correspondence between the crystal basis and the basis of local states, Eq. (1):

$$|i^s; (i^f)^N\rangle = |I\rangle_{red} \leftrightarrow |I\rangle = |i^s, i^f\rangle. \quad (24)$$

Not surprisingly, the structure of the matrix elements is still given by Eq. (17). The energy spectrum consists of the spin triplet $E_0 - |\gamma| - A$ and the spin singlet $E_0 - |\gamma| + A$. In the general case of an electron with a wave vector $\mathbf{k}$, we obtain

$$E_T(\mathbf{k}) = E(\mathbf{k}) - A, \quad (25a)$$

$$E_S(\mathbf{k}) = E(\mathbf{k}) + A. \quad (25b)$$

We observe that the initial spectrum of the s-electrons, Eq. (21), is split into two lines (see Fig. *b*). Each line corresponds to a many-electron coupled state of the localized and a conduction electron. The splitting is expected to consist of many lines for more complex electron systems like sf^n, pf^n, or df^n (here, n = 1–13 is the number of localized f-electrons). To describe such subbands, we have to apply an efficient limited configuration interaction approach, which we have formulated here for the s–f electron system.

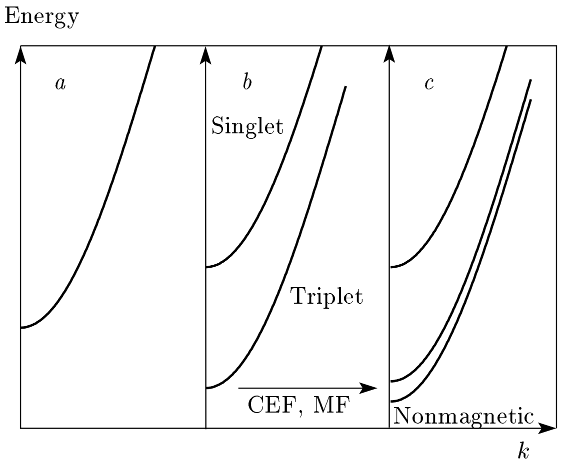
3. DISCUSSION

In the spin space, the effective Hamiltonian in Eqs. (25a) and (25b) can be written as

$$H = E(\mathbf{k}) - \frac{3}{2} A - 2A \mathbf{S}_1 \cdot \mathbf{S}_2, \quad (26)$$

where $\mathbf{S}_1$ is the spin of a conduction electron with the band energy $E(\mathbf{k})$ and $\mathbf{S}_2$ is the spin of the localized electron. (We recall that all localized electrons have the same spin projection on all sites in the model.) The Heisenberg type of Hamiltonian (26) is well known in solid state physics. Because $A > 0$ in the mean-field approximation (when $\langle \mathbf{S}_2 \rangle \neq 0$), it leads to a ferromagnetic ground state.

We stress that initially, in considering the problem with one conduction electron, the ground state was a triplet. Therefore, there is a more complex picture here, and it is more appropriate to speak of spin-triplet-like states and spin-singlet-like states, meaning that both types of pair correlations are represented in the electron spectrum. We recall that for a triplet, the spin components are $M_z = -1, 0, +1$ (in μ_B), and $M_z = 0$ for a singlet. Therefore, the spin-triplet-like states can



Energy spectrum of itinerant electrons: a — no interaction with localized f-electrons; b — triplet–singlet splitting due to the intrasite Coulomb interaction; c — further splitting of the triplet line due to the CEF or mean field (MF). The lowest subband can be nonmagnetic

be further lifted by other, weaker interactions. The main candidates here are the crystal field and mean-field effects. Indeed, it is well known that even a weak crystal electric field (CEF) splits energy levels of highly degenerate states [16, 17]. It is also worth noting that the CEF for many-electron states, or, more precisely, two-electron s–f states, is understood here [2]. In what follows, we consider the symmetry aspects of the problem in more detail.

The CEF and mean field for lanthanide and actinide ions have been extensively discussed in the literature [16–20]. In connection with the present approach, it is worth noting that the CEF is regarded as the first meaningful term of the intersite multipole expansion, when all neighbors of a lanthanide ion are considered in the spherical approximation ($l = 0$) [3]. The CEF is a single-particle potential [18]. In reality, the CEF should be considered on equal footing with the spin–orbit coupling, as has been extensively discussed in the literature [16–18]. But the influence of the spin–orbit coupling on energy levels is very specific. As was shown in Ref. [3], the combined effect of the CEF and spin–orbit coupling in the field with a cubic symmetry is as follows. 1) The orbital momenta of localized f states are not free. They are strongly coupled to the spin degrees of freedom. The possible degeneracies (irreducible representations) of the two-electron states are A, T_1, T_2, and E. 2) The spin triplet ground state keeps being triply degenerate, but the magnetic moments are $-\mathcal{M}$, 0 and $\mathcal{M}$, where $\mathcal{M}$ can take any positive value, not necessarily $1\mu_B$ as before. The triplet ground state belongs to the T_1 or T_2 irreducible representation of cubic symmetry.

The triply degenerate electron band state is close to the ferromagnetic order. If the CEF splitting is such that the lowest subband is a magnetic doublet ($\pm\mathcal{M}$), then the transition to a ferromagnetic state is straightforward. But we are presently more interested in other possibilities, where the effective ground state is a single subband with the quenched magnetic moment, $\mathcal{M} = 0$. We consider two different cases.

First, the nonmagnetic state can appear as a result of a symmetry lowering (for example, from cubic to hexagonal or trigonal). (Both cubic and hexagonal structures are typical for lanthanides and actinides.) Then the degeneracy of the ground state changes according to the scheme

$$T_1(T_2) \to E + A_1(A_2). \qquad (27)$$

The reason is that the double degeneracy is the highest supported by the threefold symmetry C_3 or the sixfold C_6. The doubly degenerate level of the E symmetry has the magnetic moments $\pm\mathcal{M}$, while the level of the A symmetry is nonmagnetic. Which level becomes the ground state depends crucially on the details of the CEF and the intersite interaction driving the symmetry lowering. Here, we do not discuss the driving forces behind the phase transition. There are many options: the cooperative Jahn–Teller effect [21] (translation–orientation coupling [2, 22]), quadrupole–quadrupole interactions [23], etc. The actual source of symmetry lowering is immaterial for our analysis in what follows. Again, if the E level happens to be the lowest, the electron system becomes ferromagnetic at some temperature, as first was discussed by Zener. Equally important is another possibility, when the ground level has the A symmetry. In this case, the ground state is nonmagnetic even if it does have the magnetic moments $-\mathcal{M}$, 0, and $\mathcal{M}$ above the phase transition. Then the phase transition is accompanied by a loss of these magnetic moments. In magnetic susceptibility measurements, it is to manifest itself as the Curie law above the transition ($T > T_c \sim \Delta E = E_A - E_E$) and a constant and low magnetic susceptibility below the phase transition ($T < T_c$). Such unusual behavior is found in some actinide and lanthanide compounds (Ce [24], $\mathrm{YbInCu_4}$ [25], $\mathrm{NpO_2}$ [26]), although theoretical interpretations remain controversial.

The second case occurs if there is no structural phase transition, but the lowest level is nonmagnetic (the A symmetry) due to the CEF. Then the magnetic susceptibility follows the Curie law at sufficiently large temperatures ($T > \Delta E = E_E - E_A$), but deviates considerably at low temperatures ($T < \Delta E$). The magnetic susceptibility decreases and saturates as $T \to 0$, with a pronounced maximum at $T \sim \Delta E$. Such unusual behavior was also found in some correlated metals including actinide and lanthanide compounds, and in alkali-doped fullerides [27].

The idea of the disappearance of magnetic moments is also provided by the Kondo and Anderson models and is often referred to as the Kondo effect [1]. Our consideration here is different. It is based on the intrasite interactions treated at the *ab initio* level, while the Anderson hybridization [28] (which is linear in the creation/annihilation operators for valence and localized electrons) is zero from symmetry considerations. In our model, the interaction between conduction and localized electrons takes the form of the Coulomb intrasite repulsion, which, being a density–density coupling, is bilinear in these operators.

The present model is a classical configuration interaction approach to solids, which captures correlation effects such as the double exchange and Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction [29]. For a single atomic-like site, it is common to use the configuration interaction, but for solids even the Hartree–Fock treatment free of exchange approximations is rare. We note that an alternative approach to the HIA problem has been developed in Refs. [8–10]. It combines the density functional theory (LDA) treatment of conduction electrons with an atomistic description of equivalent localized f-electrons. Our model is similar to HIA in assuming an effective one-electron interaction between delocalized electrons. We note, however, that the multipole expansion of the Coulomb repulsion and a multideterminant basis set are implicitly used for the f-block in the HIA. On the other hand, in our model, we do not consider processes that change the occupation number of f-electrons (such as $f \to f^2$) included in the HIA.

There have been attempts to incorporate Hund's rules into the band structure calculation scheme through orbital polarization [30] or self-interaction correction (SIC) in the local spin density approximation (LSD) framework [31]. The orbital polarization mimics Hund's rules via a phenomenologically introduced one-electron eigenvalue shift ($-E^3 L m_l$) for the state m_l. (Here, E^3 is the Racah parameter [30].) Also, as claimed in Ref. [31], the SIC–LSD approximation can reproduce Hund's rules for f-states of γ-Ce. But it is not clear how good this description is for other elements or in the cases where Hund's rules are violated. We recall that Hund's rules are just empirical observations, while the real driving force behind them is the Coulomb interaction. The latter is fully described by the multipole expansion in a many-electron basis set, which accounts for the atomic term structure in all cases.

4. CONCLUSIONS

The presented picture of coupling between localized and delocalized electrons at the same site is close to the original idea of Zener, who considered that just Hund's rules are responsible for the coupling [6]. Furthermore, the treatment derived from first principles remains valid even when some of Hund's rules fail (see, e.g., atomic Ce in [2]). The effective interaction between localized f-electrons at different sites can also be considered a variant of the RKKY mechanism [29]. The coupling appears as a natural correlation effect that requires a multideterminant basis set to be captured. This many-electron determinant basis set is easy to supply for a singular (atomic-like) site as shown in Ref. [3], but it is then a localized basis set. Here, we have explicitly demonstrated that such interactions are present for the corresponding delocalized basis set. The conclusion is not surprising, taking into account that in the tight-binding approximation, a delocalized basis set is constructed from local functions.

It is also worth noting that the on-site interactions between conduction (s) and localized (f) electrons are obtained from first principles. Part of this interaction results in an octupole repulsion (f–s transitions), which disappears if one averages this interaction in order to introduce an effective mean-field potential. Indeed, such a potential $U(\mathbf{r})$ should have the full crystal (cubic) symmetry and even parity under the inversion symmetry. This implies that $\langle s|U|f\rangle = 0$ in contradistinction to Eqs. (16) and (23).

We have added the CEF to the model and have shown that the role of the CEF is crucial in determining the magnetic response of the electron system. The resulting ground state can be either ferromagnetic or nonmagnetic. Thus, the ground state and the excitation spectrum of f-states are dominated by the combined effect of the CEF and their interaction with delocalized electron states.

REFERENCES

1. P. Fulde, *Electron Correlations in Molecules and Solids*, Springer Heidelberg, (1995).

2. A. V. Nikolaev and K. H. Michel, Phys. Rev. B **66**, 054103 (2002).

3. A. V. Nikolaev, Phys. Rev. B **71**, 165102 (2005).

4. A. V. Nikolaev and K. H. Michel, J. Chem. Phys. **117**, 4761 (2002).

5. E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Univ. Press, Cambridge (1967).

6. C. Zener, Phys. Rev. **81**, 440 (1951); *ibid* **82**, 403 (1951).

7. Yu. Ralchenko, A. E. Kramida, J. Reader, and NIST ASD Team (2008). *NIST Atomic Spectra Database (version 3.1.5)*, Online, http://physics.nist.gov/asd3 [2008, October 6]. National Institute of Standards and Technology, Gaithersburg, MD.

8. S. Lebègue, A. Svane, M. I. Katsnelson, A. I. Lichtenstein, and O. Eriksson, Phys. Rev. B **74**, 045114 (2006).

9. S. Lebègue, G. Santi, A. Svane, O. Bengone, M. I. Katsnelson, A. I. Lichtenstein, and O. Eriksson, Phys. Rev. B **72**, 245102 (2005).

10. A. I. Lichtenstein and M. I. Katsnelson, Phys. Rev. B **57**, 6884 (1998).

11. D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method*, Kluwer, Boston (1994).

12. L. L. Hirst, Adv. Phys. **27**, 231 (1978).

13. C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids*, Clarendon, Oxford (1972).

14. A. V. Nikolaev and P. N. Dyachkov, Int. J. Quant. Chem. **89**, 57 (2002).

15. J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

16. M. T. Hutchings, in *Solid State Physics: Advances in Research and Applications*, ed. by F. Seitz and D. Turnbull, Acad. Press, New York (1964), Vol. 16, p. 227.

17. J. Mulak and Z. Gajek, *The Effective Crystal Field Potential*, Elsevier, Amsterdam (2000).

18. D. J. Newman, Adv. Phys. **20**, 197 (1971); D. J. Newman, J. Phys. F: Met. Phys. **13**, 1511 (1983).

19. K. W. H. Stevens, Proc. Phys. Soc. A **65**, 209 (1952).

20. P. Fulde and M. Loewenhaupt, Adv. Phys. **34**, 589 (1986).

21. G. A. Gehring and K. A. Gehring, Rep. Progr. Phys. **38**, 1 (1975).

22. R. M. Lynden-Bell and K. H. Michel, Rev. Mod. Phys. **66**, 721 (1994).

23. P. Wachter, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. by K. A. Gschneidner, Jr., L. Eyring, G. H. Lander, and G. R. Choppin, Elsevier Sci., Amsterdam (1994), Vol. 19, p. 177.

24. D. C. Koskenmaki and K. A. Gschneidner, Jr., *Handbook on the Physics and Chemistry of Rare Earths*, ed. by K. A. Gschneidner, Jr., and L. Eyring, Amsterdam, North-Holland (1978), p. 337.

25. J. L. Sarrao, Physica B **259–261**, 128 (1999).

26. J. A. Paixão, C. Detlefs, M. J. Longfield, R. Caciuffo, P. Santini, N. Bernhoeft, J. Rabizant, and G. H. Lander, Phys. Rev. Lett. **89**, 187202 (2002).

27. L. Forró and L. Mihály, Rep. Progr. Phys. **64**, 649 (2001).

28. P. W. Anderson, Phys. Rev. **124**, 41 (1961).

29. M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); T. Kasuya, Progr. Theor. Phys. **16**, 45 (1956); K. Yosida, Phys. Rev. **106**, 893 (1957); J. H. Van Vleck, Rev. Mod. Phys. **34**, 681 (1962).

30. O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 7311 (1990).

31. S. V. Beiden, W. M. Temmerman, Z. Szotek, and G. A. Gehring, Phys. Rev. Lett. **79**, 3970 (1997).