Multipole decomposition of LDA+U energy and its application to actinide compounds

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A general reformulation of the exchange energy of 5f shell is applied in the analysis of the magnetic structure of various actinides compounds in the framework of LDA+U method. The calculations are performed in a convenient scheme with essentially only one free parameter, the screening length. The results are analyzed in terms of different polarization channels due to different multipoles. Generally it is found that the spin-orbital polarization is dominating. This can be viewed as a strong enhancement of the spin-orbit coupling in these systems. This leads to a drastic decrease in spin polarization in accordance with experiments. The calculations are able to correctly differentiate magnetic and nonmagnetic Pu system. Finally, in all magnetic systems an unusual multipolar order is observed, whose polarization energy is often larger in magnitude than the one of spin polarization.

I. INTRODUCTION

The magnetism of actinide systems shows a very rich variety of magnetic properties.[1] There are variations from itinerant magnetic systems to systems showing characteristics of localized magnetism. In the border between these extremes one have the so-called heavy fermions, which show many peculiar and anomalous properties, one of which is the co-existence of superconductivity and magnetism.[2] One aspect that makes the magnetism of the actinides unique is the presence of strong spin-orbit coupling (SOC) together with strong exchange interactions for the 5f electrons, which are the ones responsible for the magnetism.

From a theoretical point of view, a standard density-functional approach, either in the local-density approximation (LDA) or generalized gradient approximation (GGA) , describes quite well the equilibrium properties of at least metallic systems. However, these functionals are known to underestimate the orbital moments which are induced by the relatively strong SOC.[3–5] This can be remedied by allowing for the so-called orbital polarization,[5] responsible for Hund's second rule in atomic physics, either through adding an appropriate orbital depending term to the Hamiltonian or by adopting the so-called LDA+U approach.[6–8] In the latter method a screened Hartree-Fock (HF) interaction is included among the 5f states only.

There is a drastic difference between the itinerant magnetism of a 3d shell and that of the 5f shell. In the former the orbital degrees of freedom are quenched due to the process of hopping between different atoms while in the latter case the stronger SOC unquenches them again. Magnetic ordering is relatively abundant among actinide systems due to the strong exchange interactions but generally the spin moments are strongly reduced compared to a fully spin-polarized value, which sometimes is ascribed to crystal-field effects and other times to hybridization.

This paper will focus on the role of the local screened exchange interactions and it will aim to convincingly argue that these interactions, together with an appreciable SOC interaction, are responsible for the reduced spin polarizations as well as for a large orbital moment. This is analyzed in terms of tensor moment polarizations of the 5f shell. First we describe the method we employ, the LDA+U method in its most general form with a minimum of free parameters--one. This is accomplished by using screened Slater parameters together with an interpolating optimal double-counting (DC) term.[9] This last degree of freedom can be chosen to be, for instance, the lowest Slater integral U, which is used as a varying parameter. This general LDA+U scheme has been implemented within the state-of-the-art full-potential augmented plane-wave plus local orbitals (FP-APW+lo) method[10,11] in the ELK code.[12] This linearized augmented plane-wave method is one of the most accurate scheme to treat the complicated behavior of 5f electrons in actinides.[13,14] Second, we present an analysis method for the resulting ground state. This analysis is based on an exact multipole decomposition of the density matrix as well as of the HF exchange energy. We have tested the generality of the method by considering actinides systems with different degree of localization of their 5f electrons; the itinerant features in U compounds, the more localized behavior in Pu compounds and finally the intermediate one in Np-based materials. The calculations show reasonable comparison with experiments as well to other beyond LDA calculations. By applying our tensor-moment decomposition, we observe several clear trends regarding the favored polarizations in these actinide systems. For instance it is clear that the Hund's rules break down in the sense that other channels are more significant than the spin polarization.

II. METHOD

A. A General Form of LDA+U Method

In the most general version of LDA+U (Refs. 6, 7, and 15) a HF correction to the energy enters with the form

$$E_{\text{HF}} = \frac{1}{2} \sum_{abcd} \rho_{ac} [\langle ab|g|cd \rangle - \langle ab|g|dc \rangle] \rho_{bd}, \quad (1)$$

where ρ_{ab} is one element of the density matrix with dimension $D=2(2\ell+1)$, which acts as an occupation matrix and a, b, c, and d are single-electron states. The interaction term is of the form

$$\langle ab|g|cd \rangle = \int \psi_a^\dagger(1)\psi_b^\dagger(2)g(r_{12})\psi_c(1)\psi_d(2)d(1)d(2) \quad (2)$$

with one-electron states a and wave function $\psi_a(1) = R_\ell(r_1)Y_{\ell m_a}(\Omega_1)\chi_{s_a}(1)$, where the relevant quantum numbers, m and s, are the magnetic quantum number and spin component, respectively. The interaction can be expanded in a series,

$$g(r_{12}) = \sum_{k=0}^{\infty} g_k(r_1, r_2)P_k(\cos\theta_{12}), \quad (3)$$

where the Legendre function P_k in turn can be expanded by the use of the addition theorem for spherical harmonics,

$$P_k(\cos\theta_{12}) = \frac{4\pi}{2k+1}\sum_{q=-k}^{k} Y_{kq}^*(\Omega_1)Y_{kq}(\Omega_2). \quad (4)$$

B. Calculation of Slater integrals through a Yukawa potential

The radial part of the interaction is then contained in the Slater integrals

$$F^{(k)} = \int dr_1 r_1^2 R_\ell^2(r_1) g_k(r_1, r_2) R_\ell^2(r_2) r_2^2 dr_2. \quad (5)$$

For a f shell there are four independent parameters, $F^{(0)} = U$, $F^{(2)}$, $F^{(4)}$, and $F^{(6)}$. It is very unpractical to stay with these four parameters. A common practice within LDA+U or HF calculations[6,15,16] is to have the screened Slater parameters determined by the choice of two linear combinations of parameters, U and J, and by fixing two ratios, $A_1 = F^{(4)}/F^{(2)}$ and $A_2 = F^{(6)}/F^{(2)}$. In the present work we will instead follow the ideas of Norman[17] and calculate the Slater parameters directly from a screened Coulomb interaction in the form of a Yukawa potential $g(r_1, r_2) = e^{-\lambda r_{12}}/r_{12}$. Then

$$g_k(r_1, r_2, \lambda) = -(2k+1)\lambda j_k(i\lambda r_<)h_k^{(1)}(i\lambda r_>), \quad (6)$$

where j_k is a spherical Bessel function, $h_k^{(1)}$ is a spherical Hankel function of the first kind and $r_<$ and $r_>$ are, respectively, the smaller and the larger radius entering in the double integral in Eq. (5). This type of approach has two advantages; it determines the ratio between the different Slater parameters in a more realistic way than by choosing U and J individually, and there is only one independent parameter, the screening length λ.

Since in APW+lo basis set $R_\ell(r, \varepsilon)$ is energy dependent, we decided to use the energy ε at the center of the band of the localized shell ℓ. We set the atomic muffin-tin (MT) radius to a value large enough such that the integrals in Eq. (5) are well converged. In the upper part of Fig. 1 we plot the calculated Slater parameters for US. These values are in perfect agreement with ones calculated for the ion U^{4+} by Norman[17] with the same screened potential. In the lower part of Fig. 1 we compare the Slater integrals ratios A_1 and A_2 obtained for US with the fixed ratios commonly used in most LDA+U studies.[6,18] There is a good agreement only at small values of the screening length. For $\lambda \gtrsim 0.5$ a.u.$^{-1}$ there start
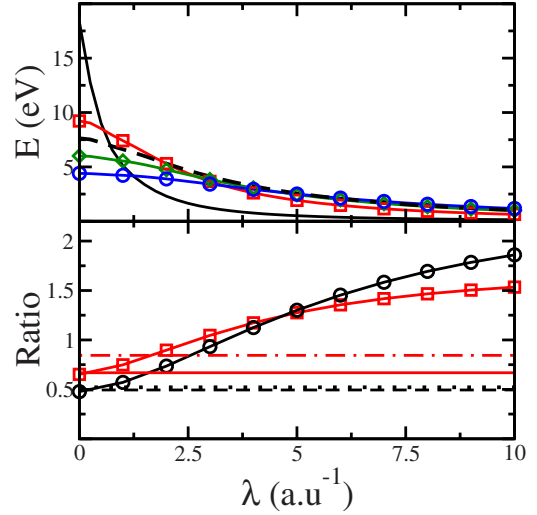

FIG. 1. (Color online) Upper panel: Slater parameters $F^{(0)}$ (full black line), $F^{(2)}$ (red line with squares), $F^{(4)}$ (green line with diamonds), $F^{(6)}$ (blue line with circles), and parameter J 10 times (dashed black line) as function of screening length λ of the Yukawa potential in US. Lower panel: comparison of Slater parameters ratios $A_1 = F^{(4)}/F^{(2)}$ (red lines) and $A_2 = F^{(6)}/F^{(2)}$ (black lines) calculated by a screened Yukawa potential (full line with squares for A_1 and full line with circles for A_2) with the fixed ones in Refs. 6 and 18 (full line for A_1 and dashed line for A_2) and in Refs. 16 and 17 (dashed-dotted line for A_1 and dotted line for A_2). The radial wave function used for the calculation of Slater integrals in Eq. (5) corresponds to the energy at the center of 5f band and the MT radius of U is $R_{MT}^U = 2.79$ a.u.

to be a significative difference that turns out to be relevant in the calculation of US magnetic moments. If the $F^{(k)}$ are calculated individually with Eqs. (5) and (6), the spin moment (M_{sp}) and orbital moment (M_{orb}) show a more dramatic variation as a function of U (or λ) than ones determined by fixing A_1 and A_2 (see Fig. 2). This fact indicates how relevant the individual determination of every Slater integral might be in many systems. Finally, we verified that one can reproduce the LDA moments in the limit of large screening length ($F^{(k)} \to 0$ for $\lambda \to \infty$), i.e., by slowly changing the parameter λ one increases the localization of the 5f electrons from the LSDA limit in a continuos way.

A parameter-free method to screen the Slater parameter has been suggested by Brooks,[19] where the screening parameter λ is identified as the Thomas-Fermi screening, which depends on the local-charge density. A more appropiate but time-consuming scheme to calculate the Slater parameters from the screened Coulomb potential is within the random-phase approximation (RPA), as it has been recently accomplished by Solovyev *et al.*[20]

C. Calculation of LDA+U potential

The contribution to the orbital potential from the LDA+U correction is defined as

$$V_{ij} = \frac{\delta E_{HF}}{\delta\rho_{ji}} = \sum_{ab}[\langle ja|g|ib \rangle - \langle ja|g|bi \rangle]\rho_{ab}. \quad (7)$$

We note that the potential so defined is the complex conjugate of the one sometimes stated in literature. The correct
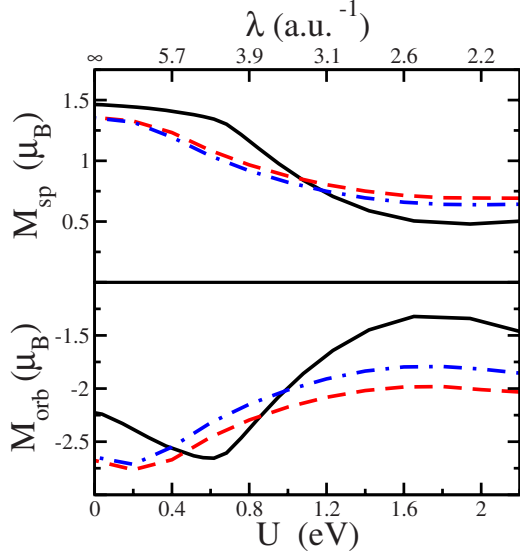
FIG. 2. (Color online) Spin (upper panel) and orbital magnetic moment (lower panel) of US, a=10.36 a.u., calculated with LDA+SOC+U approach and INT DC (see DC corrections in the method section). We compare the results obtained by calculating the $F^{(k)}$ with a screened Yukawa potential (full black line and screening length in the upper axis) with ones obtained by fixing the ratios A_1 and A_2 to ones of Refs. 6 and 18 (dashed red line) and to ones of Refs. 16 and 17 (dashed-dotted blue line). In the fixed ratios calculations we fixed the parameter J=0.46 eV to one in Ref. 16. The MT radii of U and S are set, respectively, to R_{MT}^U=2.79 a.u. and R_{MT}^S=2.13 a.u.. The parameter $R_{MT}^U|\vec{G}+\vec{k}|_{max}$, governing the number of plane waves in the APW+lo method, is chosen to be 9.76. The Brillouin zone (BZ) is sampled with 1728 k points uniformly spaced.

definition becomes crucial to evaluate off-diagonal spin terms in all calculations in which the coordinate system is not rotated to the local one, i.e., in all calculations in which the density matrix is not diagonal.

D. Double-counting corrections

A major obstacle in the LDA+U approach is that the electron-electron interaction has already been included in LDA potential, thus a simple addition of the orbital-dependent HF potential would lead to DC terms. One may want to individuate those terms in the LDA potential that correspond to the interaction already considered in the HF Hamiltonian and subtract them. A direct connection between the two formalisms is not possible and in addition it would not be useful. In fact LDA approximation treats very accurately spatial variations of the exchange-correlation potential but it neglects the orbital dependence of the Coulomb interaction. Thus the best recipe would be to identify the mean-field part of the HF potential and subtract it, leaving only an orbital-dependent correction to the mean-field-type LDA potential. Czyżyk and Sawatzky[21] suggested a prescription that is exact in the case of uniform occupancies [around mean-field (AMF)] and that would be realistic for weakly correlated systems, however not exact because of the presence of the crystalline field. The AMF correction is implemented by

redefining a new density matrix without the charge n and the magnetization $\vec{m}$ contributions,

$$n = \mathrm{Tr}\, \rho, \qquad (8)$$

$$\vec{m} = \mathrm{Tr}\, \vec{\sigma}\rho, \qquad (9)$$

in the following way

$$\widetilde{\rho}_{ab} = \rho_{ab} - (\delta_{ab}n + \vec{\sigma}_{ab} \cdot \vec{m})/D. \qquad (10)$$

The AMF double-counting corrected LDA+U energy and potential terms become in our formalism

$$E_{\mathrm{HF-dc}}^{\mathrm{AMF}} = \frac{1}{2}\sum_{abcd} \widetilde{\rho}_{ac}[\langle ab|g|cd\rangle - \langle ab|g|dc\rangle]\widetilde{\rho}_{bd}, \qquad (11)$$

$$V_{ij}^{\mathrm{AFM}} = V_{ij} - \sum_{ab}[\langle ja|g|ib\rangle - \langle ja|g|bi\rangle](\delta_{ab}n + \vec{\sigma}_{ab} \cdot \vec{m})/D$$

$$= \sum_{ab}[\langle ja|g|ib\rangle - \langle ja|g|bi\rangle]\widetilde{\rho}_{ab}. \qquad (12)$$

For strongly correlated systems it exists another prescription for the DC, the fully localized limit (FLL),[6] that would correspond to subtract the average effect for a localized state, with integer occupation number. The most general expressions for energy and potential are

$$E_{dc}^{\mathrm{FLL}} = \{2Un(n-1) - 2Jn(n/2-1) - J\vec{m}\cdot\vec{m}\}/4, \qquad (13)$$

$$V_{ij}^{\mathrm{FLL}} = V_{ij} - \left[\frac{U(2n-1)}{2} - \frac{J(n-1)}{2}\right]\delta_{ij} + \frac{J\vec{m}\cdot\vec{\sigma}_{ij}}{2}. \qquad (14)$$

Most of LDA+U calculations use one of these approaches while the real occupation numbers lie somewhere between the two limits. Petukhov *et al.*[9] proposed a linear interpolation (INT DC) between these two limits;

$$E_{\mathrm{HF-dc}}^{\mathrm{INT}} = \alpha E_{U-dc}^{\mathrm{FLL}} + (1-\alpha)E_{U-dc}^{\mathrm{AMF}}, \qquad (15)$$

$$V_{ij}^{\mathrm{INT}} = \alpha V_{ij}^{\mathrm{FLL}} + (1-\alpha)V_{ij}^{\mathrm{AMF}}, \qquad (16)$$

in which the parameter α is a material-dependent constant determined in a self-consistent (SC) way following a constrained DFT philosophy. In our formalism the expression of α in Ref. 9 is generalized to take into account the off-diagonal spin terms of the density matrix,

$$\alpha = \frac{D\,\mathrm{Tr}\,\widetilde{\rho}^2}{Dn - n^2 - m^2}, \qquad (17)$$

where n and m are defined, respectively, in Eq. (8) and Eq. (9).

In the present study we prefer to use the INT DC approach for two reasons. First, it reduces one further free parameter. The results do depend on the choice of DC but if we stay consequently with the INT DC this degree of freedom is gone since we can in principle treat both more itinerant and more localized system. Second, it turns out that the use of the INT DC is very important to reproduce the correct magnetic structure of monopnictides Pu compounds. In Fig. 3 we com-
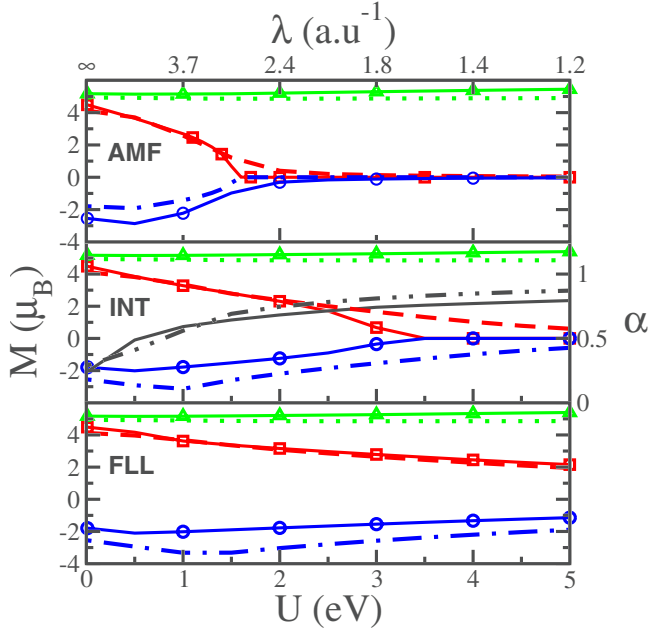
FIG. 3. (Color online) Spin M_{sp} (red lines) and orbital M_{orb} (blue lines) magnetic moments of paramagnetic PuS (full line with squares for M_{sp}, full line with circles for M_{orb}), $a=10.46$ a.u., and ferromagnetic PuP (dashed line for M_{sp}, dashed-dotted line for M_{orb}), $a=10.49$ a.u., as function of U for different types of DC. The Slater parameters are calculated SC by using a Yukawa potential with screening length λ reported in the upper axis. For AMF DC the moments vanish in both compounds at $U \approx 2.0$ eV, for FLL DC both compounds stay magnetic for all values of U. Only for the INT DC there is a range of U ($U \gtrsim 3.5$ eV) for which we obtain the experimental magnetic structure of both compounds (Ref. 1); PuS becomes nonmagnetic while PuP stays magnetic. The green lines refer to the $5f$ charge of PuS (full line with triangles) and PuP (dotted line). The black lines refer to INT DC factor α of PuS (full line) and PuP (dashed-two-dots line). The MT radii of Pu and S(P) are set, respectively, to $R_{MT}^{Pu}=2.82$ a.u. and $R_{MT}^{S(P)}=2.15$ a.u.; the basis set cut off $R_{MT}^{Pu}|\vec{G}+\vec{k}|_{max}$ is set to be 9.1. The integration in the BZ is performed with 1728 with k points uniformly spaced.

pare M_{sp} and M_{orb} calculated for the paramagnet PuS (Ref. 1) with ones calculated for the ferromagnet PuP.[1] For AMF type of DC, M_{sp} and M_{orb} of both compounds decrease dramatically until they disappear at $U \approx 2.0$ eV. Instead, by using FLL DC, M_{sp} and M_{orb} decrease significantly but they never disappear for any value of U. Finally, only by using the INT type of DC, we find a range of values for U ($U \gtrsim 3.5$ eV) in which PuS is nonmagnetic and PuP is magnetic.

In conclusion we have implemented the LDA+U method in the most general form, taking into account the off-diagonal spin terms of the density matrix and the correct definition of the potential for those terms. By using the interpolated DC of Petukhov *et al.*[9] and by calculating SC the $F^{(k)}$s with a Yukawa potential, our LDA+U approach has only one free parameter left, i.e., the screening length λ or if preferable U.

E. Multipole representation of LDA+U energy

The formalism up to now is standard and have been used several times before, although some studies have neglected the spin-mixing terms in Eq. (1). Within this formalism the density matrix plays a crucial role. In the following we will decompose this fairly large matrix into the most important and physical relevant terms. We will find that this decomposition largely simplifies the analysis, as well as it gives many new insights into the magnetism of the actinides, where the SOC has a crucial contribution. The interaction term in Eq. (1) have been studied in detail, for example by Slater,[22] Racah,[23–26] Condon, and Shortly.[27] By expanding the interaction in spherical harmonics and by making use of the Wigner $3j$ symbols[27] the interaction can be expressed as

$$
\langle ab|g|cd \rangle = \delta_{s_a s_c} \delta_{s_b s_d} (2\ell+1)^2 \sum_{k=0}^{2\ell} \sum_{q=-k}^{k} (-1)^{m_a+m_b+q}
$$

$$
\times \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} \ell & k & \ell \\ -m_a & -q & m_c \end{pmatrix} F^{(k)} \begin{pmatrix} \ell & k & \ell \\ -m_b & q & m_d \end{pmatrix}.
$$

(18)

The spin dependence is given by the two delta functions of the spin quantum numbers of states a, b, c, and d. The radial dependence is confined in the Slater integrals $F^{(k)}$ and the Wigner $3j$ symbols take care of the angular part of the integral. We now introduce a multipole momentum tensor $\mathbf{w}^k$ defined as the expectation values of a tensor operator $\mathbf{v}^k$,

$$
w_x^k = \mathrm{Tr}\, v_x^k \rho, \tag{19}
$$

$$
v_x^k \equiv \langle m_b | v_x^k | m_a \rangle = (-1)^{\ell-m_b} \begin{pmatrix} \ell & k & \ell \\ -m_b & x & m_a \end{pmatrix} n_{\ell k}^{-1}, \tag{20}
$$

$$
n_{\ell k} = \frac{(2\ell)!}{\sqrt{(2\ell-k)!\,(2\ell+k+1)!}}, \tag{21}
$$

where the tensor component index x runs from $-k$ to k. The spin-independent part of the HF energy (the Hartree term) can be rewritten as

$$
E_H = \frac{(2\ell+1)^2}{2} \sum_{k=0}^{2\ell} n_{\ell k}^2 \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 F^{(k)} \mathbf{w}^k \cdot \mathbf{w}^k. \tag{22}
$$

In order to take care of the spin dependence we may introduce a double tensor

$$
w_{xy}^{kp} = \mathrm{Tr}\, v_x^k t_y^p \rho, \tag{23}
$$

$$
t_y^p = (-1)^{s-s_b} \begin{pmatrix} s & p & s \\ -s_b & y & s_a \end{pmatrix} n_{sp}^{-1}, \tag{24}
$$

where the index y runs from $-p$ to p. It is easy to verify that $\mathbf{w}^{k0}=\mathbf{w}^k$. Then the exchange energy can also be written as a function of the tensor components rather than the density matrix (see the Appendix),

$$E_X = -\sum_{k=0}^{2\ell} F^{(k)} \sum_{k_1=0}^{2\ell} \frac{(2\ell+1)^2(2k_1+1)}{4}(-1)^{k_1} n_{\ell k_1}^2$$

$$\times \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} \ell & \ell & k_1 \\ \ell & \ell & k \end{Bmatrix} \sum_{p=0}^{1} \mathbf{w}^{k_1 p} \cdot \mathbf{w}^{k_1 p}, \quad (25)$$

where the {…} symbol is the Wigner $6j$ symbol. Notice that the Wigner $3j$ symbols are defined such that the contribution from odd k vanish so only Slater parameters of even k are needed. This type of expression was derived by Racah.[24] However, since it was derived for atomic configurations only, it has not been fully realized that it is as valid for noninteger occupations.

F. The coupling of indices—irreducible spherical tensor

It is useful to introduce the irreducible spherical tensors $\mathbf{w}^{kpr}$ from the double tensors $\mathbf{w}^{kp}$ for two reasons. First, the double tensors are not true spherical tensors and, second, in the presence of SOC the spin and orbital degrees of freedom are not longer decoupled. The three-index tensors $\mathbf{w}^{kpr}$ is defined through a coupling of the indices of the double tensor $\mathbf{w}^{kp}$,

$$w_t^{kpr} = \underline{n}_{kpr}^{-1} \sum_{xay} (-)^{k-x+p-y} \begin{pmatrix} k & r & p \\ -x & t & -y \end{pmatrix} w_{xy}^{kp}, \quad (26)$$

where the index r runs from $|k-p|$ to $|k+p|$ and where the normalization factor $\underline{n}_{abc}$ is given, as in Ref. 28, by

$$\underline{n}_{abc} = i^g \left[\frac{(g-2a)!\,(g-2b)!\,(g-2c)!}{(g+1)!} \right]^{1/2}$$

$$\times \frac{g!!}{(g-2a)!\,!(g-2b)!\,!(g-2c)!\,!} \quad (27)$$

with $g = a+b+c$.

These tensor moments have a very nice feature, they are proportional to the moment expansions of the charge (k even and $p=0$), spin magnetization (k even and $p=1$), current (k odd and $p=0$), and spin-current (k odd and $p=1$) densities. For instance, $\mathbf{w}^{000}$ gives the total charge, $\mathbf{w}^{011}$ gives the spin moment, and $\mathbf{w}^{101}$ is proportional to the orbital moment.[28]

The exchange energy E_X of the shell ℓ in terms of the irreducible spherical tensor moments is now

$$E_X = -\sum_k F^{(k)} \sum_{k_1 pr} \frac{(2\ell+1)^2(2k_1+1)(2r+1)}{4}$$

$$\times (-1)^{k_1} |\underline{n}_{k_1 pr}|^2 n_{\ell k_1}^2 \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} \ell & \ell & k_1 \\ \ell & \ell & k \end{Bmatrix}$$

$$\times \mathbf{w}^{k_1 pr} \cdot \mathbf{w}^{k_1 pr}. \quad (28)$$

It is convenient to rewrite Eq. (28) in a simplified form,

$$E_X = \sum_{k_1 pr} E_X^{k_1 pr} = \sum_{k_1 pr} K_{k_1 pr} \mathbf{w}^{k_1 pr} \cdot \mathbf{w}^{k_1 pr}, \quad (29)$$

where

$$K_{k_1 pr} = -\sum_{2k=0}^{4\ell} F^{(k)} \frac{(2\ell+1)^2(2k_1+1)(2r+1)}{4}(-1)^{k_1} |\underline{n}_{k_1 pr}|^2 n_{\ell k_1}^2$$

$$\times \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} \ell & \ell & k_1 \\ \ell & \ell & k \end{Bmatrix}. \quad (30)$$

In Eq. (29) the exchange energy of the shell ℓ is expressed as a sum of independent terms involving different spherical tensors. We will refer to these terms as different exchange *channels*.

One of the most important types of polarization is the so-called spin polarization (SP), often referred to as Stoner exchange or Hund's first rule, which corresponds to a polarization of channel 011. Since $\mathbf{w}^{011} \cdot \mathbf{w}^{011} = m_{\mathrm{spin}}^2$, we get that the SP energy E_{SP} is given by

$$E_{\mathrm{SP}} = E_X^{011} = K_{011} m_{\mathrm{spin}}^2 = -\frac{1}{4}\left(\frac{U-J}{2\ell+1} + J\right) m_{\mathrm{spin}}^2. \quad (31)$$

Hence, the so-called Stoner parameter I, defined by $E_{\mathrm{SP}} = -\frac{1}{4} I m_{\mathrm{spin}}^2$, is given by

$$I = \frac{U-J}{2\ell+1} + J \quad (32)$$

as it is already known. In this expressions we have adopted the convention to use certain linear combinations of the Slater parameters, the "Hubbard" parameters, $U = F^{(0)}$, and J, that for d and f electrons is given by, respectively,

$$J^d = \frac{1}{14}(F^{(2)} + F^{(4)}), \quad (33)$$

$$J^f = \frac{2}{45}F^{(2)} + \frac{F^{(4)}}{33} + \frac{50}{1287}F^{(6)}. \quad (34)$$

In our multipole expansion in Eq. (29) it is also included an exact formulation of the orbital polarization (OP) exchange energy E_{OP},

$$E_{\mathrm{OP}} = E_X^{101} + E_X^{110} = K_{101}\mathbf{w}^{101} \cdot \mathbf{w}^{101} + K_{110}\mathbf{w}^{110} \cdot \mathbf{w}^{110}, \quad (35)$$

where $K_{101} = 3K_{110}$ and $\mathbf{w}^{101} \cdot \mathbf{w}^{101} = \frac{m_{\mathrm{orb}}^2}{\ell^2}$. This expression is a sum of two terms, one that breaks the time-reversal symmetry,[29] 101 (OP odd), and a second one that does not, 110 (OP even). Consequently 101 is associated with the presence of an orbital moment while 110 is compatible with a nonmagnetic solution.[30] Finally, the prefactor K_{101} has a simple expression in terms of Racah parameters;[18] this is for d and for f electrons, respectively,

$$K_{101}^d = -\frac{E^0 + 21E^2}{10}, \quad (36)$$

$$K_{101}^f = -\frac{9E^0 + 297E^3}{112}. \quad (37)$$

III. RESULTS

In this section we shall apply our method to calculate the magnetic structure of some metallic U, Np, and Pu compounds, for which the behavior of $5f$ electrons varies from itinerant to more localized.

A. Application to US

We selected US as a prototype system to compare the results obtained by calculating the $F^{(k)}$ through a screened Yukawa potential with other common procedures,[6,16] in which U and J are provided as inputs and the ratios $A_1 = F^{(4)}/F^{(2)}$ and $A_2 = F^{(6)}/F^{(2)}$ are fixed. US shows a ferromagnetic order with $T_C = 178$ K and a strong anisotropy along [111] direction.[31,32] Many experiments have proven $5f$ electrons of US to be itinerant.[33–35] Neutron scattering experiments have measured the $5f$ total moment to be $1.7\mu_B$ (Ref. 36) while measurements of the magnetization in the bulk have shown that the total moment per f.u. is $1.55\mu_B$.[37] On the theoretical side there have been many investigations of magnetic properties of US, making this system a good benchmark case for our method. Recent LDA calculation with SOC correction seem to underestimate the orbital moment[5] while orbital polarization[5] and Hartree-Fock tight-binding calculations reproduce the correct size of M_{orb}.[16] We have investigated the magnetic and electronic structure of this compound using our optimized LDA+SOC+U method and its multipole decomposition. As anticipated in the method section, we compared the behavior of magnetic moments obtained by calculating $F^{(k)}$ through a Yukawa potential $[M_{sp}^{Yukawa}(\lambda)$ and $M_{orb}^{Yukawa}(\lambda)]$ with ones determined by fixing the ratios A_1 and A_2. In the fixed ratios calculations, first, we fixed the value of J to 0.46 eV (Ref. 16) for any values of λ (Fig. 2), second, we varied J as function of λ to the value $J(\lambda)$ determined by the screened calculation (Fig. 4). If the $F^{(k)}$ are determined individually, $M_{sp}^{Yukawa}(\lambda)$ and $M_{orb}^{Yukawa}(\lambda)$ change dramatically as function of λ (or U), while the moments are much more constant by fixing A_1, A_2, and J. If then J is varied to $J(\lambda)$, and only A_1 and A_2 are kept constant, the moments vary in a similar way to $M_{sp}^{Yukawa}(\lambda)$ and $M_{orb}^{Yukawa}(\lambda)$. This is because in the latter case the values of $F^{(k)}$ become fairly similar to ones calculated with the screened potential, as we show in Table I.

Let us now analyze the decomposition in multipoles of the HF-E_X energy in Eq. (29), that we report in Fig. 5. We found three main contributions: the SP term 011, the OP even term 110, and finally the high multipole of $\vec{m}(\vec{r})$ 615. For small U the SP 011 is the dominant contribution until it starts to decrease rapidly. At $U \approx 0.8$ eV the OP-even 110 crosses 011 and it becomes the largest term. Such a term has been detected in all our LDA+SOC+U calculations on actinides and it has been found responsible for the vanishing of magnetic moments in δ-Pu, both in a LDA+U investigation[30] as well as in a dynamical mean-field theory (DMFT) study.[40] Finally, at $U \approx 1.0$ eV the 615 contribution becomes the largest. Few other terms are present but they are much smaller than the others; 101, OP-odd term, that refers to the E_X associated to the presence of an orbital moment, 211 and
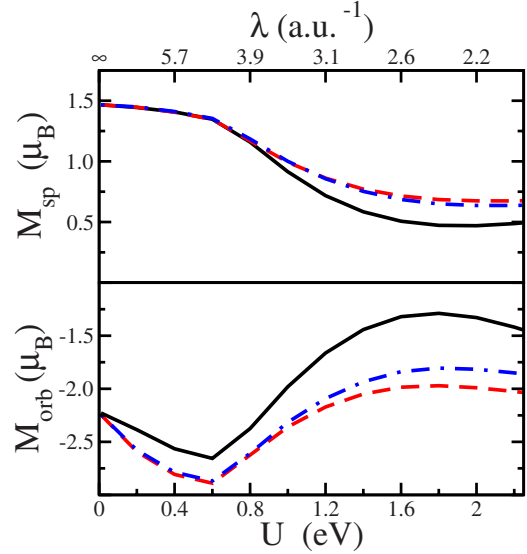

FIG. 4. (Color online) Spin (upper panel) and orbital magnetic moment (lower panel) of US, $a = 10.36$ a.u., calculated with LDA+SOC+U approach. We compare the results obtained by calculating the $F^{(k)}$ with a screened Yukawa potential (full black line and screening lenght in the upper axis) with ones obtained by fixing the ratios $A_1 = F^{(4)}/F^{(2)}$ and $A_2 = F^{(6)}/F^{(2)}$ to ones of Refs. 6 and 18 (dashed red line) and to ones of Refs. 16 and 17 (dashed-dotted blue line). In the fixed ratios calculations we varied J to the one determined by Yukawa potential at every different screening length, $J(\lambda)$. Other calculation details are the same as the ones reported in Fig. 2.

413, related to the multipoles of the $\vec{m}(\vec{r})$, 505, corresponding to an high multipole of the current density.

B. Application to Np compounds

The $5f$ electrons in Np compounds are expected to have intermediate features between the itinerant behavior in U compounds and the more localized behavior in Pu compounds. We calculated the electronic and magnetic structure of two Np compounds, NpN and NpSb. NpN is reported to be a ferromagnet with easy axis along [111] direction, $T_C = 87$ K and a total magnetic moment of $1.4\mu_B$,[1] NpSb is reported to be an antiferromagnet in AFM-3k structure and easy axis along [111] direction with a total moment of $2.5\mu_B$.[1] In Figs. 6 and 7 we plot M_{sp} and M_{orb} as functions of the parameter U and the corresponding screening length λ. Both compounds are magnetic for all values of λ. In the same figures we also report the different multipole components of E_X as defined in Eq. (29). For $0 \leq U \leq 1.5$ eV the SP 011 term dominates in both compounds. For $U \gtrsim 1.5$ eV, 110 and 615 become the largest terms. In both materials there is also a significant OP-odd 101 that is related to the presence of an orbital moment. Finally, in NpN we observe a significant 211 contribution that corresponds to an high multipole of $\vec{m}(\vec{r})$. We note that the relevant channels in these Np compounds are similar to ones present in US, however the 110 term is larger and the 615 term is slightly smaller.

C. Application to Pu compounds

We have investigated the magnetic structure of some Pu compounds belonging to the actinides monopnictides, whose

TABLE I. Comparison of Slater integrals of US and U^{4+} calculated with different methods. The fixed ratios A_1 and A_2 are from Refs. 6 and 18; in those calculations the parameters U and J are provided as input equal to ones calculated with Yukawa potential for $\lambda = 1.6$ a.u.$^{-1}$. The Slater integrals of US are evaluated using the $5f$ radial functions with an energy corresponding to the center of the band. The MT of U is 2.79 a.u.

	Method	$F^{(0)}$	$F^{(2)}$	$F^{(4)}$	$F^{(6)}$	J
Present work US	$\lambda = 1.6$ a.u.$^{-1}$	3.114	6.128	5.110	4.060	0.585
Present work US	Fixed A_1 and A_2	3.114	6.973	4.659	3.446	0.585
Ref. 17 U^{4+}	$\lambda = 1.6$ a.u.$^{-1}$	3.309	6.377	5.281	4.185	0.606
Refs. 38 and 39 U^{4+}	Experiment	2.3,2.6	6.440	5.296	3.441	0.580

$5f$ electrons are expected to have more localized features compared to Np and U compounds. These materials have the fcc NaCl crystal structure and the determination of their magnetic structure has been object of many experimental studies.[1] PuS, PuSe, and PuTe, are paramagnets like δ-Pu; PuSb, PuP, and PuAs are ferromagnets; PuBi is an antiferromagnet. We have found that the use of the INT DC is essential to correctly reproduce the magnetic structure of those compounds. In addition we reproduced the nonmagnetic ground state of the high-T_c superconductor PuCoGa$_5$ and we analyzed it through the multipole decomposition of E_X in Eq. (29). We already discussed in the method section the ability of INT DC to correctly describe the magnetic structure of two prototype Pu compounds, the paramagnet PuS, and the ferromagnet PuP (see Fig. 3). The results of a similar calculation for the ferromagnets PuAs and PuSb, for the antiferromagnet PuBi, and for the paramagnets PuSe and PuTe are summarized in Table II. By using the INT type of DC, M_{sp} and M_{orb} decrease significantly faster for nonmagnetic compounds until they disappear, while for magnetic compounds the moments decrease slower and do not disappear.

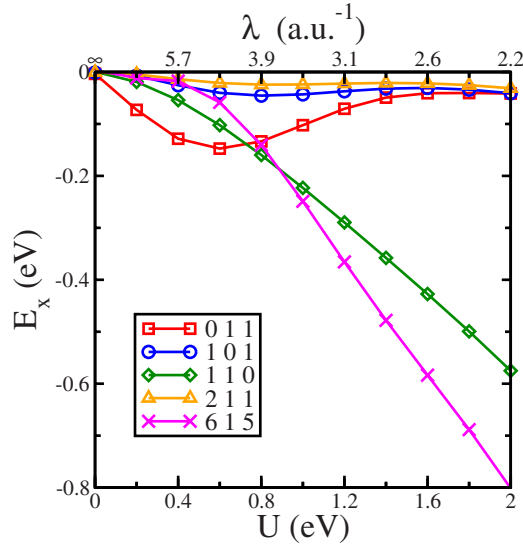Let us now discuss the decomposition in multipoles of the HF E_X. Again we will refer to the two prototype materials

PuS and PuP calculated with INT DC. In both compounds the dominant term is SP 011 for $0 \leq U \lesssim 1.5$ eV. With increasing U the OP-even term 110 starts to increase and it soon becomes the dominant contribution for $U \gtrsim 1.5$ eV. In PuS the OP-even 110 term completely takes over the SP 011 contribution, as we already found in the case of δ-Pu.[30] Also in PuP the 011 channel decreases, however it does not become zero and few other significant channels are opened. The most relevant one (after 110) is the 615 contribution that is related to a high multipole of $\vec{m}(\vec{r})$. However, the 615 term is lower than one present in magnetic U and Np compounds, while 110 channel is clearly larger. This mechanism is clearly shown in Figs. 3 and 8, where we compare the magnetic moment and HF-E_X contributions of PuS, nonmagnetic, and PuP, ferromagnetic, as function of the parameter U and corresponding screening length λ.

Finally, we applied our one-parameter LDA+U method to the superconducor PuCoGa$_5$. Previous LDA+U calculations
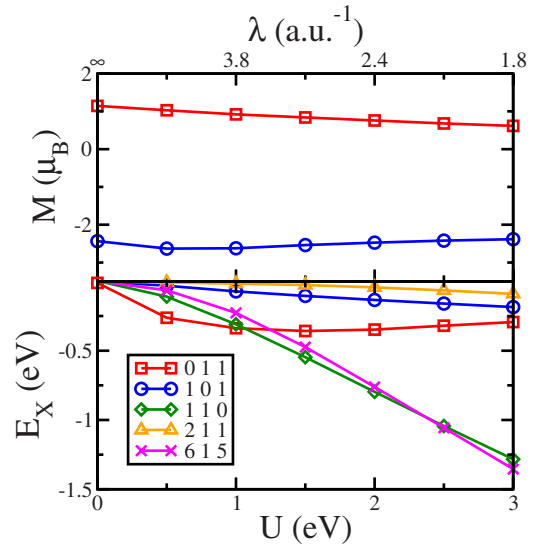

FIG. 6. (Color online) Upper panel: spin (red line with squares) and orbital (blue line with circles) moment of ferromagnetic NpN, $a = 9.25$ a.u.. Lower panel: relevant exchange energy channels in Eq. (29), $E_X^{k_1 pr}$, of NpN calculated with LDA+SOC+U approach and INT DC. The Slater parameters are calculated SC by using a screened Yukawa potential with screening length λ reported in the upper axis. The MT radii of Np and N are set, respectively, to $R_{MT}^{Np} = 2.60$ a.u. and $R_{MT}^{N} = 1.80$ a.u.; the parameter $R_{MT}^{Np} |\vec{G} + \vec{k}|_{max}$ is set to 9.4. The integration in the BZ is performed with 1728 k points uniformly spaced.

FIG. 5. (Color online) Relevant exchange energy channels in Eq. (29), $E_X^{k_1 pr}$, of US calculated with LDA+SOC+U method and INT DC. The Slater parameters are calculated SC by using a screened Yukawa potential with screening length λ reported in the upper axis. Other calculation details are reported in Fig. 2.
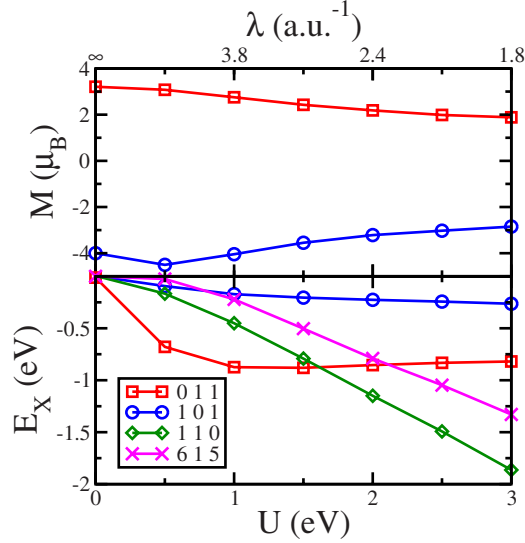
FIG. 7. (Color online) Upper panel: spin (red line with squares) and orbital (blue line with circles) moment of NpSb in AFM-3k structure, $a = 11.82$ a.u.. Lower panel: relevant exchange energy channels in Eq. (29), $E_X^{k_1 pr}$, of NpSb calculated with LDA+SOC+U and INT DC. The Slater parameters are calculated SC by using a screened Yukawa potential with screening length λ reported in the upper axis. The MT radii of Np and Sb are set, respectively, to $R_{MT}^{Np} = 2.95$ a.u. and $R_{MT}^{Sb} = 2.65$ a.u.; the parameter $R_{MT}^{Np}|\vec{G} + \vec{k}|_{max}$ is set to be 9.2. The integration in the BZ is performed with 1728 k points uniformly spaced.

of this compound have stabilized a nonmagnetic solution with AMF type of DC, $U = 3$ eV and $J = 0.6$ eV, and fixed A_1 and A_2.[41] We also stabilized a nonmagnetic solution for $U = 3.2$ eV, corresponding to $\lambda = 1.79$ a.u.$^{-1}$, (see Fig. 9 and Table II). In the E_X multipole decomposition the OP-even 110 term, that corresponds to an enhancement of SOC interaction, is again the dominant one and it takes over the whole SP 011 contribution once the system becomes nonmagnetic. This mechanism is completely analogous to the one present in the others paramagnetic Pu monopnictides we calculated in this work and in δ-Pu.[30]

IV. CONCLUSIONS

The purposes of this paper are twofold. First, we advocate an approach to LDA+U calculations that reduces the number of free parameters in a well-defined way. This involves the use of screened Yukawa potential to describe the HF interaction within an atomic shell with a single parameter. In addition we argue to systematically use the INT approach to DC, which takes away the ever existing choice between AMF or FLL, especially since the results depend on the choice of DC. This approach ought to facilitate fast and systematic LDA+U calculations. The results of which would be comparable between different computations, without having to dwell on the used values of, e.g., J.

Second, we present a method, the decomposition in tensor moments of the density matrix, that facilitates the analyses of the results from an LDA+U calculation. This is an exact approach which gives both the different polarization chan-

TABLE II. Table of screening length λ used to determine Slater integrals through a screened Yukawa potential in LDA+SOC+U calculations of Pu compounds with INT type of DC. We report the smallest value of U and corresponding screening length λ that are necessary to obtain vanishing magnetic moments (less than $0.1\mu_B$ for both M_{sp} and M_{orb}) in nonmagnetic Pu compounds. For the first three nonmagnetic compounds PuX, with X$=$S, Se, Te, we considered the corresponding ferromagnetic compounds PuY, with Y $=$P, As, Sb, where X and Y are chosen to be neighbors elements in the periodic table. We then report the magnetic moments of PuY using the same value of U that makes the corresponding compound PuX nonmagnetic. For the antiferromagnet PuBi we used the same value of U of PuSb. We also write down the INT DC interpolation factor α that is determined SC. Values of experimental magnetic moments are from Ref. 1.

Paramagnets		
	U [eV]	λ [a.u.$^{-1}$]	α
PuS	3.2	1.74	0.75
PuSe	3.6	1.57	0.79
PuTe	4.1	1.38	0.83
δ-Pu	3.7	1.51	0.78
PuCoGa$_5$	3.2	1.79	0.69

Ferromagnets						
	U [eV]	λ [a.u.$^{-1}$]	M_{spin} [μ_B]	M_{orb} [μ_B]	M_{tot} [μ_B]	M_{tot}^{exp} [μ_B]	α
PuP	3.2	1.76	1.60	-1.52	0.08	0.75	0.82
PuAs	3.6	1.60	1.67	-1.54	0.13	0.64	0.86
PuSb	4.1	1.40	1.57	-1.47	0.1	0.67	0.9

Antiferromagnets						
	U [eV]	λ [a.u.$^{-1}$]	M_s [μ_B]	M_{orb} [μ_B]	M_{tot} [μ_B]	M_{tot}^{exp} [μ_B]	α
PuBi	4.1	1.42	1.38	-1.29	0.09	0.50	0.89

nels as well as the corresponding Hartree and exchange energies.

Finally, we apply these combined approaches to a few metallic actinide systems whose $5f$ electrons show different degrees of localization; from the itinerant features in US to the more localized behavior in Pu compounds and the intermediate one of Np-based materials. The results show that our one-parameter approach catches the ground-state properties of these system, such as spin and orbital moments. Here it is worth mentioning that an even better agreement with experiments can be obtained by tweaking the individual Slater parameters differently for the different systems. But that would rather reduce than increase the physical understanding of these systems.

Most importantly, our results signal that these systems are not as well understood as believed. For instance, Hund's
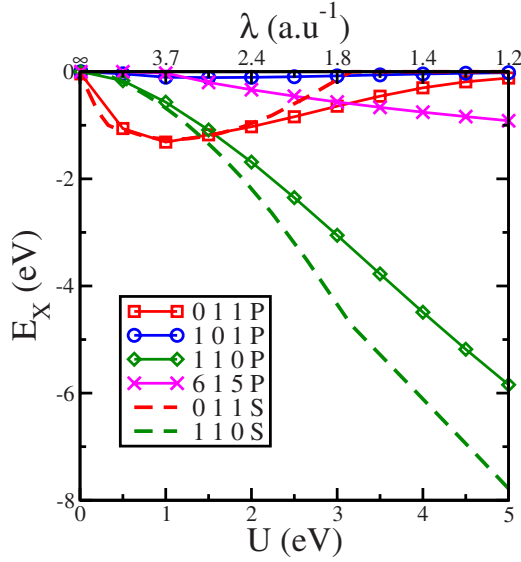
FIG. 8. (Color online) Relevant exchange energy channels in Eq. (29), $E_X^{k_1pr}$, for paramagnetic PuS, $a=10.46$ a.u., and ferromagnetic PuP, $a=10.49$ a.u., as function of U for INT DC. The Slater parameters are calculated SC by using a Yukawa potential with screening lenght λ reported in the upper axis. Other calculation details are reported in Fig. 3.
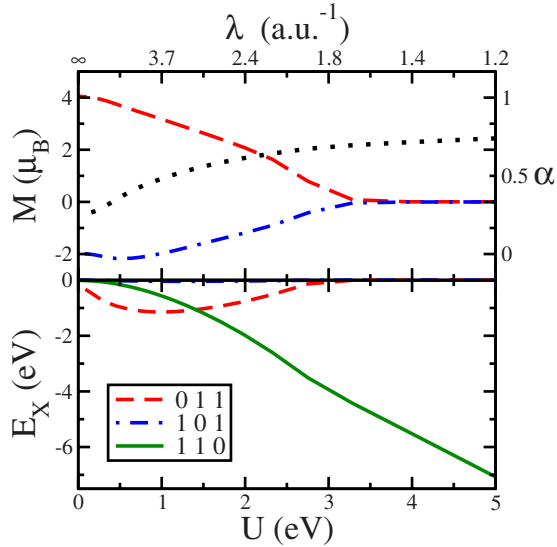

FIG. 9. (Color online) Upper panel: spin (dashed red line) and orbital (dashed-dotted blue line) magnetic moments of high-T_c superconductor PuCoGa$_5$, $a=7.84$ a.u and $c=12.57$ a.u., calculated with LDA+SOC+U and INT DC, as function of parameter U. The interpolation factor α is plotted with a dotted black line. The Slater parameters are calculated SC by using a Yukawa potential with screening lenght λ reported in the upper axis. We used an AFM-1k structure with $\mathbf{q}=(0,0,1/2)$. Lower panel: relevant exchange energy channels in Eq. (29), $E_X^{k_1pr}$, of PuCoGa$_5$. The MT radii of Pu, Co, and Ga are set, respectively, to $R_{MT}^{Pu}=2.7$ a.u. and $R_{MT}^{Co,Ga}=2.2$ a.u.. The parameter $R_{MT}^{Pu}|\vec{G}+\vec{k}|_{max}$ is set to 9.5. The integration in the BZ is performed with 576 k points uniformly spaced.

rules are far away from fulfilled since the SP does not play the dominant role as always assumed. On one hand the LDA calculations show large SP which leads to an overestimation of the spin moments. On the other hand, when including the HF interaction of the LDA+U functional, another polarization channel dominates, the one of spin-orbital currents, the OP-even 110 channel. The tensor moment associated with such channel, $\mathbf{w}^{110}$, is even close to the saturation limit of $-\frac{4}{3}\mathbf{w}^{000}$ for all systems considered. Large values of this tensor moment are in good accordance with the rising number of experiments that point to large $\mathbf{w}^{110}$ for actinide systems.[42–44] This fact corresponds to a large enhancement of SOC in all these systems by the HF-exchange interaction. The SP 011 channel, however, decreases drastically, and in some Pu compounds even disappears. Instead, to some surprise, a third polarization plays an important role, the 615 channel; this corresponds to an high multipole of the magnetization density.

APPENDIX

The transformation Eq. (23) can be reversed through orthogonality relations of the Wigner 3j symbols. Hence, the density matrix ρ can be expanded in the double tensors $\mathbf{w}^{k_ip_i}$,

$$\rho_{ac} = \sum_{k_ix_i} (2k_i+1)n_{lk_i}(-1)^{m_c-\ell}\begin{pmatrix} \ell & k_i & \ell \\ -m_c & x_i & m_a \end{pmatrix}\sum_{p_iy_i}(2p_i+1)$$

$$\times n_{sp_i}(-1)^{s_c-s}\begin{pmatrix} s & p_i & s \\ -s_c & y_i & s_a \end{pmatrix}w_{x_iy_i}^{k_ip_i}. \tag{A1}$$

When this form, together with Eq. (18), are inserted in the exchange part of Eq. (1), we get an expression where the complications essentially arise from the orbital summations in the factor

$$\mathcal{Q} = \sum_{m_am_bm_cm_dq} (-1)^q\begin{pmatrix} \ell & k_1 & \ell \\ -m_c & x_1 & m_a \end{pmatrix}\begin{pmatrix} \ell & k & \ell \\ -m_a & -q & m_d \end{pmatrix}$$

$$\times\begin{pmatrix} \ell & k_2 & \ell \\ -m_d & x_2 & m_b \end{pmatrix}\begin{pmatrix} \ell & k & \ell \\ -m_b & q & m_c \end{pmatrix}, \tag{A2}$$

where the indeces on k and x stem from the two different density-matrix expansions. The spin dependence of the exchange energy is simpler due to the Kronecker delta symbols in Eq. (18), i.e., the relevant factor becomes

$$\mathcal{S} = \sum_{s_a s_b s_c s_d} (-1)^{-s_c - s_d} \begin{pmatrix} s & p_1 & s \\ -s_c & y_1 & s_a \end{pmatrix} \delta_{s_a s_d} \begin{pmatrix} s & p_2 & s \\ -s_d & y_2 & s_b \end{pmatrix} \delta_{s_b s_c}$$

$$= \sum_{s_a s_b} (-1)^{1+s_a - s_b} \begin{pmatrix} s & p_1 & s \\ -s_a & -y_1 & s_b \end{pmatrix} \begin{pmatrix} s & p_2 & s \\ -s_a & y_2 & s_b \end{pmatrix}$$

$$= (-1)^{1-y_1} (2p_1 + 1)^{-1} \delta_{p_1 p_2} \delta_{y_1 - y_2} \tag{A3}$$

by use of orthogonality relations. To simplify $\mathcal{Q}$ we start with an identity for the Wigner $6j$ symbols, see, e.g., Ref. 18, and we reshuffle a little,

$$\begin{Bmatrix} \ell & \ell & k_1 \\ \ell & \ell & k \end{Bmatrix} \begin{pmatrix} \ell & \ell & k_1 \\ m_b & -m_c & -x_1 \end{pmatrix} = \sum_{m_a m_d q} (-1)^{k+m_a+m_d+q}$$

$$\times \begin{pmatrix} \ell & k & \ell \\ -m_d & -q & m_b \end{pmatrix} \begin{pmatrix} \ell & k & \ell \\ -m_c & q & m_a \end{pmatrix} \begin{pmatrix} \ell & k_1 & \ell \\ m_d & -x_1 & -m_a \end{pmatrix}. \tag{A4}$$

Then we multiply by

$$\begin{pmatrix} \ell & \ell & k_2 \\ m_b & -m_c & x_2 \end{pmatrix}$$

and we sum over m_b and m_c, by obtaining

$$\begin{Bmatrix} \ell & \ell & k_1 \\ \ell & \ell & k \end{Bmatrix} \sum_{m_b m_c} \begin{pmatrix} \ell & \ell & k_1 \\ m_b & -m_c & -x_1 \end{pmatrix} \begin{pmatrix} \ell & \ell & k_2 \\ m_b & -m_c & x_2 \end{pmatrix}$$

$$= \sum_{m_a m_b m_c m_d q} (-1)^{k_1+k+x_1+q} \begin{pmatrix} \ell & k_1 & \ell \\ -m_d & x_1 & m_a \end{pmatrix} \begin{pmatrix} \ell & k & \ell \\ -m_a & -q & m_c \end{pmatrix} \begin{pmatrix} \ell & k_2 & \ell \\ -m_c & x_2 & m_b \end{pmatrix} \begin{pmatrix} \ell & k & \ell \\ -m_b & q & m_d \end{pmatrix}. \tag{A5}$$

On the left-hand side we use an orthogonality relation for the Wigner $3j$ symbols and on the right-hand side we identify $\mathcal{Q}$ from Eq. (A2),

$$\begin{Bmatrix} \ell & \ell & k_1 \\ \ell & \ell & k \end{Bmatrix} (2k_1 + 1)^{-1} \delta_{k_1 k_2} \delta_{x_1 - x_2} = (-1)^{k_1 + x_1 + k} \mathcal{Q}. \tag{A6}$$

The phase factors of Eqs. (A3) and (A6) are then used to form the scalar product of the double tensors in the final form of exchange energy, Eq. (25) as

$$\mathbf{w}^{k_1 p_1} \cdot \mathbf{w}^{k_1 p_1} = \sum_{x_1 y_1} (-1)^{x_1 + y_1} w^{k_1 p_1}_{x_1 y_1} w^{k_1 p_1}_{-x_1 - y_1}. \tag{A7}$$

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