

# Obtaining correct orbital ground states in $f$ -electron systems using a nonspherical self-interaction-corrected LDA+ $U$ method

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The electronic structure of lanthanide and actinide compounds is often characterized by orbital ordering of localized  $f$  electrons. Density-functional theory studies of such systems using the currently available local-density approximation (LDA)+ $U$  method are plagued by significant orbital-dependent self-interaction, leading to erroneous orbital ground states. An alternative scheme that modifies the exchange, not Hartree, energy is proposed as a remedy. We show that our LDA+ $U$  approach reproduces the expected degeneracy of  $f^1$  and certain  $f^2$  states in free ions and the correct ground states in solid PrO<sub>2</sub>. We expect our method to be useful in studying electronic excitations and entropies in  $f$  and heavy- $d$  elements.

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## I. INTRODUCTION

Interesting physical phenomena associated with the strongly correlated  $f$  electrons in lanthanide and actinide compounds continue to attract lively interest.<sup>1,2</sup> Strong on-site interactions between the  $f$  electrons in these materials present serious challenges to modern density-functional theory (DFT)-based electronic-structure techniques, causing most approximate functionals, such as the local density approximation (LDA) or generalized gradient approximation (GGA), to fail qualitatively. To overcome the deficiencies of the LDA/GGA in studying  $f$ -element compounds, several recent studies have employed the self-interaction (SI)-corrected LDA (Ref. 3), e.g., in Refs. 4–6, the hybrid functional method<sup>7,8</sup> in Refs. 9–13 or the dynamical mean-field theory (DMFT) (Ref. 14) in Refs. 15 and 16. The LDA+ $U$  method<sup>17</sup> has emerged as a well-established model to deal with strong electron correlations in  $d$  and  $f$  systems, combining high efficiency with an explicit treatment of correlation within a Hubbard-type model for the localized electrons. This method has been very successful in transition-metal oxides (for a review, see Ref. 18) and has yielded promising results for band gaps in  $f$  systems.<sup>13,19,20</sup> However, systematic studies of its effectiveness remain inconclusive, with issues of orbital ordering<sup>21</sup> and multiple self-consistent solutions attracting heightened attention.<sup>19,22–25</sup>

Here, we show that the currently popular versions of LDA+ $U$ , by Liechtenstein *et al.*<sup>26</sup> and Dudarev *et al.*,<sup>27</sup> respectively, encounter serious difficulties in  $f$  systems due to large orbital-dependent SI effects, which result in an unphysical splitting of up to 0.4 eV between degenerate  $f^1$  multiplets. Since the SI errors (SIE) are typically larger than the crystal-field (CF) splitting energies and comparable to the strength of the spin-orbit coupling (SOC), they lead to qualitatively incorrect electronic ground states in solids. We propose an orbital SI-free form of the LDA+ $U$  method that leaves the LDA Hartree term intact and only replaces the LDA exchange with the Hartree-Fock exchange. In our method, the Hartree-Fock exchange term cancels the LDA self-interaction energy to a high degree of accuracy, ensuring near degeneracy of real- and complex-valued orbitals in free ions and correctly reproducing the  $\Gamma_8$  ground state and  $\Gamma_8$

$\rightarrow\Gamma_7$  excitation energies in the PrO<sub>2</sub> solid. The accuracy of this functional is sufficient for evaluating high-temperature electronic entropies of  $f$ -electron systems.

## II. METHOD AND COMPUTATIONAL DETAILS

All DFT calculations were carried out using the VASP package<sup>28,29</sup> with projector augmented wave potentials,<sup>30</sup> energy cutoff of 450 eV, and without any constraint symmetry or ionic relaxation. For free ions, a 12 Å cubic cell containing one ion and uniform compensating background charge were used. For the PrO<sub>2</sub> solid, we consider a primitive cell of the fcc supercell [lattice constant of 5.386 Å (Ref. 31)]. The term “LDA+ $U$ ” is used irrespective of the  $X_c$  functional since the LDA and GGA results are found similar. Each calculation was initialized in a specific atomic orbital and self-consistently converged to either states very close to the initial orbital with the results reported or distinctly different states with lower energy. SOC was excluded from the calculations unless its inclusion is stated explicitly to make realistic comparison with experiment. Finally, we fix the  $U$  parameter in the LDA+ $U$  method to 6 eV and leave the discussions of this choice to the end.

### A. Aspherical self-interaction error of LDA+ $U$ for $f$ electrons

We begin by showing that the conventional LDA+ $U$  approach fails to reproduce the degeneracy of different  $|m\rangle$  orbitals of  $f^1$  ions. First consider real orbitals with angular dependence of real  $y_{3m}^R = \sqrt{2}\mathcal{Y}_{3m}$  without spin-orbit effects to simplify the presentation of our method. Complex orbitals and SOC are discussed later. Figure 1 shows the energies of different  $y_{3m}^R$  orbitals (with the exception of  $y_{31}^R$ , which converges to  $y_{32}^R$ ) in several lanthanide and actinide ions calculated using the LDA+ $U$  scheme of Liechtenstein *et al.*<sup>26</sup> with  $J=0.5$  and  $U=6$  eV. Contrary to the expected degeneracy, the energies of the different  $y_{3m}^R$  orbitals differ substantially, up to 0.4 eV, and the  $y_{31}^R$  orbital was found unstable and converged to  $y_{32}^R$ . Varying  $J$  between 0 (i.e., the Dudarev scheme<sup>27</sup>)  $\sim 1$  eV changes the results by only a few meV.

The above results demonstrate that the conventional LDA+ $U$  approach commits large errors of up to 0.4 eV/

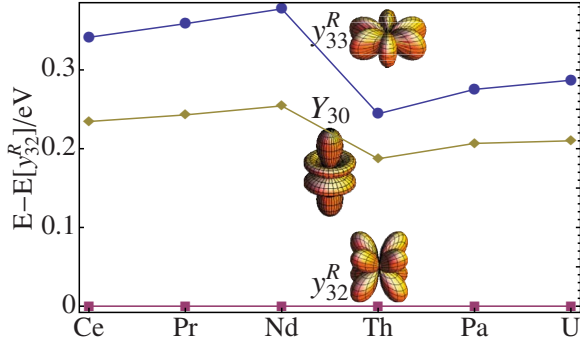


FIG. 1. (Color online) LDA+ $U$  total energies for different orbital filling of  $f^1$  ions with the Liechtenstein scheme (Ref. 26) relative to  $y_{32}^R$ .

electron in the predicted relative orbital energies of  $f$  electrons. To understand the reasons for the unphysical splitting of the  $f^1$  states, we examine the conventional LDA+ $U$  total-energy functional<sup>17</sup>

$$E^{\text{LDA}+U} = E^{\text{LDA}} + E_U - E_{\text{dc}}, \quad (1)$$

where the LDA description of the on-site interaction, approximately represented by the so-called double-counting term  $E_{\text{dc}}$ , is replaced with a Hubbard-type  $E_U$ . The latter is essentially the Hartree-Fock energy, expressed in a rotationally invariant form by Liechtenstein *et al.*<sup>26</sup> as a sum of the Hartree (H) and exchange (X) terms,  $E_U = E_H + E_X$ , where

$$E_H = \frac{1}{2} \sum_{\{m\}} \langle m, m'' | V_{\text{cc}} | m', m''' \rangle n_{mm'} n_{m''m'''}, \quad (2)$$

$$E_X = -\frac{1}{2} \sum_{\{m\}, \sigma} \langle m, m'' | V_{\text{cc}} | m''', m' \rangle n_{mm'}^\sigma n_{m''m'''}^\sigma. \quad (3)$$

The on-site density matrix  $n_{mm'}^\sigma$ , is obtained by projecting the Kohn-Sham orbitals  $\psi_\alpha^\sigma$  of occupancy  $f_\alpha^\sigma$  onto atomic states  $|nlm(m')\rangle$ ,

$$n_{mm'}^\sigma = \sum_\alpha f_\alpha^\sigma \langle \psi_\alpha^\sigma | nlm' \rangle \langle nlm | \psi_\alpha^\sigma \rangle, \quad (4)$$

while the Slater integrals  $\langle mm' | V_{\text{cc}} | m''m'''\rangle$  are evaluated in terms of the Gaunt coefficients and the screened Coulomb  $U$  and exchange  $J$  parameters (the diagonal  $m=m'=m''=m'''$  terms are given in Table I). A simplified version by Dudarev *et al.*<sup>27</sup> adopts the  $J=0$  limit.

For a free  $f^1$  ion, the Hartree-Fock energy  $E_U$  in Eq. (1) naturally vanishes while  $E_{\text{dc}}$  in the Liechtenstein and Dudarev schemes depends only on the number of electrons,  $N^\sigma = \sum_m n_{mm}^\sigma$ , and not on the type of the occupied orbital. Therefore, Eq. (1) becomes

$$E^{\text{LDA}+U} = E^{\text{LDA}} + \text{const} \approx E_H + \text{const}.$$

In the above approximation we assumed (1) the LDA exchange is not sensitive to orbital filling (more on this later) and (2) the Hartree energy difference comes mainly from the on-site Hartree term  $E_H$  of Eq. (2). The resulting error in the relative orbital energies is then entirely due to the orbital dependence of the SIE of the LDA, which is reflected in  $E_H$ . To see the validity of our argument, we list in Table I the on-site  $E_H$  calculated from Eq. (2) for atomic orbitals; these expressions are expected to closely approximate the SI for localized orbitals in the LDA+ $U$ . Even though  $E_H$  is identical for all real  $p$  or  $d$  orbitals, it is orbital dependent for  $f$  multiplets and in all cases splits the SI energies of real vs complex orbitals. The predicted ordering of  $E_H$  is  $y_{32} < y_{30} < y_{31} < y_{33}$ , in agreement with the LDA+ $U$  results shown in Fig. 1, demonstrating that the unphysical splitting of  $f^1$  states in conventional LDA+ $U$  is due to orbital-dependent SIE. Note that with real orbitals the problem of orbital-dependent SIE does not affect  $p$  or  $d$  electrons. We will show later that complex  $p$  and  $d$  orbitals are affected. According to Table I, the SIE is proportional to  $J$ ; for typical values of  $J$  in the range of 0.1–1 eV, it is comparable to or even larger than other important on-site effects, such as CF and SOC, which can lead to qualitatively incorrect predictions of electronic ground states in solids by the current LDA+ $U$  methods. These deficiencies of the conventional LDA+ $U$  approach can be traced back to its treatment of the Hartree and exchange energies. The LDA+ $U$  approach replaces the LDA Hartree energy with an on-site model expression  $E_H$  given by

TABLE I. Hartree energy  $E_H$ , Eq. (2), and LSD exchange energy  $E_X^{\text{LSD}}$ , Eq. (7), for one  $l$  electron in orbitals with real ( $y_{lm}^R, Y_{l0}$ ) and complex ( $Y_{lm}$  for  $m > 0$ ) angular wave functions.

	$y_{l3}^R$	$y_{l2}^R$	$y_{l1}^R$	$Y_{l0}$	$Y_{l1}$	$Y_{l2}$	$Y_{l3}$
$l$	Value of $a$ in $E_H = \langle mm   V_{\text{cc}}   mm \rangle / 2 = U/2 + aJ$						
1			0.4	0.4	0.1		
2		0.571	0.571	0.571	0.186	0.358	
3	0.880	0.422	0.807	0.716	0.332	0.194	0.696
$l$	Value of $a$ in LSD exchange $E_X^{\text{LSD}} = -aK$						
1			0.409	0.409	0.364		
2		0.364	0.364	0.356	0.324	0.324	
3	0.339	0.328	0.335	0.323	0.298	0.292	0.302

Eq. (2). Even though the  $E_H$  term is capable of reproducing the correct orbital energetics, the LDA+ $U$  double-counting energy  $E_{dc}$  is *orbital independent* and fails to properly account for the orbital dependence of the LDA SIE in open-shell systems. Similar considerations hold for the orbital dependence of the LDA exchange energy, which is mainly sensitive to the choice of real vs complex orbitals (see Table I); this factor acquires importance in systems with strong SOC, when the orbitals with a definite value of the total angular momentum  $J$  are necessarily complex.

### B. Reformulated LDA+ $U$

To correct the orbital-dependent SIE in the Hartree and exchange terms, we propose a formulation of the LDA+ $U$

$$\begin{aligned} E_X^{\text{LSD}} &= -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \sum_{\sigma} \int d^3r (\rho^{\sigma})^{4/3} = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \sum_{\sigma} \int R_l^{8/3}(r) r^2 dr d\Omega [n_{mm'}^{\sigma} \bar{Y}_{lm}(\Omega) Y_{lm'}(\Omega)]^{4/3} \\ &= -\left( \frac{4\pi}{2l+1} \right)^{1/3} \frac{K}{2} \sum_{\sigma} \int d\Omega [n_{mm'}^{\sigma} \bar{Y}_{lm} Y_{lm'}]^{4/3} = -\left( \frac{4\pi}{2l+1} \right)^{1/3} \frac{K}{2} \sum_{\sigma} \int d\Omega [\tilde{\rho}^{\sigma}(\Omega)]^{4/3} \end{aligned} \quad (7)$$

where  $c$  is the interpolation coefficient,  $\rho^{\sigma}$  is the charge density of spin component  $\sigma$ , which can be obtained from the on-site-occupation matrix  $n_{mm'}^{\sigma}$ , as well as radial function  $R_l(r)$  and spherical  $Y_{lm}(\Omega)$ ,  $K$  is the LSD exchange strength parameter and  $\tilde{\rho}$  represents the angular part of  $\rho$ . Only the  $E_X^{\text{LSD}}$  term in Eq. (6) is orbital dependent. The linear interpolation is conceptually similar to hybrid functional approaches and serves the purpose of subtracting the orbital dependence of the LDA exchange energy. The potential corresponding to the correction energy  $E_X - E_{dcX}$ , obtained by differentiating with respect to the on-site density matrix  $n_{mm'}$ , is then

$$\begin{aligned} \Delta V_{mm'}^{\sigma} &= \frac{2c}{3} \left( \frac{4\pi}{2l+1} \right)^{1/3} K \int d\Omega [\tilde{\rho}^{\sigma}(\Omega)]^{1/3} \bar{Y}_{lm} Y_{lm'} \\ &+ (1-c) \left( \frac{U-J}{2} + n^{\sigma} J \right) \delta_{mm'} \\ &- \langle m, m'' | V_{ee} | m'' m' \rangle n_{m'' m''}^{\sigma}. \end{aligned} \quad (8)$$

It is possible to reduce the number of independent parameters by requiring that  $E_X - E_{dcX}$  vanishes for full  $l$  shells ( $n_{mm'}^{\uparrow} = n_{mm'}^{\downarrow} = \delta_{mm'}$ ),

$$E_X - E_{dcX} = -c(2l+1)(U+2lJ) + c(2l+1)K = 0,$$

which gives

$$K = U + 2lJ. \quad (9)$$

The main advantage of Eqs. (5)–(7) is that the LDA self-interaction energy is canceled by the corresponding ex-

change term in  $E_X$ . As a result, the proposed method is self-interaction free to high accuracy.

## III. RESULTS AND DISCUSSIONS

In this section, we analyze the parameter dependence of the proposed method and then present results for the example of PrO<sub>2</sub> solid.

### A. Determination of parameters to remove aspherical SIE

We demonstrate orbital degeneracy for free Pr ions with one or two  $f$  electrons. Figure 2(a) displays the energy of Pr<sup>4+</sup> in real atomic orbitals calculated with our method (assuming  $c=0$ ) as a function of the exchange parameter  $J$ . At  $J=0$ , a splitting of more than 0.3 eV is found, similar to the behavior of the original LDA+ $U$  in Fig. 1. The splitting is reduced by increasing  $J$  and at the optimal value of  $J^0 = 0.783$  eV, it is less than 40 meV, i.e., the four real orbitals  $y_{3m}^R$  are almost degenerate. The  $y_{31}^R$  orbital can only be stabilized in the vicinity of  $J^0$ , relaxing otherwise to the more stable  $y_{32}^R$  or  $y_{33}^R$ . Hence, just one point for  $y_{31}^R$  is shown in the inset of Fig. 2(a).

The energy of the Pr<sup>3+</sup> ion ( $f^2$ ) is shown in Fig. 2(b) (also at  $c=0$ ). Consider three distinct  $f^2$  states with  $S=1$  and degenerate Hartree-Fock energy  $E_U$ . Using the basis defined by real-valued spherical harmonics,  $\{y_{l|m}^I = \sqrt{2} \mathcal{Y}_{l|m}(-l \leq m < 0), Y_{l0}, y_{l|m}^R (0 < m \leq l)\}$  [shown for  $l=3$  in Fig. 4(b)], the first of these states, designated by  $\phi_{13}$ , has electrons in orbitals  $y_{31}^I$  and  $y_{33}^I$ , or  $n_{mm'}^{\sigma} = 0$  except  $n_{11}^{\uparrow} = n_{33}^{\uparrow} = 1$ , while the other two  $f^2$  states, designated by  $\phi_{14}$  and  $\phi_{15}$ , correspond to  $n_{11}^{\uparrow}$

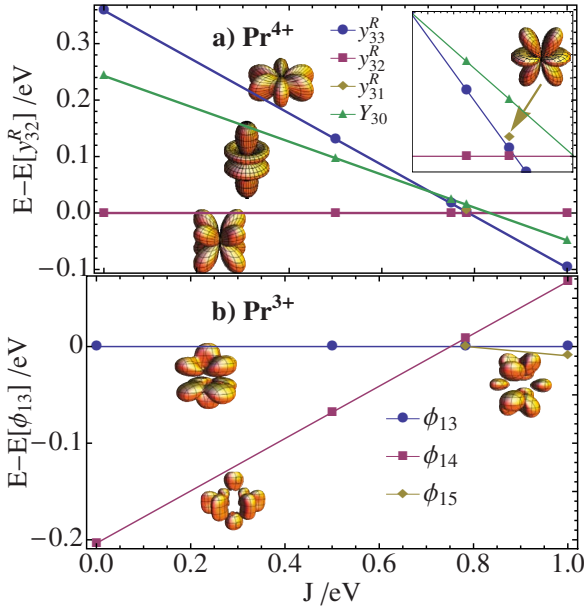


FIG. 2. (Color online) LDA+ $U$  energy of the  $\text{Pr}^{3+}$  and  $\text{Pr}^{4+}$  ions as a function of  $J$  for  $c=0$  calculated with our method. (a)  $f^1$  in orbitals  $y_{3m}^l$ , with the optimal  $J$  region magnified in the inset and (b)  $f^2$  in three degenerate (in terms of  $E_U$ ) two-electron states.

$=n_{44}^\uparrow=1$  and  $n_{11}^\uparrow=n_{55}^\uparrow=1$ , respectively. Their angular wave functions are shown in Fig. 2(b). Similar to the  $f^1$  case, the energy splitting is large at  $J=0$  and gets reduced to less than 30 meV at the optimal value  $J^0$ . Note that  $\phi_{15}$  can be stabilized only for  $J \geq J^0$ .

So far, we have used  $c=0$ , assuming that the LSD exchange functional is insensitive to the orbital and can be ignored. The lower part of Table I proves this assumption for the real orbitals:  $E_X^{\text{LSD}}$  varies by less than  $0.02K$ . However, Table I also shows that  $E_X^{\text{LSD}}$  of complex orbitals is substantially lower (by  $\sim 0.3K$ ), indicating a large lowering of the exchange energy in states with nonzero orbital current. Since  $E_X^{\text{LSD}} \sim -\rho^{4/3}$  is concave, it favors inhomogeneous charge distributions (such as real orbitals compared to complex ones) and therefore the LDA exchange energies in Table I of real orbitals are lower than those for complex orbitals. The difference may play an important role in systems with strong SOC, when the resulting electronic states are complex combinations of real  $y_{lm}$ 's with the orbital angular momentum unsuppressed. In Fig. 3, we show the dependence of the energies of real- and complex-valued orbitals for  $\text{Pr}^{4+}$  on the mixing coefficient  $c$  in Eq. (7), using the optimal value of the exchange parameter,  $J^0$ . It is seen that at  $c=0$ , the energies of real and complex orbitals differ by more than 0.2 eV due to their different LSD exchange and the spurious splitting is minimized to approximately 70 meV at the optimal  $c \approx 0.6$ .

In our approach, the  $J$  and  $c$  parameters are *a priori* determined by the physical requirement of degeneracy once the  $U$  parameter is given (6 eV in this work). They hardly change when  $U=4$  eV is used, suggesting that our method is relatively insensitive to the choice of  $U$ .

### B. Eigenstates of $\text{PrO}_2$ without SOC

Finally, we demonstrate the advantages of our method for extended solids by considering  $\text{PrO}_2$  in the cubic fluorite

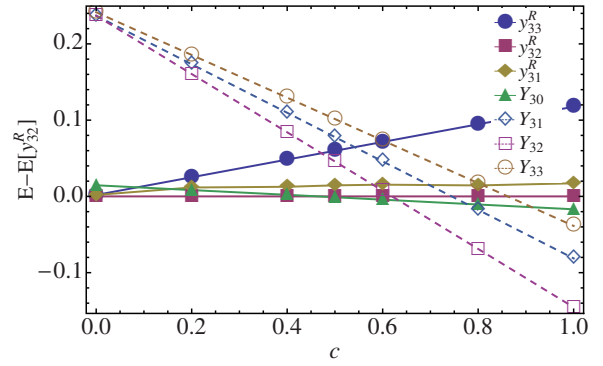


FIG. 3. (Color online) LDA+ $U$  energy of the  $\text{Pr}^{4+}$  ion as a function of  $c$  at fixed  $J^0=0.783$  eV calculated with our scheme, including both real- and complex-valued (no SOC) orbitals.

structure. The  $\text{Pr}^{4+}$  ion is coordinated by eight oxygen atoms in a cube. Figure 4 shows the  $f^1$  energy-level splitting scheme in the presence of cubic CF and SOC. Without SOC, the cubic CF splits the  $f^1$  states into the  $t_{1u}$  ground state and  $t_{2u}$  and  $a_{2u}$  excited states [see Figs. 4(a) and 4(c)]. Table II lists the CF eigenvalues of these states (small sixth-order CF ignored) and the calculated LDA+ $U$  energies using the conventional approaches and our scheme at the optimal values of  $J=0.783$  eV and  $c=0.6$ . The conventional schemes predict orbital energies that deviate dramatically from the expected CF order: the Liechtenstein approach predicts almost degenerate  $t_{1u}$  and  $t_{2u}$  while  $t_{2u}$  is the ground state in the Dudarev method. In contrast, our method successfully finds the correct  $t_{1u}$  ground state.

### C. Eigenstates of $\text{PrO}_2$ with SOC

The physics of orbital ordering in  $f$  systems is affected by strong relativistic effects,<sup>21</sup> necessitating the inclusion of

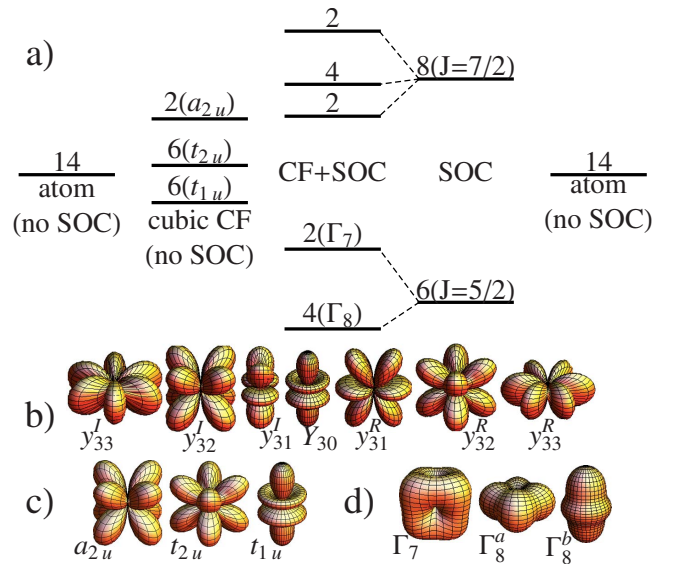


FIG. 4. (Color online) (a) Schematics of  $f^1$  energy levels (with multiplicity) split by SOC and cubic CF. The angular wave functions are shown for (b) real-valued atomic orbitals  $\Psi_3$ , CF eigenstates (c) without and (d) with SOC.

TABLE II. Comparison of the LDA+ $U$  energy of PrO<sub>2</sub> and crystal-field eigenvalues. Ground-state energy is given in bold.

	$Y_{30}(t_{1u})$	$y_{32}^R(t_{2u})$	$y_{32}^I(a_{2u})$
Energy eigenvalue in cubic CF (arbitr. unit)	-3	1	6
LDA+ $U$ energy in different schemes (eV)			
Liechtenstein	<b>-23.848</b>	<b>-23.843</b>	-23.488
Dudarev	-23.693	<b>-23.877</b>	-23.458
This work	<b>-24.260</b>	-24.128	-23.834

SOC to make direct comparisons with experiment. Including SOC, our method predicts that the energies of the CF degenerate  $\Gamma_8^a$  and  $\Gamma_8^b$ , and the excited  $\Gamma_7$  states in PrO<sub>2</sub> [Fig. 4(d)] are 0 (reference), 69, and 142 meV, respectively. The spurious 69 meV splitting between the two degenerate  $\Gamma_8$  states is consistent with the accuracy shown in Fig. 3. Neglecting Jan-Teller lattice distortions and magnetic ordering effects, we estimate that the  $\Gamma_7/\Gamma_8$  CF splitting is between 73 and 142 meV, in good agreement with the measured value of 131 meV from neutron diffraction.<sup>32</sup>

#### D. Aspherical SIE in other methods

Our method bears some likeness to the hybrid functional approach. The difference in the latter is that the exchange interactions are calculated directly from the wave functions, with the amount of the exact or Fock exchange ( $U/2+aJ$  for one localized electron in terms of LDA+ $U$ ), as well as the replaced LDA/GGA exchange controlled by a fixed parameter  $a_{\text{EXX}}$ . However,  $a_{\text{EXX}}$  in the hybrid functional method is often system dependent and fitted to experimental data, just like  $U$  in LDA+ $U$ . For instance, Ref. 33 found that in  $f$  systems good results were obtained using 40–70 % Fock exchange while  $d$  systems typically require 20–50 %.<sup>34</sup> However, such an  $a_{\text{EXX}}$  may not necessarily lead to accurate removal of the aspherical SIE. Figure 5 shows the energy of the Pr<sup>4+</sup> ion as a function of  $a_{\text{EXX}}$  calculated with the hybrid functional (HSE06).<sup>35</sup> Nearest degeneracy is obtained at  $a_{\text{EXX}} \approx 85\%$ . Given the sensitive orbital dependence of SI demonstrated in this work, in general the accuracy of hybrid functional calculations for  $f$ -electron systems may still suffer from incomplete removal of the aspherical SIE. After the first submission of this paper, we became aware that the idea of removing on-site  $E_{\text{H}}$  from LDA+ $U$  was previously proposed from a different perspective in Ref. 36 in which the

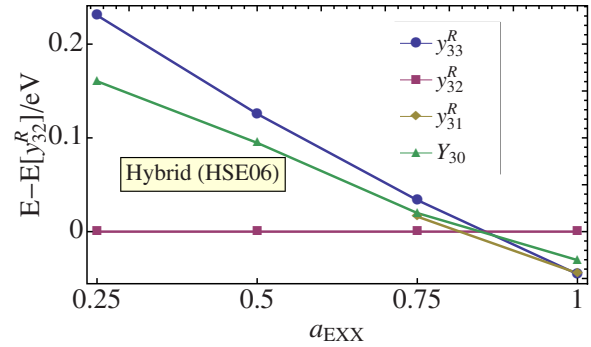


FIG. 5. (Color online) Total energy of the Pr<sup>4+</sup> ion for different filling of real orbitals as a function of  $a_{\text{EXX}}$ , the fraction of exact exchange, with the HSE06 method. Most calculations for complex orbitals  $Y_{3m}$  converged to very different states and are not shown.

exchange double-counting is independent of the orbital filling, an important difference from our approach. Therefore, the method of Ref. 36 is not expected to give accurate removal of the orbital-dependent SIE.

#### IV. SUMMARY

In summary, we have identified a serious problem in applying the LDA+ $U$  method to  $f$ -electron systems: the degeneracy of atomic orbitals is lifted, resulting in qualitatively incorrect electronic ground states and orbital excitation spectra. Aspherical orbital-dependent self-interaction is identified as the main source of error. To correct it, an LDA+ $U$  scheme is proposed, which leaves the Hartree intact and only replaces the LDA exchange with the Hartree-Fock exchange. Our method has one adjustable parameter  $U$ , with the other two ( $J$  and  $c$ ) being determined from the condition of orbital degeneracy in free ions. The computational expense is approximately the same as in the conventional LDA+ $U$  and very competitive compared to hybrid functional approaches.<sup>37</sup> We expect that our method will scale to large systems and will significantly improve the accuracy of first-principles studies of  $f$  as well as heavy  $d$  systems with significant relativistic effects. Additionally, more advanced methods such as GW and DMFT could benefit from the correct input ground-state orbitals generated by our method.

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<sup>1</sup>M. Pepper and B. E. Bursten, Chem. Rev. (Washington, D.C.) **91**, 719 (1991).

<sup>2</sup>M. Dolg and H. Stoll, in *Handbook of Chemistry and Physics of Rare Earths*, edited by K. A. Gschneidner and L. Eyring (Elsevier, Amsterdam, 1996), Vol. 22, pp. 607–729.

<sup>3</sup>J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

<sup>4</sup>A. Svane, W. M. Temmerman, Z. Szotek, J. Laegsgaard, and H. Winter, Int. J. Quantum Chem. **77**, 799 (2000).

<sup>5</sup>L. Petit, A. Svane, Z. Szotek, and W. M. Temmerman, Science **301**, 498 (2003).

<sup>6</sup>A. Svane, L. Petit, Z. Szotek, and W. M. Temmerman, Phys. Rev. B **76**, 115116 (2007).

- <sup>7</sup>A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
- <sup>8</sup>A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- <sup>9</sup>K. N. Kudin, G. E. Scuseria, and R. L. Martin, Phys. Rev. Lett. **89**, 266402 (2002).
- <sup>10</sup>I. D. Prodan, G. E. Scuseria, J. A. Sordo, K. N. Kudin, and R. L. Martin, J. Chem. Phys. **123**, 014703 (2005).
- <sup>11</sup>P. J. Hay, R. L. Martin, J. Uddin, and G. E. Scuseria, J. Chem. Phys. **125**, 034712 (2006).
- <sup>12</sup>I. D. Prodan, G. E. Scuseria, and R. L. Martin, Phys. Rev. B **73**, 045104 (2006).
- <sup>13</sup>J. L. F. Da Silva, M. V. Ganduglia-Pirovano, J. Sauer, V. Bayer, and G. Kresse, Phys. Rev. B **75**, 045121 (2007).
- <sup>14</sup>W. Metzner and D. Vollhardt, Phys. Rev. Lett. **62**, 324 (1989).
- <sup>15</sup>L. V. Pourovskii, B. Amadon, S. Biermann, and A. Georges, Phys. Rev. B **76**, 235101 (2007).
- <sup>16</sup>D. Jacob, K. Haule, and G. Kotliar, EPL **84**, 57009 (2008).
- <sup>17</sup>V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).
- <sup>18</sup>V. I. Anisimov, *Strong Coulomb Correlations in Electronic Structure Calculations: Beyond the Local Density Approximation, Advances in Condensed Matter Science* (Gordon and Breach, Amsterdam, The Netherlands, 2000).
- <sup>19</sup>P. Larson, W. R. L. Lambrecht, A. Chantis, and M. van Schilf-gaarde, Phys. Rev. B **75**, 045114 (2007).
- <sup>20</sup>F. Tran, J. Schweifer, P. Blaha, K. Schwarz, and P. Novak, Phys. Rev. B **77**, 085123 (2008).
- <sup>21</sup>T. Hotta, Rep. Prog. Phys. **69**, 2061 (2006).
- <sup>22</sup>A. B. Shick, W. E. Pickett, and A. I. Liechtenstein, J. Electron Spectrosc. Relat. Phenom. **114–116**, 753 (2001).
- <sup>23</sup>G. Jomard, B. Amadon, F. Bottin, and M. Torrent, Phys. Rev. B **78**, 075125 (2008).
- <sup>24</sup>B. Amadon, F. Jollet, and M. Torrent, Phys. Rev. B **77**, 155104 (2008).
- <sup>25</sup>E. R. Ylvisaker, W. E. Pickett, and K. Koepernik, Phys. Rev. B **79**, 035103 (2009).
- <sup>26</sup>A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).
- <sup>27</sup>S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57**, 1505 (1998).
- <sup>28</sup>G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).
- <sup>29</sup>G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
- <sup>30</sup>P. E. Blochl, Phys. Rev. B **50**, 17953 (1994).
- <sup>31</sup>C. H. Gardiner, A. T. Boothroyd, P. Pattison, M. J. McKelvy, G. J. McIntyre, and S. J. S. Lister, Phys. Rev. B **70**, 024415 (2004).
- <sup>32</sup>A. T. Boothroyd, C. H. Gardiner, S. J. S. Lister, P. Santini, B. D. Rainford, L. D. Noailles, D. B. Currie, R. S. Eccleston, and R. I. Bewley, Phys. Rev. Lett. **86**, 2082 (2001).
- <sup>33</sup>D. Torumba, P. Novak, and S. Cottenier, Phys. Rev. B **77**, 155101 (2008).
- <sup>34</sup>F. Cora, M. Alfredsson, G. Mallia, D. S. Middlemiss, W. C. Mackrodt, R. Dovesi, and R. Orlando, Struct. Bonding (Berlin) **113**, 171 (2004).
- <sup>35</sup>J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 219906 (2006).
- <sup>36</sup>D.-K. Seo, Phys. Rev. B **76**, 033102 (2007).
- <sup>37</sup>P. Novák, J. Kuneš, L. Chaput, and W. E. Pickett, Phys. Status Solidi B **243**, 563 (2006).