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Anisotropy and magnetism in the LSDA+U method

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Consequences of anisotropy (variation in orbital occupation) and magnetism, and their coupling, are analyzed for local-spin-density approximation (LSDA) plus interaction term U (LSDA+U) functionals, with both the commonly used ones as well as less commonly applied functionals. After reviewing and extending some earlier observations for an isotropic interaction, the anisotropies are examined more fully and related to use with the local-density approximation or with the LSDA. The total energies of all possible integer configurations of an open f shell are presented for three functionals, where some differences are found to be dramatic. Differences between how the commonly used "around mean-field" (AMF) and "fully localized limit" (FLL) functionals perform are traced to such differences. The LSDA+U interaction term, when applied self-consistently, usually enhances spin magnetic moments and orbital polarization, and the double-counting terms of both functionals provide an opposing moderating tendency ("suppressing the magnetic moment"). The AMF double-counting term gives magnetic states a significantly larger energy penalty than does the FLL counterpart.

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I. INTRODUCTION

Density-functional theory (DFT) and its associated local-(spin-) density approximation [L(S)DA] are used widely to describe the properties of a wide variety of materials often with great success. However there exists a class of materials which are poorly described, sometimes qualitatively, by LDA. These so-called strongly correlated materials typically contain atoms with open d or f shells, in which the corresponding orbitals are in some sense localized. The LSDA plus interaction term U (LSDA+U) approach was introduced by Anisimov *et al.*[1] to treat correlated materials as a modification of LDA ("on top of LDA") that adds an intra-atomic Hubbard U repulsion term in the energy functional. Treated in a self-consistent mean-field ("Hartree-Fock") manner, in quite a large number of cases the LDA+U result provides a greatly improved description of strongly correlated materials.

At the most basic level, the LSDA+U correction tends to drive the correlated orbital m occupation numbers $n_{m\sigma}$ (σ denotes spin projection) to integer values 0 or 1. This in turn produces, under appropriate conditions, insulating states out of conducting LSDA states, and the Mott insulating state of several systems is regarded as being well described by LSDA+U at the band theory level. Dudarev *et al.*[2] and Petukhov *et al.*[3] provided some description of the effect of the spin dependence of two different double-counting terms within an isotropic approximation. Beyond this important but simple effect, there is freedom in which of the spin orbitals ($m\sigma$) will be occupied, which can affect the result considerably and therefore makes it important to understand the effects of anisotropy and spin polarization in LSDA+U. After the successes of providing realistic pictures of the Mott insulating state in La_2CuO_4 and the transition-metal monoxides,[1] the anisotropy contained in the LSDA+U method produced the correct orbitally ordered magnetic arrangement for $KCuF_3$ that provided an understanding of its magnetic behavior.[4]

The anisotropy of the interaction, and its connection to the level of spin polarization, is a topic that is gaining interest and importance. One example is in the LSDA+U description of the zero-temperature Mott transition under pressure in the classic Mott insulator MnO. The first transition under pressure is predicted to be[5] an insulator-insulator (not insulator-metal) transition, with a $S=\frac{5}{2}\rightarrow S=\frac{1}{2}$ moment collapse and a volume collapse. The insulator-to-insulator aspect is surprising, but more surprising is the form of moment collapse: each orbital remains singly occupied beyond the transition, but the spins of electrons in two of the orbitals have flipped direction. This type of moment collapse is totally unanticipated (and hence disbelieved by some), but it is robust against crystal structure (occurring in both rocksalt and NiAs structures) and against reasonable variation in the interaction strength. Detailed analysis indicates that it is a product of the anisotropy of the LSDA+U interaction and the symmetry lowering due to antiferromagnetic order.

Another unanticipated result was obtained[6] in $LaNiO_2$, which is a metal experimentally. This compound is also a metal in LSDA+U over a very large range of interaction strength U rather than reverting to a Mott insulating Ni^{1+} system which would be isovalent with $CaCuO_2$. For values of U in the range expected to be appropriate for the Ni ion in this oxide, the magnetic system consists of an atomic singlet consisting of antialigned $d_{x^2-y^2}$ and d_{z^2} spins on each Ni ion. Again the anisotropy of the interaction evidently plays a crucial role in the result, with its effect being coupled thoroughly with band mixing effects.

The addition of a Hubbard U interaction also introduces the need for "double-counting" correction terms in the energy functional to account for the fact that the Coulomb energy is already included (albeit more approximately) in the LSDA functional. All double-counting schemes subtract an averaged energy for the occupation of a selected reference state depending only on $\{N_\sigma\}$, which largely cancels the isotropic interaction of the E_I term (2). Several forms for these double-counting terms have been proposed[1,7,8] but primarily two are commonly used. These LDA+U functionals are most often referred to as around mean field (AMF) and the fully localized limit (FLL), which is also referred to as the atomic limit (AL). The distinctions between these forms have attracted some discussion but without consideration of the full anisotropy of the interaction.

The need for double-counting corrections is not unique to the LDA+U method; any other method that adds correlation terms to the LSDA functional, such as the dynamical LDA +DMFT (dynamical mean-field theory) approach, will also require double-counting corrections. This is an unfortunate consequence of LDA's success; LDA works too well, even in correlated systems where it usually gets interatomic charge balance reasonably, to just throw it away.[9] The common approach has been to use LSDA for correlated materials and to include a double-counting correction. There are techniques being developed which do not build on a correction to DFT-LDA, but it remains to be seen whether these approaches will be successfully applied to a broad range of solid-state materials.

Although there has been much study on the performance of these LDA+U functionals in the context of real materials, and an early review of the method and some applications was provided by Anisimov *et al.*[10] relatively little has been done to understand, qualitatively and semiquantitatively, how the functionals operate based solely on their energetics distinct from DFT-LSDA effects. In this paper we analyze the functionals that are commonly used, as well as others which were introduced early on but are not so commonly used. Some of the nomenclature in the literature are confusing, so we try to clarify these confusions where we can.

II. LSDA+U CORRECTION ΔE

The LDA+U functional is usually coded in a form in which the choice of coordinate system is irrelevant, often referred to as the rotationally invariant form.[4] This form involves Coulomb matrix elements that have four orbital indices and the orbital occupation numbers are matrices in orbital space (viz. $n_{mm'}$). One can always (after the fact) rotate into the orbital Hilbert space in which the occupations are diagonal, in which case the interactions have only two indices. In our discussion we will work in the diagonal representation.

The LDA+U functionals considered here can all be written in the form

$$\Delta E = E_I - E_{\mathrm{dc}}, \tag{1}$$

where the direct interaction is

$$E_I = \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} W_{mm'}^{\sigma\sigma'} n_{m\sigma} n_{m'\sigma'} \tag{2}$$

and E_{dc} is the double-counting correction. The Coulomb matrix elements are given in terms of the direct and (spin-dependent) exchange contributions as

$$W_{mm'}^{\sigma\sigma'} = (U_{mm'} - J_{mm'}\delta_{\sigma,\sigma'}). \tag{3}$$

By the convention chosen here, E_I and E_{dc} are both positive quantities as long as the constants U and J (which define the matrix elements $U_{mm'}$ and $J_{mm'}$ but are not the same) are chosen conventionally, with U much larger than J.

Note that the orbital+spin diagonal term has been omitted in Eq. (2); there is no self-interaction in E_I. However, it is formally allowed to include the diagonal "self-interaction" term because the matrix element vanishes identically (self-interaction equals self-exchange: $U_{mm}=J_{mm}$) and it can simplify expressions (sometimes at a cost in clarity) if this is done. The double-counting correction depends only on the orbital sum N_σ, which appears up to quadratic order. A consequence is that it will contain non-vanishing terms in $n_{m\sigma}n_{m\sigma}$ which are self-interactions. Thus while the LSDA +U method was not intended as a self-interaction correction (SIC) method, it is not totally self-interaction free. In fact, the underlying LSDA method also contains self-interaction, and the double-counting term may serve to compensate somewhat this unwanted effect. We discuss self-interaction at selected points in this paper.

A. Short formal background to the LSDA+U method

The "LSDA+U method" is actually a class of functionals. Each functional has the same form of interaction E_I, with differences specified by

(1) Choice of the form of double-counting term.

(2) Choice of constants U and J. For a given functional, these are "universal" constants such as $\hbar, m, e$; i.e., they are not functional of the density in current implementations. Possibilities for doing so, that is, determining them self-consistently within the theory, have been proposed.[11]

(3) Choice of projection method to determine the occupation matrices from the Kohn-Sham orbitals. Given identical choices for (1) and (2) above, there will be some (typically small) differences in results from different codes due to the projection method.

The occupation numbers (or, more generally, matrices) are functionals of the density, $n_{m\sigma}[\rho]$, through their dependence on the Kohn-Sham orbitals. Then, whereas in LSDA one uses the functional derivative

$$\mathrm{LSDA}: \frac{\partial E_{\mathrm{LSDA}}[\{\rho_s\}]}{\partial \rho_\sigma(r)} \tag{4}$$

in minimizing the functional. In LSDA+U the expression generalizes to

$$\mathrm{LSDA+U}: \frac{\partial (E_{\mathrm{LSDA}}[\{\rho_s\}] + \Delta E[\{n_{ms}[\rho_s]\}])}{\partial \rho_\sigma(r)}. \tag{5}$$

Since the resulting spin densities ρ_s are changed by including the ΔE correction, the change in energy involves not only ΔE but also the change in E_{LSDA}. In practice, there is no reason to compare $E_{\mathrm{LSDA+U}}$ with E_{LSDA} as they are such different functionals. However, in the following we will be assessing the importance of the choice of the double-counting term in the LSDA+U functional, and it is of interest to compare, for fixed U and J, the energy differences between LSDA+U functionals differing only in their double-counting terms in order to understand the differing results. Even if the set of occupation numbers turn out to be the same (a situation we consider below), the densities ρ_σ will be different and the differences in E_{LSDA} may become important.

As with the nonkinetic-energy terms in E_{LSDA}, the functional derivatives of ΔE lead to potentials in the Kohn-Sham equation. These are nonlocal potentials, which (via the same projection used to define the occupation numbers) give rise to orbital-dependent (nonlocal) potentials

$$v_{m\sigma} \equiv \frac{\partial \Delta E}{\partial n_{m\sigma}} = v^{I}_{m\sigma} - v^{\mathrm{dc}}_{m\sigma},$$

$$v^{I}_{m\sigma} = \sum_{m'\sigma' \neq m\sigma} W^{\sigma\sigma'}_{mm'} n_{m'\sigma'}. \tag{6}$$

The double-counting orbital potential is discussed later.

The corresponding contribution to the eigenvalue sum E_{sum} is

$$\Delta E_{\mathrm{sum}} = \sum_{m\sigma} v_{m\sigma} n_{m\sigma}, \tag{7}$$

which is subtracted from the eigenvalue sum to obtain the Kohn-Sham kinetic energy. However, there are indirect effects of the orbital potentials that affect all of the kinetic and (LSDA) potential energies; these will be different for different ΔE functionals because the orbital potentials, which depend on the derivative of ΔE and not simply on the values of $n_{m\sigma}$, differ for each functional. This makes it necessary, for understanding the effects of the ΔE correction and the change in energy, to analyze the orbital potentials. We provide a brief discussion in Sec. V.

B. Fluctuation forms of LSDA+U

First we consider the class of functionals that can be written in what is termed here as a *fluctuation form*. The original LDA+U functional was introduced in 1991 by Anisimov *et al.*[1] and was written as

$$\Delta E^{\text{Fl-nS}} = \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} W^{\sigma\sigma'}_{mm'} (n_{m\sigma} - \bar{n})(n_{m'\sigma'} - \bar{n}), \tag{8}$$

where $\bar{n}=N^{\mathrm{corr}}/2(2l+1)$ is the average occupation of the correlated orbitals. (Henceforth $N \equiv N^{\mathrm{corr}}$.) Note that the energy is changed only according to *angular* "fluctuation" away from the (spin-independent) angular average occupation. This form is properly used with LDA (the "LDA averages" $\bar{n}$ are the reference) and not LSDA. This form was originally advocated with generic $(U - J\delta_{\sigma,\sigma'})$ matrix elements instead of the full Coulomb matrix, but we use the full $W^{\sigma\sigma'}_{mm'}$ here for comparison with other functionals.

In 1994, Czyzyk and Sawatzky[8] introduced a change to Eq. (8) and also proposed a new functional. The motivation for changing Eq. (8) was to use an LSDA exchange-correlation (xc) functional to treat spin-splitting effects rather than LDA. This change motivated the following equation:

$$\Delta E^{\text{Fl-S}} = \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} W^{\sigma\sigma'}_{mm} (n_{m\sigma} - \bar{n}_\sigma)(n_{m'\sigma'} - \bar{n}_{\sigma'}) = \Delta E^{\mathrm{AMF}}, \tag{9}$$

where $\bar{n}_\sigma = N_\sigma/(2l+1)$ is the average occupation of a single spin of the correlated orbitals. Here the energy correction is due to angular fluctuations away from the spin-dependent angular mean and hence must be used with LSDA. We point out that the authors in Ref. 8 refer to Eq. (8) as $E^{\mathrm{LDA+AMF}}$ and Eq. (9) as $E^{\mathrm{LSDA+AMF}}$. This wording may have caused subsequent confusion due to the way these terms have come to be used, and also because a discussion of the "+U" functionals requires explicit specification of whether LDA or LSDA is being used just to understand which functional is being discussed. Also confusing is that Solovyev *et al.*[12] re-justified Eq. (8) using "atomic limit" terminology.

The fluctuation forms of LSDA+U are automatically particle-hole symmetric since $n_{m\sigma} \to 1 - n_{m\sigma}$ and $\bar{n}_\sigma \to 1 - \bar{n}_\sigma$ gives $n_{m\sigma} - \bar{n}_\sigma \to -(n_{m\sigma} - \bar{n}_\sigma)$ and the expression is quadratic in these fluctuations. The general form of Eq. (1) need not be particle-hole symmetric.

Many authors (present authors included) have used the term LDA+U where the term LSDA+U would be more appropriate, which is especially confusing when discussing the AMF functional. We choose to depart from this confusing nomenclature by giving Eqs. (8) and (9) unique names specifying their fluctuation forms and their connection to LSDA (Fl-S) or to LDA (Fl-nS). We collect the double-counting terms for the various functionals, along with their connection to LDA or LSDA, in Table I.

C. FLL functional

The second functional introduced by Czyzyk and Sawatzky[8] is the FLL functional. (A $J=0$ version of FLL was introduced in 1993 by Anisimov *et al.*[7]) The authors referred to it (confusingly, as terminology has progressed) as the around mean-field functional but the atomic limit double-counting term; in the literature it is now referred to as the atomic limit or FLL functional. This functional cannot be written in the fluctuation form of the previous two functionals (the fluctuation form is exhausted by the -S and -nS cases). The FLL functional is written in the form (1), with the double-counting term given in Table I.

There is yet another LDA+U functional that is available, which was introduced in 1993 by Anisimov *et al.*[7] There is no clear name for it, but since it can be obtained by using $N_\sigma = N/2$ in E_{dc} for FLL, one might consistently refer to it as FLL-nS, corresponding to FLL with no spin dependence. The authors in Ref. 7 indicate that this functional is to be used with LDA, in accordance with the lack of spin dependence in the double-counting term.

D. Implementation of LSDA+U in some widely used codes

The Fl-nS functional is implemented in the WIEN2K code, as nldau=2, and called HMF (Hubbard in mean field);[13] however, it is apparently not often used. The Fl-S (AMF) functional is implemented in the WIEN2K code[13] as nldau=0

TABLE I. The double-counting terms of various LDA+U functionals. In the second expression two of them are rewritten to reflect how they are (somewhat deceptively) identical in form, but in one case a distinction between spin up and spin down (relative to half of N: $N_\sigma \leftrightarrow N/2$) is made. Note that while the first two forms appear to contain an isotropic self-interaction $[\frac{1}{2}UN^2$ rather than $\frac{1}{2}N(N-1)]$ they are derived from a form which *explicitly* has *no* self-interaction between the orbital fluctuations $\delta_{M\sigma}$. See text for more discussion.

LDA+U Functional	E_{dc}=E_{dc} (rewritten)	DFT xc Functional
Fl-nS	$\frac{1}{2}UN^2-\frac{U+2lJ}{2l+1}\frac{1}{4}N^2=\frac{1}{2}UN^2-\frac{U+2lJ}{2l+1}\frac{1}{2}\Sigma_\sigma(\frac{N}{2})^2$	LDA
Fl-S (AMF)	$\frac{1}{2}UN^2-\frac{U+2lJ}{2l+1}\frac{1}{2}\Sigma_\sigma N_\sigma^2=\frac{1}{2}UN^2-\frac{U+2lJ}{2l+1}\frac{1}{2}\Sigma_\sigma N_\sigma^2$	LSDA
FLL	$\frac{1}{2}UN(N-1)-\frac{1}{2}J\Sigma_\sigma N_\sigma(N_\sigma-1)=\frac{1}{2}UN(N-1)$ $-\frac{1}{2}J\Sigma_\sigma(N_\sigma^2-N_\sigma)$	LSDA
FLL-nS	$\frac{1}{2}UN(N-1)-\frac{1}{4}JN(N-2)=\frac{1}{2}UN(N-1)-\frac{1}{2}J\Sigma_\sigma[(\frac{N}{2})^2$ $-N_\sigma]$	LDA

and the FPLO code[14] as AMF. It is also available in the ABINIT code[15] when using a PAW basis set[16] by setting usepawu =2.

The FLL functional is implemented in several general-purpose DFT codes such as WIEN2K (nldau=1),[13] FPLO (select AL in fedit),[14] VASP, PW/SCF, and ABINIT (usepawu=1) when using a PAW basis set. The FLL-nS functional is available in VASP.

E. General remarks

When the Fl-nS and Fl-S functionals are written in their fluctuation form, there is no separate double-counting term; hence, one does not need the double-counting interpretation. They can of course be expanded to be written in the "interaction minus double-counting" form (2), which is useful especially for comparing with functionals that can only be written in that form. A comparison of the double-counting terms is given in Table I. Reducing all to interaction minus double-counting form makes the difference between the functionals most evident. Since they all have the same "direct-interaction" term, the *only difference* between the functionals is what double-counting energy is used; the uninteresting tail seems to be wagging the exciting dog, which is in fact the case. The double-counting terms can be reduced to dependence only on N and N_σ thanks summation rules (there is at least one free index) on the $U_{mm'}$ and $J_{mm'}$ matrices,

$$\sum_m U_{mm'} = (2l+1)U \tag{10}$$

$$\sum_m J_{mm'} = U + (2l)J, \tag{11}$$

that is, the sum over any column (or row) of the U and J matrices is a fixed simple value, which depends on the input parameters U and J. One can then simply see that a sum over a column of W is $(2l+1)U$ if $\sigma \neq \sigma'$ and $2l(U-J)$ if $\sigma = \sigma'$.

The $U_{mm'}$ and $J_{mm'}$ matrices satisfy, by definition, $U_{mm} - J_{mm} = 0$, so that there is no self-interaction, whether or not the (vanishing) diagonal term $m\sigma = m'\sigma'$ is included in the interaction term. As mentioned earlier, the following analysis assumes that the occupation matrix has been diagonalized. While this can always be done, the transformed matrix elements $U_{mm'}$ and $J_{mm'}$ will not be exactly what we have used in Sec. VI.

III. ANALYSIS OF THE FUNCTIONALS

A. J=0 simplification

It is not uncommon for practitioners to use "effective" values $\tilde{U} = U - J, \tilde{J} = 0$ and insert these constants (for U, J) into LDSA+U. For J=0, of course Hund's coupling (intra-atomic exchange) is lost, but J also controls the anisotropy of the interaction, and for J=0 anisotropy also is lost ($U_{mm'} \equiv U$ as well as $J_{mm'} \equiv 0$ for $m \neq m'$). This case is relatively simple. It seems that it should provide the "big picture" of what LSDA+U does with simple Coulomb repulsion, and it has been discussed several times before. With J=0, the fluctuation functionals simplify to

$$\begin{aligned}
\Delta E_{J=0}^{\mathrm{Fl}\text{-}\kappa} &= \frac{U}{2} \sum_{m\sigma \neq m'\sigma'} \delta n_{m\sigma} \delta n_{m'\sigma'} \\
&= \frac{U}{2}\left[\left(\sum_{m\sigma} \delta n_{m\sigma}\right)^2 - \sum_{m\sigma} (\delta n_{m\sigma})^2\right] \\
&= -\frac{U}{2}\sum_{m\sigma} (\delta n_{m\sigma})^2 \\
&\equiv -\frac{U}{2}\Gamma_\kappa^2 \leq 0,
\end{aligned} \tag{12}$$

because the sum of fluctuations vanishes by definition for either form κ=nS or S; note the "sign change" of this expression when the diagonal terms are added, and subtracted, to simplify the expression. Here Γ^2 is the sum of the squares of the fluctuations bounded by $0 \leq \Gamma_\kappa^2 \leq N$. For integer occupations the energy corrections for Fl-nS and Fl-S (AMF) can be written as

$$\Delta E_{J=0}^{\mathrm{Fl}\text{-}\mathrm{S}} = -\frac{U}{2}\left[N(1-\bar{n}) - \frac{M^2}{2(2l+1)}\right],$$

$$\Delta E^{\text{Fl-nS}}_{J=0} = -\frac{U}{2}N(1-\bar{n}). \tag{13}$$

There are two things to note here.

1. In Fl-nS, the energy is independent of both the spin and orbital polarization of the state, which lacks the basic objective of what LSDA+U is intended to model. Considering the form of its double-counting term (see Table I) with its self-interaction term (proportional to N^2), Fl-nS for $J=0$ becomes simply a self-interaction correction method.

2. In Fl-S (AMF), configurations with magnetic moments are energetically *penalized proportionally* to U and quadratically with M. In Secs. V and VI we will discuss the partial cancellation with the LSDA magnetic energy.

Under the same conditions, the FLL functional becomes

$$\Delta E^{\text{FLL}} = \frac{U}{2}\sum_{m\sigma} n_{m\sigma}(1-n_{m\sigma}) \geq 0. \tag{14}$$

Solovyev *et al.*[12] noted the important and easily recognizable characteristics of this expression. Besides being nonnegative, for integer occupations the energy vanishes. It is a simple inverted parabola as a function of each $n_{m\sigma}$. From the derivative, the orbital potentials are linear functions of $n_{m\sigma}$, with a discontinuity of U when $n_{m\sigma}$ crosses an integer value. These characteristics underlie the most basic properties of the LSDA+U method: integer occupations are energetically preferred, and discontinuities in the potentials model realistically the Mott insulator gap that occurs in strongly interacting systems at (and only at) integer filling.

B. $J \neq 0$ but isotropic

Simplification of the full expression for functional results by separating out the isotropic parts of the interaction,

$$U_{mm'} = U + \Delta U_{mm'}, \tag{15a}$$

$$J_{mm'} = U\delta_{mm'} + J(1-\delta_{mm'}) + \Delta J_{mm'}. \tag{15b}$$

The isotropic parts simplify, giving

$$\Delta E^{\text{Fl-nS}} = -\frac{U-J}{2}\sum_{m\sigma} n^2_{m\sigma} - \frac{J}{4}M^2 + \frac{U-J}{2}N\bar{n} + \Delta E^{\text{aniso}}, \tag{16}$$

$$\Delta E^{\text{Fl-S}} = -\frac{U-J}{2}\sum_{m\sigma} n^2_{m\sigma} + \frac{U-J}{4}\frac{M^2}{2l+1} + \frac{U-J}{2}N\bar{n} + \Delta E^{\text{aniso}}, \tag{17}$$

$$\Delta E^{\text{FLL}} = -\frac{U-J}{2}\sum_{m\sigma} n^2_{m\sigma} + \frac{U-J}{2}N + \Delta E^{\text{aniso}}, \tag{18}$$

with the universal anisotropy contribution

$$\Delta E^{\text{aniso}} = \frac{1}{2}\sum_{mm'\sigma\sigma'} \Delta W^{\sigma\sigma'}_{mm'} n_{m\sigma} n_{m'\sigma'}, \tag{19}$$

$$\Delta W^{\sigma\sigma'}_{mm'} \equiv \Delta U_{mm'} - \Delta J_{mm'}\delta_{\sigma\sigma'}. \tag{20}$$

being the anisotropic part of the interaction matrix elements. These equations, up to the ΔW term, are the extensions of Eq. (13) to include isotropic exchange in explicit form.

The first term in each of these expressions contains $-\frac{1}{2}\tilde{U}n^2_{m\sigma}(\tilde{U}\equiv U-J)$ and hence has the appearance of a self-interaction correction. Since the diagonal term of the interaction E_I is specifically excluded, it does not actually contain any self-interaction; in fact, the sign of the interaction E_I is *positive*. (The double-counting term does contain terms quadratic in N which must be interpreted as self-interaction.) Nevertheless, the rewriting of the functional leads to a self-interaction-like form and that part of the functional will have an effect related to what appears in the self-interaction-corrected LDA method, but by an amount proportional to $\tilde{U}$ rather than a direct Coulomb integral, depending on the difference of $n_{m\sigma}$ from the reference occupation (see Sec. IV).

C. Fl-nS

For Fl-nS, if we are restricted to integer occupations (so $n^2_{m\sigma}=n_{m\sigma}$), then Γ^2 depends only on N, so the first term in $\Delta E^{\text{Fl-nS}}$ above depends only on N. Then, up to corrections in ΔU and ΔJ, the state with the largest total spin moment will be favored; this is Hund's first rule. In fact, even with the ΔU and ΔJ terms, the $-JM^2/4$ term is still strongly dominant. Except for $N=7$, there are many ways to arrange electrons in orbitals which maximize S. Energy differences between these arrangements arise only from anisotropy (ΔU and ΔJ) and spin-orbit (SO) coupling.

D. Fl-S

In Fl-S, instead of having the $-JM^2/4$ term from Fl-nS which *favors* magnetism, there is a term $\frac{(U-J)}{4(2l+1)}M^2$ which *opposes* magnetism. This term (as in the $J=0$ case) comes from the occupation variance which wants to evenly distribute electrons across both spin channels. Within LSDA there is something like a Stoner term of the form $-\frac{1}{4}IM^2$ which will compete with this Fl-S magnetic penalty. We return to this aspect in Secs. IV–VII and in the Appendix.

E. Spin-orbit coupling and particle-hole symmetry

Without spin-orbit interaction, for a given N there are many states that are degenerate for both double-counting schemes. Every value of N has at least four degeneracies those with $\pm L_z$, $\pm S_z$.

Any state which has the same number of spin-up as spin-down electrons ($M=0$) gives the same energy from Fl-nS and Fl-S; since then $\bar{n}_\uparrow=\bar{n}_\downarrow=\bar{n}$ (the orbital potentials are distinct however). Of course this fixed $N, M=0$ specification may contain many different configurations. Looking at results mentioned later, for Fl-S the ground state for an even number of electrons is $S_z=0$ (so $\bar{n}_\sigma=\bar{n}$); thus, the configuration which gives the Fl-S ground state has the same energy in Fl-S and Fl-nS.

IV. FRACTIONAL OCCUPATIONS

Here we briefly discuss the effect of noninteger occupations in LSDA+U. Taking a general set of occupations as $\{n_{m\sigma}\}$, we define a set of integer occupations $\{\hat{n}_{m\sigma}\}$ and the fractional part of the occupations as $\gamma_{m\sigma}=n_{m\sigma}-\hat{n}_{m\sigma}$. For illustration purposes we will choose the simplest possible scenario, where charge is transferred to an empty orbital a from an occupied orbital b both of the same spin, so that $0<\gamma_{a\uparrow}=-\gamma_{b\uparrow}$, $\hat{n}_{a\uparrow}=0$, and $\hat{n}_{b\uparrow}=1$. With this selection, N_σ is unchanged (and therefore N and M as well), so that E_{dc} is unchanged. Thus, the effect of the charge transfer is entirely contained in the E_I term. Expanding E_I for the general occupation set gives

$$E_I[\{n_{m\sigma}\}]-E_I[\{\hat{n}_{m\sigma}\}]=U\gamma_{a\uparrow}(1-\gamma_{a\uparrow}) \tag{21}$$

for the $J=0$ case, and for $J\neq 0$ we find

$$E_I[\{n_{m\sigma}\}]-E_I[\{\hat{n}_{m\sigma}\}]=\sum_{m\sigma}(W_{am}^{\uparrow\sigma}-W_{bm}^{\uparrow\sigma})\hat{n}_{m\sigma}\gamma_{a\uparrow}-W_{ab}^{\uparrow\uparrow}\gamma_{a\uparrow}^2. \tag{22}$$

The dominant term in Eq. (22) is where $m\sigma=b\uparrow$. This term gives a contribution $W_{ab}^{\uparrow\sigma'}\gamma_{a\uparrow}\sim U\gamma_{a\uparrow}$ (since $U\gg J$ for typical parameter choices, where other terms give contributions proportional to $(W_{am}^{\uparrow\sigma}-W_{bm}^{\uparrow\sigma})\gamma_{a\uparrow}\propto J\gamma_{a\uparrow}$. The term with $m\sigma=a\uparrow$ is killed off by the factor of $\hat{n}_{a\uparrow}$ and the term in γ^2 is significantly smaller than the others for $\gamma<0.5$.

This shows that there is an energy penalty for fractional occupation proportional to U and *linear* in γ at small γ. Thus, in configuration space, the LSDA+U functionals have many local minima around configurations with integer occupations. This result is fairly general. Even for charge transfer between orbitals of opposite spins, the linear energy penalty in γ is still dominant over any additional terms coming from the double counting or spin-orbit.

In practice, this gives the possibility that LSDA+U will get "stuck" in a local minimum with some configuration that may not be the true ground state. This behavior is not uncommon; LSDA+U has been reported[17] to find multiple local minima depending on the starting configuration.

V. ORBITAL POTENTIAL MATRIX ELEMENTS

Up to now only the energy functionals themselves were discussed. Now we return to the derivatives: the orbital potentials $v_{m\sigma}$. It is simple to derive the exact expressions, and the interaction term E_I common to all forms gives a potential $\Delta v_{m\sigma}$ which depends only on the occupations of the *other* orbitals $n_{m'\sigma'}, m'\sigma'\neq m\sigma$. The potential resulting from the double-counting term is functional specific and may contain a contribution from $n_{m\sigma}$ itself, i.e., a self-interaction.

We confine our observations here to the subdivision (introduced just above) of the interaction into a unitarily invariant isotropic part and into an anisotropic part (2) that is much smaller and more difficult to analyze. As for the energy itself, it is convenient to add and subtract the diagonal self-Coulomb and self-exchange, which makes the effect of the potential much more transparent at the cost of introducing the misleading self-interaction interpretation.

The potential matrix elements are

$$\Delta v_{m\sigma}^{\text{Fl-nS}}=-(U-J)[n_{m\sigma}-\bar{n}]-\frac{J}{2}M\sigma+\Delta v_{m\sigma}^{\text{aniso}}, \tag{23}$$

$$\Delta v_{m\sigma}^{\text{Fl-S}}=-(U-J)[n_{m\sigma}-\bar{n}_\sigma]+\frac{U-J}{2}\frac{M}{2l+1}\sigma+\Delta v_{m\sigma}^{\text{aniso}}, \tag{24}$$

$$\Delta v_{m\sigma}^{\text{FLL}}=-(U-J)\left[n_{m\sigma}-\frac{1}{2}\right]+\Delta v_{m\sigma}^{\text{aniso}}, \tag{25}$$

with the anisotropic potential term

$$\Delta v_{m\sigma}^{\text{aniso}}=\sum_{m'\sigma'}\Delta W_{mm'}^{\sigma\sigma'}n_{m'\sigma'}. \tag{26}$$

The main-occupation-number-dependent term, proportional to $n_{m\sigma}$, has a self-interaction appearance and effect, as discussed above for the functionals. The differences in this term arise from the "reference" occupation with which $n_{m\sigma}$ is compared to determine the potential shift. The fluctuation $n_{m\sigma}-n_{\text{ref}}$ is smaller for Fl-S (AMF) than for Fl-nS because the occupation for a given spin direction tends to be closer to $\bar{n}_\sigma$ than to $\bar{n}$. The reference occupation for FLL is, like Fl-ns, spin independent; in fact, the reference is half filling. In this sense, FLL seems more like a single-band Hubbard model treatment than the other two functionals.

The other difference that is evident in this form is the spin dependence. Fl-nS additionally has a spin-orientation-dependent potential shift proportional to J and to M (similar to an LSDA treatment but using J instead of the Stoner I) and enhances spin splitting of the eigenenergies ε accordingly. In Fl-S (AMF) the analogous term is $+(U-J)\frac{M}{2(2l+1)}\sigma$, with a sign that impedes magnetism. It can be simplified to $\approx\frac{J}{2}M\sigma$ when $U\approx 2(l+1)J$. This expression illuminates the reason that AFM is sometimes found to *decrease* the magnetic moment. This term more or less cancels the spin splitting of LSDA due to the opposite sign. What is left is a splitting of occupied and unoccupied levels due to the $n_{m\sigma}$ term, which is almost independent of M. The effect is to support a spin-polarized solution but to provide little discrimination between different M. Since the spin-polarization energy does not favor large M, we end up with a tendency of a near degeneracy of different M values, as we already pointed out from purely energetic arguments. For the case of a half-filled fully polarized shell $n_{ms}=\delta_{\sigma,1}$ (the case of $N=M=7$ in Sec. VI), the potential matrix vanishes, which can be seen from $\bar{n}=\frac{1}{2}\frac{M}{2(2l+1)}=\bar{n}=\frac{1}{2}$. However, at the same time the energy contribution also vanishes $\Delta E^{\text{Fl-S}}=0$ (for integer occupations) and the Fl-S functional has no effect at all.

The SIC term in FLL splits occupied and unoccupied states symmetrically, while in the fluctuation functionals the splitting happens with respect to the averaged occupation, which is seen in the overall energy positions in Fig. 3.

VI. NUMERICAL RESULTS

Following common terminology, for the remainder of the paper we refer to the Fl-S functional simply as the AMF form. We have taken values for $U_{mm'}$ and $J_{mm'}$ (used for Eu) from Ref. 18 (recalculated to include more significant figures). These matrices are generated using $U=8$ and $J=1$ (values typical of rare earths) following the procedure given in the appendix of Ref. 8.

In our analysis of the AMF and FLL functionals, which are based on an LSDA reference state, we include a Stoner term

$$E(M) = -\frac{1}{4}IM^2 \tag{27}$$

to model the magnetic effects of LSDA on the total energy. The addition of this term helps us to give a picture of the degree to which the functionals reproduce Hund's first rule. Typical values of I for ionized lanthanides are 0.75 eV, so we use this value for the calculations of this section. Further discussion of the Stoner I is included in the Appendix.

Spin-orbit interaction is included in the form

$$E_{\mathrm{SO}} = \lambda\vec{S}\cdot\vec{L} \rightarrow \sum_{m\sigma} S_z L_z, \tag{28}$$

where the second form applies when only z components of moments are treated, as is done in current implementations of the LSDA+U method. Due to this restriction, LSDA+U often does not produce the correct multiplet energies in the atomic limit. The visible result in LSDA+U band structures is splittings of occupied, or unoccupied, correlated suborbitals that can be as large as a few times J, and understanding the splittings is not straightforward. For $4f$ systems these splittings[18,19] may not be of much interest unless one of the correlated bands approaches the Fermi level. In heavy-fermion compounds, for example, LSDA+U results are used to infer which parts of the Fermi surface have a larger amount of f character.[20] The same effects (eigenvalue splittings) occur in $3d$ or $5f$ systems, however, where they are expected to become more relevant but are masked by stronger banding tendencies.

Here we consider values of λ of 0 and 0.2 eV. The magnitude of the spin-orbit interaction is not critical to the results; it mainly serves to break degeneracies. Without the spin-orbit interaction, the ground state for any of the functionals at a given N is degenerate with several other states. For instance with $N=6$, the AMF functional has states with $L_z=1, S_z=0$ and $L=11, S_z=0$ with the same lowest energy.

In Fig. 1 the ground states for both AMF and FLL with $U=8$, $J=1$, and $I=0.75$ are shown. The FLL and Fl-nS (not shown) schemes both reproduce Hund's rules exactly with these parameters. AMF does not reproduce Hund's rules (in fact penalizes magnetism) until I is increased to around 1.5, which is somewhat larger than reasonable values of I. If one expects LSDA+U to reproduce Hund's rules, then the AMF scheme performs rather poorly. For instance, at $N=7$, Hund's rules ask that all electrons be spin aligned, but the AMF ground state has only one unpaired spin due to the magnetic penalty appearing in Eq. (13). With these parameter choices, $U/(2l+1) > I$, so the AMF magnetic penalty wins over the Stoner energy. This is likely to be the case for $3d$ transition metals as well since $U_{3d}/(2l+1) \sim 1$ eV, but it may not be as significant since I for $3d$ elements is larger.

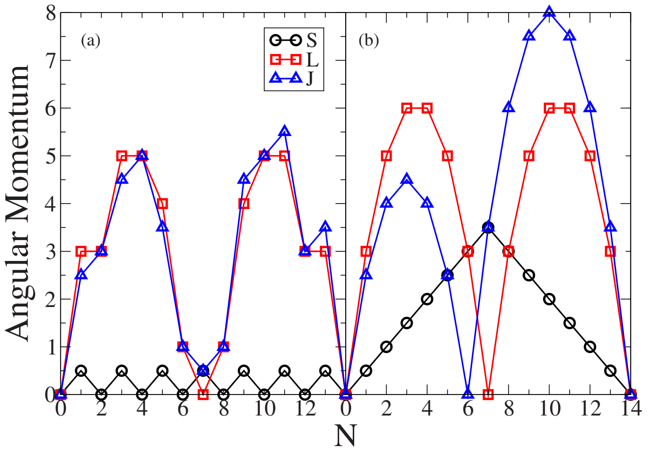

FIG. 1. (Color online) Angular momentum values of S_z, L_z, and J_z of the lowest-energy state for (a) AMF (Fl-S) and (b) FLL, with spin-orbit coupling. Parameter values are $U=8$, $J=1$, and $I=0.75$. The AMF (Fl-S) curves do not follow Hund's rules because the Stoner parameter is too small. FLL follows Hund's rules exactly with these parameters.

We examine the energetics in more detail in Fig. 2, where ΔE for the AMF and FLL functionals is plotted for every configuration for $N=7$. The configurations fall into separate lines for each spin moment M since E_{dc} depends only on N and M for both functionals. For the case of $J=0$, all the states with a particular M value collapse to a single energy value (the orbital index loses any impact). This is shown with the open squares. A value of I was chosen so that the cancellation discussed in the previous paragraph is slightly broken.

If we examine the $J=0$ case first (the large open squares in Fig. 2), we see that the separation of states in FLL is much larger than AMF (9 versus 3 eV), with $M=7$ as the lowest energy for FLL but highest for AMF. This is a direct consequence of the magnetic penalty of AMF discussed previ-

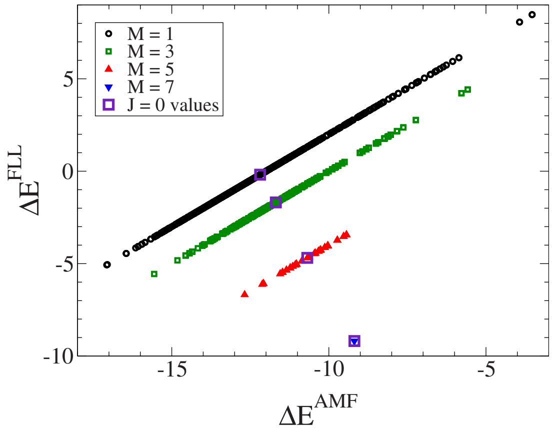

FIG. 2. (Color online) Shown here is ΔE^{FLL} plotted vs $\Delta E^{\mathrm{Fl\text{-}S}}$ for each of the 3432 configurations of $N=7$ electrons using $U=8, J=1, I=0.75$, all in eV. The ordering of states is shown for Fl-S by counting from left to right and for FLL by counting from bottom to top. Open squares show values for $U=7$ and $J=0$.

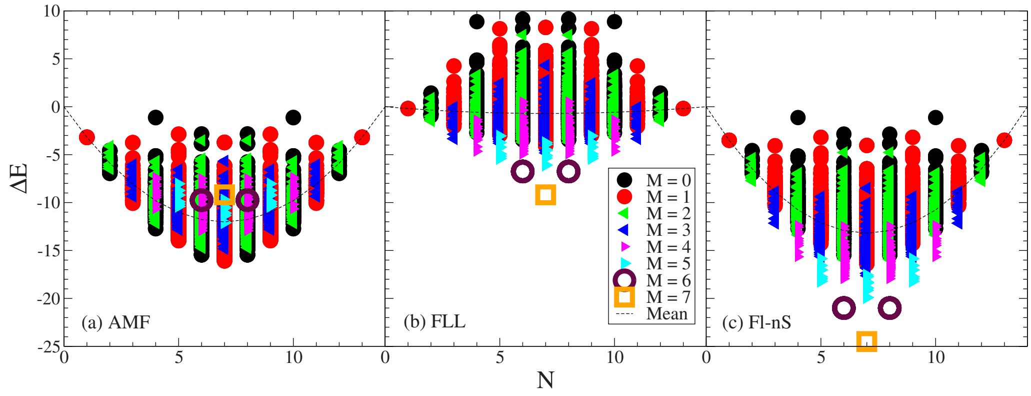

FIG. 3. (Color online) Scatter plot of all energies ΔE for all states in the (a) AMF (Fl-S), (b) FLL, and (c) Fl-nS double-counting schemes for $U=8$, $J=1$, and $I=0.75$ (FLL and AMF only). Spin-orbit is neglected here. For AMF, low-spin states (black and red circles) appear as lowest-energy configurations for all N, but this is not the case for FLL or Fl-nS. The dashed lines indicate the mean energy over configuration for each N; note that the variation with N is much less for FLL than for the other two functionals.

ously. If I were increased above 1 eV (keeping the other parameters fixed), then AMF would begin to favor the $M=7$ state by a small amount.

Once J is turned on, the degeneracy is split, and the configurations with a particular M spread out around the $J=0$ value. The spread is especially large for the highly degenerate $M=1$ value (from -5 to 8 eV), so that even if I were larger than the typical LSDA value [in which case, with $J=0$ AMF would favor a high-spin (HS) state] the large spread of $M=1$ values would cause the low-spin (LS) states to be favored in AMF. This spread is entirely coming from the E_I term and is independent of the double-counting choice. Here we see for AMF a competition between J and I. J is actually preferring a low-spin configuration in contrast to the conventional wisdom that J increases the tendency for magnetism. We see that this same tendency occurs in FLL, as for $J=0$ the separation between $M=7$ and 1 states is 9 eV, but with $J=1$ this separation is reduced to 4 eV. Since in FLL the Hubbard U does not penalize magnetic states the way AMF does, the presence of J is not able to compete with I. This makes it clear why FLL is generally accepted to perform better for systems known to have high-spin states (e.g., Eu and Gd). Conversely, FLL may be less successful at modeling low-spin states.

As mentioned previously, it is fairly common for theoretical studies to replace U and J with effective parameters $\tilde{U}$ and $\tilde{J}$. For any double-counting term chosen, using these effective parameters will lower the energy of the high-spin state relative to the low-spin state as compared to using U and J directly. With orbitals that are not highly localized, such as $3d$ or $5f$ state, it may be the case with FLL that the reduction in the energy separation between high spin and low spin caused by using U and J would allow for significant competition between magnetism and kinetic energy in LSDA+U.

We now have seen why and how FLL and AMF perform differently in assigning a magnetic moment. This may be of particular interest for studies of pressure-induced changes in magnetic moment such as that seen in MnO (Ref. 5) without changes in orbital M occupancy. Applications of LSDA+U are more thoroughly discussed in Sec. VII A.

Shown in Fig. 3 are scatter plots of the energies of all possible states for a given number of f electrons with integer occupations. SO is neglected, as it makes very minor changes to this picture by splitting some degeneracies. The particle-hole symmetry of each functional is apparent. In Fl-nS and FLL, the ground-state energy for $N=7$ is roughly 3 eV lower than the next level, which is the (degenerate) ground states for $N=6$ and 8. This is almost entirely due to the term depending on M^2 [either the J term in Eq. (8) or the Stoner term in FLL] because M is large and at its maximum with seven spins aligned. In AMF low-spin states can be seen at the low end of the range for configurations at each N; the high-spin states for $N=6$ and 7 are disfavored by 6–7 eV. We see that the trend where AMF favors low-spin configurations and FLL favors high-spin configurations shown for $N=7$ in Fig. 2 is present for all N. The large spread of values for low-spin configurations (black and red circles) is seen clearly for AMF as they appear in both the lowest-energy positions and the highest-energy positions. The high-spin configurations (large open symbols and triangles) are in the middle of each distribution for N. For, e.g., $N=5$, counting from the lowest energy, $M=1$ configurations are found first, followed by $M=3$ configurations then the $M=5$ configurations are found (with the trend reversing counting up to the highest-energy states). In FLL, the lowest-energy configurations for $N\neq 7$ are still the configurations with maximum spin for a given N, and states with lower spins are found in succession. Again using $N=5$ as an example, the $M=5$ configurations are lowest in energy and then $M=3$ configurations are seen at energies lower than $M=1$ states.

VII. DISCUSSION

In this paper we have tried to clarify the behavior of the various functionals that are used in the LSDA+U method, we have compared the functionals formally in certain limits, we have presented the orbital potentials that arise, and we have analyzed the total-energy corrections that LSDA+U functionals apply to LSDA total energies given a set of occupation numbers. The Fl-nS functional which was originally introduced strongly favors spin-polarized states as does the commonly used FLL functional. The other most commonly used functional besides FLL, Fl-S (AMF), has characteristics that tend to suppress moment formation or reduce the magnitude of the moment. When analyzed, this AMF functional shows positive-energy penalties to magnetism that compete with the magnetic tendencies of the LSDA functional, and when $J>0$ nonmagnetic solutions become even more likely to win out. We have provided a short analysis of the behavior when $J=0$ is used. While this case is instructive, we advise against its use; it is just as simple to do the full $J\neq 0$ calculation.

When LSDA+U is applied to correlated insulators in the strong-coupling regime, it provides a very good picture of the system at the band-structure (effective one-electron) level. The initial successes include the 3*d* transition-metal monoxides MnO, FeO, CoO, and NiO, for which the LSDA description is very poor. Other early successes included the insulating phases of the layered cuprates that become high-temperature superconductors when doped and the unusual magnetic insulator $KCuF_3$, which was the first case where crucial orbital ordering was reproduced. LSDA+U is not a satisfactory theory of single-particle excitations of such systems but nevertheless provides a realistic picture of the underlying electronic structure.

The more interesting, and more difficult, cases now lie between the strongly correlated limit of wide-gap magnetic insulators and weakly correlated regime that is well described by LSDA. Some of these are metals, some are unconventional insulators, and many lie near the metal-insulator borderline. It is for these intermediate cases that it becomes essential, if applying the LSDA+U approach, to understand what the method is likely to do and especially to understand the tendencies of the various choices of functional. This is what we have tried to clarify in this paper. As a summary, we will provide an overview of an assortment of results that have appeared in the literature for systems that lie somewhere in the intermediate correlation regime.

A. Examples of LSDA+U behavior from applications

1. Strongly correlated insulators

Cuprates. The insulating phase of the cuprate class of high-temperature superconductors comprised the "killer app" that served to popularize[1,21] the LSDA+U method, and in the intervening years the method has been applied to cuprates and other correlated insulators too many times to cite. Simply put, in cuprates it produces the Cu d^9 ion and accompanying insulating band structure.[21,22] The hole resides in the $d_{x^2-y^2}$ orbital and is strongly hybridized with the planar oxygen p_σ orbitals, as much experimental data was indicating.

MnO. Experimentally, MnO shows at room temperature a moment collapse from $M=5$ to 1 (or less), a volume collapse, and an insulator-to-metal transition, near 100 GPa; this is the classic Mott transition. Within LSDA, the moment decreases continuously with decreasing volume,[23] from the HS state to a LS state. The insulator-to-metal transition occurs at a much too low pressure (without any other change). A volume collapse is predicted, although the pressure is significantly overestimated (150 GPa).

The application of LSDA+U in its FLL flavor has been applied and analyzed in detail[5] and provides a different picture in several ways. The ambient pressure band gap is improved compared to experiment. The volume collapse transition occurs around 120 GPa and is accompanied by a moment collapse from $M=5$ to 1. The nature of this (zero-temperature) transition is insulator to insulator, while the experimental data indicate an insulator-to-metal transition at room temperature. The zero-temperature transition might indeed be insulator to insulator; such a phase transition would be a type that LSDA+U should work well for. It is also possible that the static mean-field approximation underlying LSDA+U, which favors integer occupations and hence insulating solutions, has a too strong tendency and fails to describe this transition. This question could be settled by studying experimentally the Mott transition at low temperature.

Even more unexpected than the insulator-to-insulator aspect is the LSDA+U prediction that the low-spin state has an unanticipated orbital occupation pattern,[5] being one in which every 3*d* orbital remains singly occupied (as in the high-spin state), but spin in two orbitals antialign with those in the other three orbitals. This state is obtained simply from the $M=5$ high-spin state by flipping the spins of two of the orbitals. The resulting density remains spherical, but the spin density exhibits an angular nodal structure leading at the same time to a high degree of polarization of the spin density but with a low total moment ($M=1$). This solution (being the high-pressure ground state in LSDA+U) can be traced[5] back to the interplay between symmetry lowering due to the antiferromagnetic order (cubic lowered to rhombohedral) and the anisotropy part of the interaction (20). The symmetry lowering lifts the cubic grouping (t_{2g} and e_g manifolds), thus allowing a higher number of allowed occupation patterns.

The anisotropic part of the interaction is responsible[5] for Hund's second rule ordering of states, which has the tendency to increase the mutual distance of each pair of electrons. If the overall energetics (band broadening and kinetic effects) reduces the gain of energy due to spin-polarization, then Hund's first rule may become suppressed and the result is a low-spin state. The anisotropic interaction is however not influenced by this suppression since it is a local term proportional to a parameter J. It will enforce a Hund's second rule like separation of the electrons under the low-spin condition and thus can be shown to result exactly in the occupation pattern observed for MnO. In a sense the low-spin state is an example of Hund's second rule without Hund's first rule.

FeO, CoO, and NiO. Together with MnO, these classic Mott (or "charge-transfer") insulators have been prime applications of the LSDA+U method.[24–27] The behavior of the open 3*d* shell in these compounds has not been analyzed in the detail that was done for MnO however.

2. Metals

Correlated metals involve carriers that can move; hence, they invariably involve fluctuations in occupation number, in magnetic moment, in orbital occupation, etc. It cannot be expected that a self-consistent mean-field treatment such as LSDA+U can answer many of the questions raised by their behavior. However, there is still the question of whether

LSDA+U can provide a more reasonable starting point than LSDA alone in understanding these metals. In our opinion, this remains an open question, but one for which some evidence is available.

The Fe-Al system has provided one platform for the application of LSDA+U to moderately correlated metals. The systems treated include the Fe impurity in Al (Kondo system experimentally) and the compounds Fe_3Al, FeAl, and $FeAl_3$. The calculated behavior is too complex to summarize here. The LSDA+U result will, generally speaking, be likely to give a good picture of a Kondo ion when it produces an integer-valent ion with a large value of U. Both FLL and AMF functionals have been applied in this regime,[28,29] with substantially differing results, leading one to question whether either is more realistic than simple LSDA. Results are also sensitive to volume, i.e., whether using the experimental lattice constant or the calculated equilibrium value, and the calculated equilibrium is different from LSDA and LSDA+U. One result was that, for moderate $U_{\mathrm{Fe}} \sim 3-4$ eV, AMF strongly reduces the magnetic moment, while FLL does not.[29] Another application found that the magnetism disappeared within a certain range of intermediate values of U_{Fe}; that is, it was magnetic around small U_{Fe} and also again at large coupling[28] but nonmagnetic between.

3. *Moderately strongly interacting oxides*

Trying to address seriously the electronic structure of intermediate coupling oxides, which are often near the metal-insulator transition, is a challenge that has begun to be addressed more directly. The peculiar Na_xCoO_2 system, which becomes superconducting when hydrated (water intercalates between CoO_2 layers) is one example. One set of studies showed no appreciable difference between FLL and AMF,[30] with both predicting charge disproportionation on the Co ion for $x=\frac{1}{3}$ and $\frac{1}{2}$ for $U \approx 2.5-3$ eV. It is likely that this compound presents a case where the interplay between LSDA and U has effects that are not fully understood. Also, it is unclear why there is so little difference between the FLL and AMF functionals in this system.

The compound Sr_2CoO_4 is another example. Both functionals show a collapse of the moment[31] around $U=2.5$ eV related to the metal–half-metal transition that occurs, but the result for the moments $[M(\mathrm{AMF}) < M(\mathrm{FLL})]$ bears out the tendency of AMF to penalize magnetic moments. The fixed spin-moment calculation in Fig. 9 in Ref. 31 is instructive too, showing the competition between LSDA magnetic energy and AMF magnetic penalty. Also it shows the creation of local minima around M=integer values that LDA+U introduces.

4. *f electron materials*

4*f systems.* These metals often display the correlated electron physics of a magnetic insulator at the band-structure level. Background conduction bands provide the metallic nature, while the correlated states have integer occupation. The LSDA+U method seems to be a realistic method for placing the f states closer to where they belong (away from the Fermi level). Gd is a good example, which has been studied at ambient pressure and compared to photoemission data[25] and magnetic dichroism data.[32,33] The LSDA+U method has also been applied up to extremely high pressure to assess where the "Mott transition" in the 4f bands is likely to occur. The LSDA+U method has also been applied to heavy-fermion metals, for example, Cu and U compounds,[34] $PrOs_2Sb_{12}$,[35] and $YbRh_2Si_2$.[20] In such systems the LSDA+U method may even provide a good estimate of which itinerant states at the Fermi level are strongly coupled to the localized f states, i.e., the Kondo coupling matrix elements. These 4f systems may become heavy-fermion metals ($YbRh_2Si_2$) or novel heavy fermion superconductors ($YbAlB_4$), or they may remain magnetic but otherwise rather uninteresting metals (Gd).

5*f systems.* A variety of applications of the LSDA+U method to 5f systems, and especially Pu, have been presented.[36–40] Given the complexity of the phase diagram of elemental Pu, together with claims that dynamic correlation effects must be included for any realistic description of Pu, a more critical study of Pu would be useful.

ACKNOWLEDGMENTS

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APPENDIX: CALCULATION OF THE STONER *I* for 3*d* and 4*f* SHELLS

The Stoner parameter I is a well-established quantity. For metals its value is obtained by a second-order expansion of the LSDA xc energy around the nonmagnetic solution, resulting in a Fermi-surface-averaged integral of the radial-wave functions with the xc kernel.[41] LSDA+U is usually applied to describe insulating states, where the Fermi surface vanishes. In the context of discussing the LSDA contribution to the energy of a correlated d or f shell, it is more natural to consider the energy contribution from the localized shell. This leads to a derivation of the Stoner I similar to the formulation of Janak[41] but adapted to atomlike situations.

Seo[42] presented the second-order perturbation theory of the spin polarization in DFT, which results in explicit expressions for the shell exchange parameter I_{nl} that are applicable to atomlike situations. In this work a numerical estimate for I_{nl} was derived indirectly from exchange splittings and spin-polarization energies taken from DFT calculations. The idea behind this perturbation theory, the expansion of the xc energy around the spherically averaged nonmagnetic density of the shell under consideration, was also discussed in the appendix of Kasinathan *et al.*[5] and leads to $\Delta E_{\mathrm{xc}} \approx -\frac{1}{4} I_{nl} M^2$ with the shell-Stoner integral

$$I_{nl} = -\frac{1}{2\pi} \int K_0(r) [R_{nl}(r)]^4 r^2 dr, \qquad \text{(A1)}$$

$$K_0(\vec{r},\vec{r}\,') = \left. \frac{\delta^2 E_{xc}}{\delta m(\vec{r})\,\delta m(\vec{r}\,')} \right|_{n^{\text{spher}},m=0} \rightarrow K_0(\vec{r})\,\delta(\vec{r}-\vec{r}\,'). \tag{A2}$$

The last expression applies for a local approximation (viz. LSDA) to E_{xc}. $K_0(\vec{r},\vec{r}\,')$ is a magnetization-magnetization interaction directly analogous to the second functional derivative of the DFT potential energy with respect to $n(\vec{r})$, which is the Coulomb interaction $e^2/|\vec{r}-\vec{r}\,'|$ plus an "xc interaction" arising from E_{xc}.

For a more detailed discussion of the parameter I_{nl} we performed LSDA calculations for free atoms and ions and explicitly calculated I_{nl} from Eq. (A1). It turns out that $\Delta E_{\text{xc}}(M)$ given above is by far the largest M-dependent term of the energy expansion. The spin-polarization energy of isolated atoms or ions with spherical M is well described by this estimate with an error smaller than (5–10)%. The resulting shell-Stoner integrals I_{nl} have very similar values compared to the ones obtained from the theory for the metallic situation. (Note, however, that there is a factor-of-2 difference in the definition of the Stoner I in some of the publications.)

For the 3d transition element series we get values I_{nl} ranging from 0.62 eV for Sc to 0.95 eV for Zn (see Fig. 4). These values increase across the series by ≈0.15–0.20 eV, when the exchange only LSDA is used, pointing to a reduction due to (LDA-type) correlation effects when the full xc kernel is used. For the 4f series the shell-Stoner integrals vary from 0.58 eV for Ce to 0.75 eV for Yb. The LDA correlation effects amount to 10% of these values. The values obtained depend on the choice of the reference system, which serves as zeroth order in the functional expansion. For instance for the 3^+ ions of the 4f-series I_{4f} is increased by (6–20)% with respect to the neutral atoms.

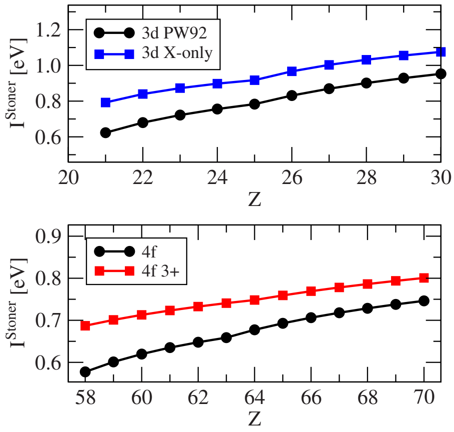

FIG. 4. (Color online) Shell-Stoner integrals for the 3d and 4f atoms. For explanations, see text.

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