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Exchange energy dominated by large orbital spin-currents in δ-Pu

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The electronic structure of the anomalous δ phase of Pu is analyzed by a general and exact reformulation of the exchange energy of the f shell. It is found that the dominating contribution to the exchange energy is a polarization of orbital spin-currents that preserves the time-reversal symmetry; hence a nonmagnetic solution in accordance with experiments. The analysis brings a unifying picture of the role of exchange in the 5f shell with its relatively strong spin-orbit coupling. The results are in good accordance with recent measurements of the branching ratio for the d to f transition in the actinides.

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The electronic structure of the actinides stands out among the elements of the periodic table as most intricate. Their 5f states form narrow bands with a comparatively large spin-orbit coupling. Rather subtle changes in the electronic structure lead to different ground states, and in various actinide compounds the 5f show itinerant, localized as well as heavy fermion behavior and are responsible for both magnetic order and superconductivity. In recent years this complexity has been exemplified by various attempts to theoretically understand the phase diagram of Pu and especially the formation of its high temperature, large volume, highly anomalous δ phase.[1–7] As a first progress, it was observed that the stability of this phase can be understood if allowed for spin polarization (SP).[1,2] However, the existence of any magnetic moment are in contrast to a large amount of experimental observations.[8] Most recently it was pointed out that orbital polarization (OP) plays a major role in stabilizing this magnetic solution.[7] In calculations utilizing the so-called LDA+U approach, i.e., a local-density approximation (LDA) to density-functional theory with an added extra local Hartree-Fock (HF) term,[3,4] it was observed that a nonmagnetic large volume phase could be stabilized in a somewhat counterintuitive way—by increasing the exchange energy, the moments vanish. Meanwhile there have also been various dynamical mean-field theoretical (DMFT) calculations,[5,6,9] which also lead to a high volume nonmagnetic state, at least when allowing for the off-diagonal spin coupling. These LDA+DMFT calculations are complex and hard to analyze. However there seems to be a consensus to attribute the high volume phase to partial localization of the 5f states[6] and a tendency to ascribe the vanishing magnetic moments to Kondo screening.[10,11]

The purpose of this Rapid Communication is to explore the relationship of the SP+OP approach with that of the general LDA+U approach with its more flexible exchange interaction and to explain how the nonmagnetic state is stabilized by the latter. This is accomplished be re-expressing the general exchange interaction of the LDA+U approach as a sum of interacting multipoles. With the aid of this expression it is argued that in the case of δ-Pu, the SP is overtaken by a variant of OP that does not break the time-reversal symmetry as is confirmed by electronic structure calculations within the LDA+U approach. In this context, there is a discussion of the nature of this exact expression for the OP and how it compares with earlier formulations.[12,13] Finally, the corresponding OP multipole is discussed in connection with existing d to f branching ratio experiments,[14,15] where it appears through a sum rule.

In the most general version of LDA+U (Ref. 16) the HF correction enters with a Hartree (H) and exchange (X) term as

$$E_H + E_X = \frac{1}{2}\sum_{abcd} (\rho_{ac}\rho_{bd} - \rho_{ad}\rho_{bc})\langle ab|g|cd\rangle, \qquad (1)$$

where ρ_{ab} is one element of the density matrix for the ℓth shell, with dimension $(4\ell+2)\times(4\ell+2)$, (or $2[\ell]\times 2[\ell]$ if we use the conventional notation, $[\ell]=2\ell+1$) which acts as an occupation matrix. Here a is a combined label for the magnetic quantum number m_a and the spin variable s_a. The interaction has the form

$$\langle ab|g|cd\rangle = \delta(s_a,s_c)\delta(s_b,s_d)[\ell]^2\sum_k E^{(k)} \times \sum_{k'q} (-)^q a_{k'k}c^{(k')}(m_a,m_c)c^{(k')}(m_b,m_d), \qquad (2)$$

where $c^{(k')}$ are the Gaunt coefficients and $E^{(k)}$ (where $k=0\ldots\ell$) are the $\ell+1$ Racah parameters[17,18] of the screened Coulomb interaction, which are given as a linear combination of the more common Slater parameters $F^{(k)}$ (where $k=0,2\ldots 2\ell$) and $E^{(k)}=\Sigma_{k'}b_{kk'}F^{(k')}$, where $\Sigma_k a_{k'k}b_{kk''}=\delta_{k'k''}$. In the exchange term the spin Kronecker-deltas will allow for a nondiagonal spin interaction between the two density matrices ρ, giving rise to a spin mixing.

This method has been implemented[19] in the full potential augmented plane wave (FP-APW) package EXCITING,[20] and the results above have essentially been verified. A straight forward density-functional approach leads to a large volume antiferromagnetic solution with large spin and orbital moments. When switching on the LDA+U HF interaction, including spin mixing terms, the moments vanish, leading to a nonmagnetic solution as displayed in Fig. 1, for a double counting of the type around mean field (AMF).[3] We also find that this nonmagnetic solution is obtained for the fully localized limit (FLL) type of double counting[4] but then for a slightly larger exchange parameter $J\gtrsim 0.8$ eV.

To analyze this nonmagnetic solution is cumbersome due to the $4[\ell]^2$ independent elements of the density matrix ρ.

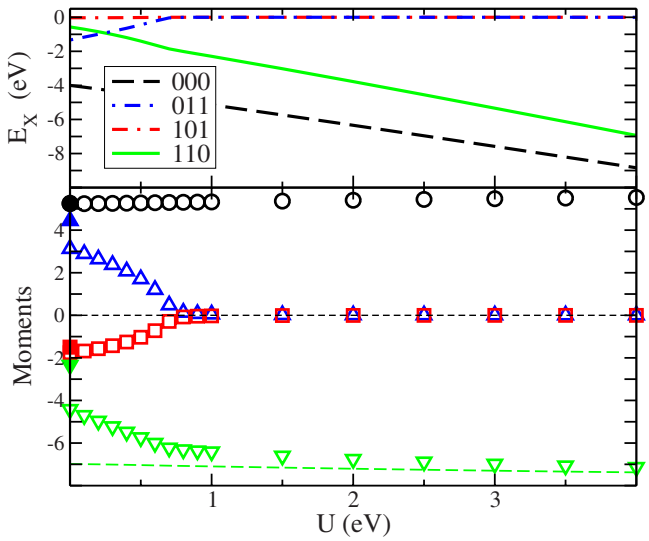

FIG. 1. (Color online) Moments and exchange energies from LDA+U-AMF calculations of fcc Pu (a=4.64 Å) within the FP-APW method. Basis set cutoffs corresponding to $R_{\mathrm{MT}}G_{\max}=9$, with muffin-tin radius $R_{\mathrm{MT}}=1.56$ Å, and a Brillouin-zone sampling of 864 points for a two atom cell were used. The Racah parameters are summarized in two parameters U and J in the same way as in Ref. 3. The spin (up-pointing triangles) and orbital (squares) moments are shown for a varying U but a constant $J=0.68$ eV, which corresponds to a varying $E^{(0)}=U-J$ and constant $E^{(3)}=53$ meV, in the bottom part. Filled symbols indicate the LDA results. Also displayed is the $5f$ occupation number (circles) as well as the $\mathbf{w}^{110}$ (down-pointing triangles) where the dashed line indicates the corresponding saturation limit. At the top, the most significant terms of the exchange energy in Eq. (8) are displayed as lines, with same notational scheme as for the moments, with the tensor rank identifying each, given in the legend.

We take the following approach. As a generalization of the fact that one gets the spin and orbital moment from the density matrix, as, e.g., $\langle S\rangle=\mathrm{Tr}\, S\rho$, we introduce the expectation value of double tensor operators $\mathbf{w}^{kp}=\mathrm{Tr}\, \mathbf{v}^k\mathbf{t}^p\rho$.[21–23] In our basis the tensor operators take the form,

$$v_x^k \equiv \langle m_b|v_x^k|m_a\rangle = (-)^{\ell-m_b}\begin{pmatrix} \ell & k & \ell \\ -m_b & x & m_a \end{pmatrix} n_{\ell k}^{-1},$$

$$t_y^p \equiv \langle s_b|t_y^p|s_a\rangle = (-)^{s-s_b}\begin{pmatrix} s & p & s \\ -s_b & y & s_a \end{pmatrix} n_{sp}^{-1}. \tag{3}$$

Here we have used the so-called Wigner $3j$ symbols $(\ldots)$ (Ref. 18) and the same normalization as in Ref. 21.

An attractive property of the multipole double tensors $\mathbf{w}^{kp}$ is their simple interpretations. As has been pointed out[21] the $\mathbf{w}^{k0}$, with k even, are related through Wigner-Eckhart theorem to the kth multipole moment of the ℓ charge density, while the $\mathbf{w}^{k1}$, with even k, are related to the multipoles of the magnetization density. Finally the odd k correspond to currents, i.e., the tensors are related to the multipole moments of the current ($p=0$) and the spin-current ($p=1$).

It is fruitful to view the introduction of $\mathbf{w}^{kp}$ as a transformation of the density matrix ρ to these double tensors. This transformation is one to one,[24] which is consistent with the fact that the number of parameters is kept. The sum of the rank of the tensor operators are $\Sigma_k[k]\times\Sigma_p[p]=4[\ell]^2$, which is equal to the number of independent (real and imaginary) components of ρ since it is Hermitian. So we keep the same information, as in the density matrix, but now distributed on $[k][p]$ independent double tensors, which turns out to be very convenient. The inverse transformation, i.e., from double tensors to the density matrix, is readily obtained by utilizing orthogonality properties of the $3j$ symbols.[18] The double tensors are not irreducible under simultaneous rotations of spin and orbitals, so in the case of the actinides with their fairly large spin-orbit coupling it is convenient to introduce the irreducible spherical tensors $\mathbf{w}^{kpr}$ through coupling of the orbital k and spin p degrees.[21,23] There still exists, of course, a one-to-one correspondence between this set of irreducible tensors and the density matrix.

As can be straightforwardly shown, with the introduction of the irreducible tensors $\mathbf{w}^{kpr}$ and its transformation from the density matrix, both the direct and the exchange terms of Eq. (1) can be put in simple forms,

$$E_{\mathrm{H}} = \sum_k E^{(k)} \sum_{k_1} a_{k_1 k} I(\ell,k_1,k_1)\mathbf{w}^{k_1 0 k_1}\cdot\mathbf{w}^{k_1 0 k_1}, \tag{4}$$

$$E_{\mathrm{X}} = -\sum_k E^{(k)} \sum_{k_1 pr} J(\ell,k,k_1)A_{k_1 pr}\mathbf{w}^{k_1 pr}\cdot\mathbf{w}^{k_1 pr}, \tag{5}$$

with $A_{k_1 pr}=(-)^{k_1+p+r}[r]\underline{n}_{k_1 pr}^2$, where $\underline{n}_{k_1 pr}$ is the normalization of the irreducible tensor as in Ref. 21,

$$I(\ell,k,k_1) = \frac{(-)^{k_1}[\ell]^2 n_{\ell k_1}^2}{2}\begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \tag{6}$$

and

$$J(\ell,k,k_1) = \frac{[k_1]}{2}\sum_{k_2} a_{k_2 k} I(\ell,k_2,k_1)\begin{Bmatrix} \ell & \ell & k_1 \\ \ell & \ell & k_2 \end{Bmatrix}, \tag{7}$$

where the $\{\ldots\}$ symbol is the $6j$ symbol.[18] This is a remarkably simple reformulation of the exchange energy. It is a straightforward generalization of the Stoner-like exchange formulation of SP, with scalar products of quantities with themselves. The final expression is actually almost identical to an expression derived by Racah[23] for a ℓ^2 configuration but is more general in that it is valid for any noninteger occupation of the ℓ shell. The interaction strengths $J(3,k,k_1)$ of Eq. (7) are tabulated in Table I. Here the advantage of using Racah parameters instead of Slater parameters becomes clear as many of the tabulated values vanish.

The independent terms in this exchange energy expansion, which can be written in the form,

$$E_{\mathrm{X}} = \sum_{kpr} K_{kpr}\mathbf{w}^{kpr}\cdot\mathbf{w}^{kpr}, \tag{8}$$

have simple physical meanings; for instance the 011 term involving $\mathbf{w}^{011}$ is the well-known Stoner-like SP. Two other terms of importance for the present study are the 101 and 011 terms, i.e., the orbital and the scalar part of the spin-orbital moment, respectively. These two terms are included in the

TABLE I. The interaction strengths $J(3,k,k_1)$ from the multipole expansion of the exchange energy in terms of Racah parameters $E^{(k)}$.

	k_1						
k	0	1	2	3	4	5	6
0	$\frac{1}{28}$	$\frac{9}{112}$	$\frac{25}{336}$	$\frac{1}{24}$	$\frac{9}{616}$	$\frac{1}{336}$	$\frac{1}{3696}$
1	$\frac{9}{28}$	0	$\frac{25}{168}$	0	$\frac{9}{308}$	0	$\frac{1}{1848}$
2	0	0	$\frac{3575}{168}$	0	$-\frac{585}{154}$	0	$\frac{5}{264}$
3	0	$\frac{297}{112}$	$-\frac{275}{336}$	0	$-\frac{9}{154}$	$-\frac{3}{112}$	$\frac{1}{528}$

OP expression suggested by Brooks[12,13] for f systems (OP-B), which in our terminology, where the orbital moment is given by $\langle \mathbf{L} \rangle = -\ell \mathbf{w}^{101}$, give expansion coefficients of the form,

$$K_{101}^{\text{OP-B}} = 3K_{110}^{\text{OP-B}} = -\frac{9E^{(3)}}{4}. \tag{9}$$

Included in our multipole expansion of the exchange energy, we now have an exact formulation of this OP of the exchange energy, valid for any noninteger system. From Eq. (5) and Table I we get the coefficients of these two OP terms as

$$K_{101} = 3K_{110} = -\frac{9E^{(0)} + 297E^{(3)}}{112}, \tag{10}$$

since $\underline{n}_{110}^2 = \underline{n}_{101}^2 = \frac{1}{3}$. We note that there are two corrections to the simplified OP-B formulation. First, there is a contribution from $E^{(0)} = U - J$ too. Second, the exact contribution proportional to $E^{(3)}$ is $\frac{297}{33} \approx 2.65$ instead of 2.25. These two corrections can in principle be compensated by using a somewhat larger effective $E^{(3)}$ parameter in OP-B. However, more severely, in the original formulation OP-B only the z components are included when obtaining $\mathbf{w}^{110}$ since the spin mixing are neglected, while in general we can get an independent contribution from each of the three spin components. In total all these three corrections lead to an effectively stronger OP than what was originally suggested by Brooks. In addition we observe that the OP is essentially two different terms; one that favors broken time-reversal symmetry states with $\mathbf{w}^{101} \neq 0$ (OP-odd), while the second term involving $\mathbf{w}^{110}$ does not break time-reversal symmetry (OP-even).

In the upper part of Fig. 1 the different energy contributions to the exchange energy of Eq. (8) are given for the LDA+U calculation of δ-Pu. As can be seen, although there are in total 26 independent terms in Eq. (8), only a very few tensors have any significant contribution to the total exchange energy. They are the terms involving $\mathbf{w}^{000}$ (total $5f$ occupation), $\mathbf{w}^{011}$ (SP), and $\mathbf{w}^{110}$ (OP-even). The OP-odd 101 term is barely detectable for low U values. It is worth noting that the total exchange energy calculated by Eqs. (1) and (5) are indistinguishable. It is evident from the graph that the OP-even term takes over the SP exchange energy when increasing the effective Coulomb interaction U. This can be understood as the polarization of $\mathbf{w}^{011}$ and $\mathbf{w}^{110}$ are mutually exclusive, i.e., both terms cannot be saturated simultaneously. When the contribution from the 110 term increases and approaches saturation, the contribution from the 011 term has to decrease and vanish.

The calculated observables are displayed in the bottom part of Fig. 1. It is worth stressing that although there is a small increase in the $5f$ occupancy from 5.2–5.5, it has little influence, in contrast to what has earlier been assumed.[3,4] It is clear from the energy contributions that it is the steep increase in the magnitude of $\mathbf{w}^{110}$ that stabilizes the nonmagnetic state. The order parameter $\mathbf{w}^{110}$ obtained is quite intriguing. It corresponds to that the three components of the spin-currents orbit, with equivalent magnitudes, around their different spin quantization axes. This lead to a time-reversal scalar order parameter, and since it arises from spin-currents it is a quantity that is difficult to observe directly in experiments.

Recently there have, however, been reports on measurements on the branching ratio for the d to $5f$ transition for several actinide systems,[14,15] from which values of $\mathbf{w}^{110}$ can be obtained through a sum rule.[25] These measurements report very large values, not least for α-Pu. In the subsequent discussion they attribute this to the strong spin-orbit coupling, which brings the $5f$ states close to a jj coupling scheme. In the light of our finding we would like to alter that analysis slightly. While the spin-orbit coupling is important in the actinides, it is not strong enough to bring the $5f$ states into a jj limit by itself. In fact without the HF term of Eq. (1), i.e., in the LDA limit, we calculate a spin-orbit-only value of −2.4 while in the presence of the HF term, and especially the OP-even term, we get enhanced values varying between −4.4 and −7.2, as seen in Fig. 1. The values for large U parameter are close to saturation, as indicated in Fig. 1, which would correspond to $-\frac{4}{3}\mathbf{w}^{000}$. These values should be compared with the measured value of −5.1 for Pu in its α phase, assuming a f^5 configuration.[14] We notice that the exchange term is essential to bring the calculated $\mathbf{w}^{110}$ to the same magnitude as the experimental value.

In summary, the present analysis in terms of different exchange terms, Eq. (8), leads to the conclusion that there is a strong competition between *different exchange channels* in the actinides, where the spin-orbit coupling plays a role since it favors the OP-even channel over the SP channel. These are in accordance with calculations on other actinide systems, where we have found that $\mathbf{w}^{110}$ have large contributions even for magnetic systems.[19]

We can also conclude that while the calculations that stabilize the large volume phase incorporate the dominant con-

tributions to exchange, the main difference between the calculations leading to a magnetic state[2,7] and the ones leading to a nonmagnetic state[3,4] is their treatment of the OP term. The former calculations utilize the simplified form of Eq. (9) without any spin mixing, while the latter allow for the correct OP-even term as in Eq. (10). With the proper form all exchange polarization goes into the OP-even term, draining all other contributions, and the resulting symmetry broken state has zero magnetic moments but nonzero spin-currents. This work illustrates a large advantage with the multipole expansion of the exchange energy of Eq. (5)—it brings forward the physically important exchange channels in a simple way.

The LDA+U approach corresponds to the static limit of a more general LDA+DMFT approach. From such studies it is clear that in order to get a good description not only of the ground-state properties, as volume and moments, but also of the spectral density, it is crucial to include dynamics in terms of an energy dependent self-energy. However, the exchange energy, which is already included in LDA+U, is a dominant part of the self-energy. In this work, which is focused on ground-state properties, we observe that it is this exchange energy that gives rise to the enhanced values of the orbital spin-currents, $\mathbf{w}^{110}$, observed in recent experiments.[14,15] The same exchange contribution is present also in the more sophisticated DMFT calculations, and our observation that the SP exchange contribution is not always dominant for the actinides with their large spin-orbit couplings, is general and ought to help to understand the anomalous electronic structure of actinide compounds in general. It would be of great interest to perform multipole expansions on the terms relevant for studies of dynamics within the f shell, e.g., the energy dependent self-energy calculated by LDA+DMFT, in order to perform a similar analysis as analyzed here.

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