

ARTICLES

Reformulation of the LDA+ U method for a local-orbital basis

W. E. Pickett,* S. C. Erwin, and E. C. Ethridge

Complex Systems Theory Branch, Naval Research Laboratory, Washington, DC 20375

(Received 13 February 1998)

We present a local orbital approach to the evaluation of the on-site repulsion energy U for use in the LDA+ U method of Anisimov and co-workers. Our objectives are to make the method more firmly based, to concentrate primarily on ground-state properties rather than spectra, and to test the method in cases where only modest changes in orbital occupations are expected, as well as for highly correlated materials. Because of these objectives, we employ a differential definition of U . We also define a *matrix* \mathbf{U} , which we find is very dependent on the environment of the atom in question. The formulation is applied to evaluate U for transition-metal monoxides from VO to NiO using a local-orbital basis set. The resulting values of U are typically only 40–65 % as large as values currently in use. We evaluate the \mathbf{U} matrix for the e_g and t_{2g} subshells in paramagnetic FeO, and illustrate the very different charge responses of the e_g and t_{2g} states. The sensitivity of the method to the choice of the d orbitals, and to the basis set in general, is discussed.

[S0163-1829(98)05427-7]

I. INTRODUCTION

The understanding and evaluation of the electronic structure of strongly correlated materials is a long-standing problem. For weakly correlated materials such as nearly-free-electron-like metals, covalent semiconductors, ionic solids, and even rather complex intermetallic transition metal compounds, the local-density approximation (the LDA, which we understand to include the spin degree of freedom as well) to the exchange-correlation functional that occurs in density-functional theory gives very reasonable ground-state properties and even band structures (which are excited-state features). For correlated materials, however, LDA can be completely wrong: the now-classic example is the canonical cuprate La_2CuO_4 , which LDA predicts to be a nonmagnetic metal^{1,2} whereas it is actually an antiferromagnetic insulator. Model many-body Hamiltonian treatments, such as the Hubbard model,³ can readily explain the observed type of ground state, but do so in terms of adjustable parameters and the neglect of many aspects of the crystal that may influence most of its properties. Evaluation of the dynamic self-energy, which gives the description of excitations, is appropriate for comparing with many experiments, but even low-order approximations can be very tedious to evaluate.⁴

Within the past few years Anisimov and co-workers have proposed an extension of the LDA approach (now called LDA+ U) based on lessons learned from Hubbard model studies³ that single out a particular local orbital and the associated on-site repulsive interaction U as the fundamental characteristic to be addressed.^{5–8} They proposed that the LDA treats the effects of U reasonably well in some average sense, even in highly correlated systems, but that one must allow a deviation from this average behavior by including a correction to the total energy, including a term like

$$\Delta E = \frac{1}{2} \sum_{m,s \neq m',s'} (U - \delta_{s,s'} J) n_{ms} n_{m's'}, \quad (1)$$

where J is the exchange constant and n_{ms} is the new charge that includes a local charge redistribution (relative to the LDA value \bar{n}_{ms}) obtained by solving the LDA+ U equations self-consistently. The local-orbital and -spin indices are m and s , respectively. It is assumed in the method that one can identify the orbitals to be treated (d orbitals of Cu in La_2CuO_4 for the example mentioned above).

The LDA+ U method achieves some spectacular successes, such as leading to an antiferromagnetic insulating state of La_2CuO_4 with band gap and atomic moment in reasonable correspondence with observed values⁹, and leading to similarly impressive descriptions of the transition-metal monoxides. There remain questions, however, such as the proper way to specify the orbitals, the correct way to obtain the interaction constants (U and J), and how, if possible, to extend the method to give an improved treatment of the metallic phase when the insulator is heavily doped. In this paper we address these questions. A primary feature is that, since the method is perforce focused on an atomic orbital, it is natural to use a local-orbital basis set. We will refer to the local orbital of interest as the “ d orbital,” although in some applications it may be an f or, rarely, an s or p orbital.

II. DESCRIPTION OF LDA+ U AS CURRENTLY PRACTICED

In extending the LDA method to account for correlations resulting from strong on-site interactions, there are several criteria that one might hope to satisfy, such as (1) it should reduce to LDA when LDA is known to be good; (2) the energy is given by a functional of the density; (3) the method specifies how to obtain the local orbital in question (perhaps

through a self-consistency procedure); (4) the definition of U and J are provided unambiguously; (5) the method predicts antiferromagnetic insulators when appropriate; and (6) the description of highly correlated metals is improved over the LDA description. This list, although perhaps still incomplete, is already very ambitious, and only certain of these desires have been addressed seriously.

Anisimov, Zaanen, and Andersen (AZA) (Ref. 6) chose to refine the LDA by including an orbital-dependent one-electron potential to account explicitly for the important Coulomb repulsions not treated fully in the LDA. This was accomplished in analogy with Hartree-Fock theory by correcting the mean-field contribution of the d - d on-site interaction with an intra-atomic correction. This correction has been applied in slightly varying forms, but a representative example of the functional to be solved is

$$E_{\text{LDA}+U} = E_{\text{LDA}}[n] - \frac{1}{2}U \sum_i N_i [n_{ms}] (N_i [n_{ms}] - 1) + \frac{1}{2} \sum_i \sum_{ms \neq m's'} U_{m,m'} n_{ims} n_{im's'}. \quad (2)$$

Here i denotes the lattice site, and terms involving J have been neglected because we do not need to specify the complete form of the functional for this paper. N_i is the site sum of the d charges, evaluated for the self-consistent LDA+ U densities. The second term is presumed to be a reasonable description of the direct Coulomb interaction energy included in the LDA expression.

Equation (2) reveals that, in the LDA+ U approach, one singles out beforehand the atomic orbitals to be treated, and decides how to specify them. Implementations to date use orbitals arising in the linearized muffin-tin orbital (LMTO) method. The d orbitals to which the U correction is applied are numerical solutions to a Schrödinger equation inside an atomic sphere, and are zero outside this sphere. In addition, LDA+ U is clearly no longer a straightforward density functional because it depends on parameters U and J that depend on the LDA density rather than the LDA+ U density.

The one-electron potential is the conventional LDA form of potential, plus an orbital-dependent shift of energy given by

$$\Delta V_{ms} = U \left(\frac{1}{2} - n_{ms} \right) \quad (3)$$

if $U_{mm'} \rightarrow U$ is orbital independent. The changes in the electronic structure are proportional to U , and the definition and calculation of U is the next topic to address.

To obtain U and J , AZA performed LMTO calculations for a supercell in which the d charge on one atom is constrained and the eigenvalue is obtained.¹⁰ The d orbitals on all atoms in the supercell are *decoupled* entirely from the remaining part of the basis set. This makes the treatment of the local orbitals an ‘‘atomiclike’’ problem, which greatly reduces the difficulty associated with constraining the occupation numbers. It also has the effect of leaving a rather artificial system to perform the screening. For example, in NiO the screening system consists of oxygen p orbitals that cannot hybridize with the Ni d orbitals, plus whatever other virtual orbitals are included in the basis set.

The discreteness of the d eigenvalues makes it simple to specify the charge in the spin-orbitals in the supercell, and U and J are determined from the relations

$$U = \varepsilon_{3d\uparrow} \left(\frac{\bar{n}}{2} + \frac{1}{2}, \frac{\bar{n}}{2} \right) - \varepsilon_{3d\downarrow} \left(\frac{\bar{n}}{2} + \frac{1}{2}, \frac{\bar{n}}{2} - 1 \right), \quad (4)$$

in which the d occupation differs by unity around a mean polarization of unity, and

$$J = \varepsilon_{3d\uparrow} \left(\frac{\bar{n}}{2} + \frac{1}{2}, \frac{\bar{n}}{2} - \frac{1}{2} \right) - \varepsilon_{3d\downarrow} \left(\frac{\bar{n}}{2} + \frac{1}{2}, \frac{\bar{n}}{2} - \frac{1}{2} \right), \quad (5)$$

which is a straightforward difference between up and down eigenvalues for unit spin polarization. Here $\varepsilon_{3d\uparrow}(n_{\uparrow}, n_{\downarrow})$ [$\varepsilon_{3d\downarrow}(n_{\uparrow}, n_{\downarrow})$] is the spin-up (spin-down) $3d$ eigenvalue for occupancies n_{\uparrow} and n_{\downarrow} .

While it is widely recognized that the on-site repulsion U is a screened quantity, the manner in which the screening should be done is not precisely specified. An early study by Cox, Coulthard, and Lloyd¹¹ for $3d$ metals used a renormalized neutral atom approach, although it was recognized that screening processes might extend over a somewhat larger region. Anisimov and co-workers chose the method presented in this section, but in this paper we pursue a different approach, with a somewhat different objective.

III. REFORMULATION OF LDA+ U FOR A LOCAL ORBITAL BASIS

We specify in following subsections the various ways in which our approach differs from that in current use.

A. LCAO basis set

We begin with a basis set of local orbitals $\{\phi\}$, whose lattice sums lead to the standard linear combination of atomic orbitals (LCAO) Bloch basis functions for the one-electron Hamiltonian.¹² To represent an occupied atomic orbital (including core states), we use a contracted set of Gaussian functions, multiplied by appropriate angular functions for s , p , or d behavior. In particular, at the beginning we choose (from a neutral atom or an ion) the d orbitals of central interest. Although we have no indication of any better choice than the d orbital of the corresponding atom (e.g., neutral Cu in La_2CuO_4), our method allows the ability to check how sensitive the results are to the form chosen for the orbital. In addition to basis functions describing filled atomic (or ionic) orbitals, we add other Gaussian functions to the basis to provide a more nearly complete basis for the valence and conduction states than a minimal basis set would provide. This feature is an advantage of our local-orbital representation, as the ability to include self-consistent screening by a crystalline density of general form in the calculations is important.

This LCAO basis set brings up an important feature. As a sum of squares of wave functions, the charge density contains two types of terms. One consists of atom-centered contributions containing the coordinate dependence $\phi_{lm}^2(\vec{r} - \vec{R})$, and is clearly identified as a contribution to the charge from angular momentum l of the atom located at \vec{R} . The other

contribution has a coordinate dependence given by $\phi_{lm}(\vec{r} - \vec{R})\phi_{l'm'}(\vec{r} - \vec{R}')$, $\vec{R} \neq \vec{R}'$, which at a particular point may be positive or negative and cannot be assigned uniquely to any atom. The Mulliken decomposition,¹³ which assigns half of each such term to charge component l, m on the atom at \vec{R} and the other half to charge l', m' of the atom at \vec{R}' , is widely used when atomic decomposition of the charge is desired. Mulliken population is well understood to be not only arbitrary, but also dependent on the flexibility of the basis set, and therefore should not be endowed with any important physical meaning.

A central fact that must be addressed is that the total charge density cannot be decomposed, precisely or meaningfully, into simple atomic contributions alone. This fact means that the orbital occupations that are the centerpiece of the LDA+ U approach unfortunately are not particularly well defined. For our LCAO basis set we will use for n_{ms} charge contributions solely of the first type, which will be called on-site charges to distinguish them from Mulliken charges. These on-site quantities also cannot properly be called occupation numbers since there is no sum rule for their total, and it is not impossible that for a given orbital the value can exceed unity.

B. On the specification of the functional

Although we do not carry out LDA+ U calculations in this paper, we are thinking in terms of a generalized LDA+ U functional that is consistent with our philosophy behind the correction. Without more formal justification than is normally done in the LDA+ U approach (and which we do not address seriously here), any change must simply be tested to see if it produces better results. The form that we envision has affected our study of how to define and evaluate the interaction constants that arise in the method. We suppose that the correction is to provide adjustment to full-potential LDA results, and therefore includes both a suborbital index and a spin index on the reference charges $\bar{n} \rightarrow \bar{n}_{ms}$. These numbers will differ, sometimes greatly, for different irreducible representations of the point group of the atom. The correction then might be written suggestively as

$$E_{\text{LDA}+U} = E_{\text{LDA}}[n] + \frac{1}{2} \sum_i \sum_{ms \neq m's'} (U_{m,m'} - \delta_{s,s'} J_{m,m'}) \times (n_{ims} - \bar{n}_{ims})(n_{im's'} - \bar{n}_{im's'}). \quad (6)$$

This change may affect the types of orbitally ordered solutions that will be obtained. This form ensures that the LDA solution is an exact stationary solution of the LDA+ U functional (for which the correction vanishes identically), which is not the case for Eq. (2), i.e., if shell-averaged values of \bar{n} are used. Aside from strongly correlated solids, another interest of ours is to ascertain whether LDA+ U can provide a useful improvement of the description of ‘‘simpler’’ systems such as the transition metals Fe and V, where anisotropy (relative amounts of t_{2g} and e_g character) is not reproduced accurately in LDA, or in correlated metals where no bandgap occurs but charge rearrangement might be appropriate.

C. Procedure for determining U and J

We take as our ansatz that the constant U (J) occurring in the LDA+ U functional should describe the cost in potential energy of charge (spin) fluctuations in the actual crystal, i.e., with all normal interactions and degrees of freedom available to the electrons. Thus we do *not* decouple the d states from surrounding states. The U and J terms are applied in precisely the same system from which they are determined. We comment below on the question of dealing with the associated cost in kinetic energy due to charge fluctuations. For the remainder of this paper we concentrate solely on U , postponing a related treatment of J such as suggested in Ref. 14 for the future.

We also take the point of view that the main purpose of LDA+ U theory, as in density-functional theory, is to obtain ground-state properties, rather than to approximate excitations with the eigenvalues. Describing the ground state may require small rearrangements of occupation numbers away from their LDA values, and usually less than one-half, so we employ a differential definition of U (also used by Solov'yev, Dederichs, and Anisimov¹⁴) rather than one employing occupation numbers differing by unity. We will see that this introduces extra richness into the charge rearrangements described by the LDA+ U method, because a small change in (say) t_{2g} population can be strongly compensated by a change in e_g population.

We employ then a generalized constrained density functional approach as proposed by Dederichs *et al.*¹⁰ to calculate the change in energy due to constraints on local-orbital densities. We minimize the local-density functional subject to the constraint that on-site local orbital charges $n_{\alpha,s}$ be equal to designated values $Q_{\alpha,s}$, where α labels an irreducible representation of the point group of the atom in question (e.g., t_{2g} or e_g), and that total charge N be conserved:

$$\mathcal{E}(Q) = \min_{n_{\uparrow}, n_{\downarrow}, n_{\alpha,s}} \left\{ E_{\text{LDA}}[n_{\uparrow}, n_{\downarrow}] + \sum_{\alpha,s} w_{\alpha,s} (n_{\alpha,s} - Q_{\alpha,s}) - \mu \left(\int n(r) d^3r - N \right) \right\}. \quad (7)$$

The Lagrange multipliers are the usual chemical potential μ and the potential shifts $w_{\alpha,s}$ necessary to satisfy the constraint $n_{\alpha,s} = Q_{\alpha,s}$. Dependence on the total number N of electrons (always conserved) will not be displayed explicitly. Variation with respect to the spin orbitals leads to a one-electron Schrödinger equation in which the potential is the LDA potential, supplemented by local orbital shifts $w_{\alpha,s}$ on the orbitals in the irreducible representation α having spin s . These additional shifts of potential can be represented as a nonlocal potential

$$V_{NL} = \sum_{\alpha,s} \sum_{m \in \alpha} |\phi_{m,s}\rangle w_{\alpha,s} \langle \phi_{m,s}|, \quad (8)$$

where $\{\phi\}$ are normalized atomic orbitals.

Evaluation of the constrained energy in Eq. (7) deserves comment. Solution for the constrained energy involves generating the Kohn-Sham equations, which have an additional potential of the form of Eq. (8) that effectively constrains the density as desired. The conventional method of evaluating

the energy is to sum the resulting eigenvalues and correct for double counting of the Hartree energy and the miscounting of exchange-correlation energy. That cannot be done directly, because the Kohn-Sham eigenvalues contain the effects of the additional potential of Eq. (8) and one does not obtain E_{LDA} . The additional term that has been included by summing the LDA+ U eigenvalues, however, contains only the additional one-body term $\sum_{\alpha,s} w_{\alpha,s} n_{\alpha,s}$, and this term can be subtracted to obtain E_{LDA} evaluated for the constrained density.

D. Constrained energy

It is convenient to introduce a vector notation for the local occupations, the constraining values, and the (Lagrange parameter) potential shifts: $n_{\alpha,s} \rightarrow \vec{n}$, and similarly for \vec{Q} and for \vec{w} . Since we will be dealing with quantities relative to their LDA values, we also use the notational conveniences

$$\begin{aligned}\vec{q} &= \vec{Q} - \vec{Q}^{\text{LDA}}, \\ \mathcal{E}_q^- &= \mathcal{E}(\vec{Q}) - \mathcal{E}(\vec{Q}^{\text{LDA}}).\end{aligned}\quad (9)$$

From the Hellmann-Feynman-like relation

$$\frac{\partial \mathcal{E}_q^-}{\partial \vec{q}} \equiv \nabla_{\vec{q}} \mathcal{E}_q^- = -\vec{w}, \quad (10)$$

we can generalize the constrained density-functional theory viewpoint of Dederichs *et al.*¹⁰ to obtain the change in energy due to constraining a set of orbital densities in the manner of Eq. (7). Since there is no change in energy if the charges are ‘‘constrained’’ to be their LDA values $\vec{Q} = \vec{Q}^{\text{LDA}}$ (so $\vec{q} = 0$), the energy change is given by

$$\mathcal{E}_q^- = \int_0^{\vec{q}} d\vec{q}' \cdot \nabla_{\vec{q}'} \mathcal{E}_{q'}^- = - \int_0^{\vec{q}} d\vec{q}' \cdot \vec{w}(\vec{q}'), \quad (11)$$

subject only to the condition that \mathcal{E}_q^- is analytic (as we assume).

The general behavior of the constrained energy can be seen by noting that \vec{w} is linear for small changes in occupation, i.e., linear in \vec{q} . Since at the minimum of Eq. (7) we have $\vec{n} \equiv \vec{Q}$, we may use these quantities interchangeably to write

$$\vec{w} = -\mathbf{U}\vec{q} + \mathcal{O}(\vec{q})^2 = -\mathbf{U}\delta\vec{n} + \mathcal{O}(\delta\vec{n})^2, \quad (12)$$

where $\delta\vec{n} = \vec{n} - \vec{n}^{\text{LDA}}$, and \mathbf{U} is the constant (matrix) of proportionality. For the remainder of this section we concern ourselves with the linear ‘‘response’’ that is implicit in the LDA+ U method, although we demonstrate in the numerical results of Sec. V A where non-linear corrections begin to arise. Then the energy shift is given by

$$\mathcal{E}_q^- = \frac{1}{2} \vec{q} \cdot \mathbf{U} \cdot \vec{q}, \quad (13)$$

where

$$\mathbf{U} \equiv -\partial \vec{w} / \partial \vec{q}. \quad (14)$$

E. Potential vs kinetic contributions

The constrained energy $\mathcal{E}(\vec{q})$ can be decomposed into the kinetic-energy term, the interaction with the external potential, and the remainder, the potential energy

$$\mathcal{E}_q^- = \mathcal{E}_{q,K}^- + \mathcal{E}_{q,\text{ext}}^- + \mathcal{E}_{q,P}^-. \quad (15)$$

$\mathcal{E}_{q,\text{ext}}^-$ is linear in \vec{q} and gives no contribution to \mathbf{U} , but the quadratic term involving \mathbf{U} contains both a kinetic-energy contribution \mathbf{U}_K and a potential-energy contribution \mathbf{U}_P ,

$$\mathbf{U} = \mathbf{U}_K + \mathbf{U}_P, \quad (16)$$

$$\mathbf{U}_{K(P)} = \nabla_{\vec{q}} \nabla_{\vec{q}} \mathcal{E}_{q,K(P)}^-$$

and cancellation between the two contributions may occur.

In a self-consistent calculation, any change in local orbital charge results in an accompanying change in kinetic energy as well as a potential energy change. Since the ‘‘ U ’’ term in the LDA+ U energy functional is a potential energy term, one might argue that it should be \mathbf{U}_P that goes into the LDA+ U calculation, and the kinetic-energy change in the constrained LDA calculation should be removed: $\mathbf{U} \rightarrow \mathbf{U}_P = \mathbf{U} - \mathbf{U}_K$ is the appropriate ‘‘ U ’’ in LDA+ U . It was a related correction, to avoid double counting of kinetic terms, that Anisimov and Gunnarsson⁵ expected to account for by disconnecting their local orbitals from all other basis functions in their prescription for the determination of U . The constrained LDA procedure we propose is in some respects closer to that of Hybertsen, Schlüter, and Christensen¹⁶ than to that of Anisimov and co-workers. However, Hybertsen, Schlüter, and Christensen were specifically interested in obtaining parameters for the Hubbard model, and their procedure was tied to the form of extended Hubbard model they wished to consider.

Using the Hellmann-Feynman relation [Eq. (10)] to obtain $\vec{w}(\vec{q})$, it is straightforward to obtain \mathbf{U} of Eq. (12) numerically: one applies a shift in potential \vec{w} and calculates the change in charge \vec{q} , and forms the finite-difference derivative in Eq. (14). To calculate the separate contributions there is no alternative to evaluating a finite difference second derivative.¹⁷ We have carried out this calculation (methods are described below) for FeO. We obtain the provocative result $U_K/\bar{U} \approx -10$, which leaves $U_P/\bar{U} \approx 11$, i.e., each contribution is an order of magnitude larger than the net result, and they have opposite sign. Clearly these individual contributions are not directly useful, nor in fact is this directly related to the kinetic-energy contribution that Gunnarsson and Anisimov treated by disconnecting d orbitals when calculating U . In the context of the Hubbard model, the term ‘‘kinetic energy’’ really denotes all of the energy except the potential energy related to U , and is very different than the kinetic energy we have evaluated. We leave the question of potential vs kinetic contributions to U for further study. The value of U that we evaluate and report below is the total (net) value $\mathbf{U} = \mathbf{U}_K + \mathbf{U}_P$.

F. Change in independent variable

It will be instructive to consider the potential shifts \vec{w} to be the independent variables in an associated energy func-

TABLE I. Calculated values of U for transition-metal oxides, compared to values of Anisimov, Zaanen, and Andersen (AZA) (Ref. 6). Empirical values include representative values from the literature.

Ref.	VO	MnO	FeO	CoO	NiO
This work	2.7	3.6	4.6	5.0	5.1
AZA	6.7	6.9	6.8	7.8	8.0
Empirical	4.0–4.8 ^a	7.8–8.8 ^a 7.0 ^d	3.5–5.1 ^a 3.9 ^c , 7.0 ^d	4.9–5.3 ^a 4.9 ^c	6.1–6.7 ^a 7.9, ^b 6.1, ^c 7.5 ^d

^aAnisimov, Zaanen, and Anderson, Ref. 6.

^bReference 19.

^cReference 20.

^dReference 21.

tional leading to $\vec{q}(\vec{w})$ rather than $\vec{w}(\vec{q})$. This is also in keeping with the practice in the constrained density approach of choosing the shifts \vec{w} and then calculating the charge response \vec{q} . This change of variable is done by a Legendre transformation

$$\hat{\mathcal{E}}_w^- = \mathcal{E}_q^- + \vec{q} \cdot \vec{w}, \quad (17)$$

which, from the differential forms

$$\delta \mathcal{E}_q^- = -\vec{w} \cdot \delta \vec{q} \Rightarrow \delta \hat{\mathcal{E}}_w^- = \vec{q} \cdot \delta \vec{w}, \quad (18)$$

leads to the energy shift

$$\hat{\mathcal{E}}_w^- = \int_0^{\vec{w}} \vec{q}(\vec{w}') \cdot d\vec{w}' \approx -\frac{1}{2} \vec{w} \cdot \mathbf{U}^{-1} \cdot \vec{w}. \quad (19)$$

This formalism brings in the *matrix* \mathbf{U}^{-1} implicit in Eq. (12), relating the charge shifts in various suborbitals to potential shifts applied to other suborbitals, e.g., a decomposition of the Hubbard U for d orbitals into e_g and t_{2g} contributions for cubic site symmetry. This result is reminiscent of the extension of the definitions of U and J [Eqs. (4) and (5)] by Solovyev, Hamada, and Terakura¹⁵ to give different values U_{e_g} and $U_{t_{2g}}$, but their procedure did not provide off-diagonal terms. The effects of differing charge response in the e_g and t_{2g} channels will be quantified in Sec. V. The concept can be extended to non-site-diagonal interactions, *viz.* d orbitals interacting with neighboring oxygen p orbitals.

We now establish a sum rule relating the matrix elements of \mathbf{U} to the conventional scalar U , which for clarity we denote $U_{dd} = \partial w_d / \partial Q_d$, where Q_d is the total d charge and w_d is a shift in potential applied to all d orbitals. Since a change in potential $w_{t_{2g}}$ acting on the t_{2g} orbitals followed by a change in potential w_{e_g} acting on only the e_g orbitals is equivalent to a potential w_d of the same magnitude acting on all d orbitals, we have, in the linear regime

$$\frac{\partial}{\partial w_{t_{2g}}} + \frac{\partial}{\partial w_{e_g}} = \frac{\partial}{\partial w_d}. \quad (20)$$

By definition $n_d = n_{t_{2g}} + n_{e_g}$, so, from the definition

$$U_{\alpha\beta}^{-1} = -\frac{\partial n_\alpha}{\partial w_\beta}, \quad (21)$$

we have a sum rule relating the matrix elements to the conventional Coulomb repulsion constant

$$U_{dd}^{-1} = \sum_{\alpha, \beta = t_{2g}, e_g} U_{\alpha\beta}^{-1}. \quad (22)$$

Below we provide a numerical test of this sum rule for NiO.

IV. METHOD OF CALCULATION

For the metallic constituents of the compounds we considered, a basis set representing six s -, four p -, and three d -type functions is expanded on a set of 16 Gaussian functions. The O basis set is expanded on a set of 12 Gaussian exponents contracted into four s - and three p -type functions. The Coulomb and exchange-correlation potentials comprise the effective potential V_{eff} , which is also described by a superposition of atom-centered Gaussian-type functions. By choosing this expansion, the matrix elements of the Hamiltonian are analytic. Details of the method, and comparison to results of the full-potential linearized augmented-plane-wave (LAPW) method, have been published elsewhere.^{12,18}

For this work it is important to obtain sufficiently well converged values of orbital densities. Tests using special point meshes in the irreducible $\frac{1}{48}$ of the simple cubic Brillouin zone (IBZ) for eight atom cells up to 56 \vec{k} points indicated that ten or 20 \vec{k} points in the IBZ gave the necessary accuracy. A temperature broadening of 0.07 eV was used to facilitate convergence to self-consistency, and it was verified that this size of broadening did not change the results.

V. EVALUATION FOR TRANSITION-METAL MONOXIDES

We have applied this approach to evaluate U for the transition metal monoxides MO , $M = \text{V, Mn, Fe, Co, and Ni}$, in the paramagnetic state and for the cubic rocksalt structure. The (experimental) lattice constants used were VO, 4.093 Å; MnO, 4.444 Å; FeO, 4.332 Å; CoO, 4.260 Å; and NiO, 4.193 Å.

A. Suborbital independent U

First, applying a potential shift w_d equally to all d suborbitals analogously to LMTO treatments, the derived value of U is shown in Table I. Comparison is provided with values obtained by the method of AZA, and it is seen that the values

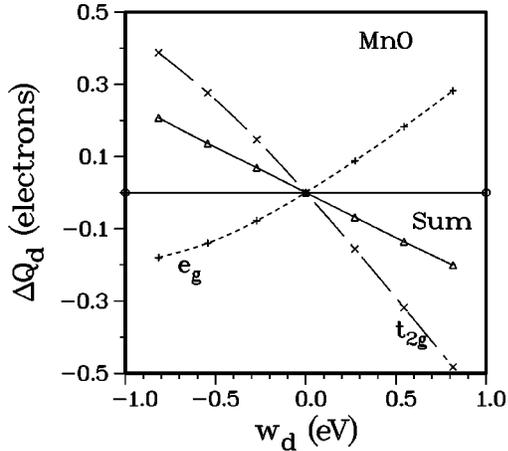


FIG. 1. Change in the on-site d charge (solid line) in MnO resulting from a potential shift w_d applied to all d states on a single Mn atom in a four molecule supercell. The total charge is decomposed into its e_g (short dashed line) and t_{2g} (long dashed line) components.

obtained are 40–65 % of the values obtained by AZA. That our values are smaller is no surprise, since our approach (of not disconnecting d orbitals from other orbitals) naturally allows additional screening to occur, by including hybridization between d orbitals and neighboring oxygen p orbitals. Moreover, charge rearrangement between e_g and t_{2g} subshells reveals that there is some intra- d -shell screening in the current approach. In addition, our definition of the d orbital is not identical with that of AZA.

Figures 1–3 for MnO, FeO, and NiO illustrate the change in subshell charge with w_d as well as the total change, which is what determines U . Taking MnO, for example, it is seen in Fig. 1 that the effect of positive w_d is to decrease $n_{t_{2g}}$ as expected, but n_{e_g} instead *increases*. Clearly charge rearrangement within the d shell is leading to a reduction in U (i.e., additional screening). A similar behavior occurs for FeO (Fig. 2), while for NiO the e_g charge remains almost unchanged as w_d is varied. Note that, besides the differences in approach and in basis sets, the values obtained in the AZA approach are evaluated for differences in d charge of unity.

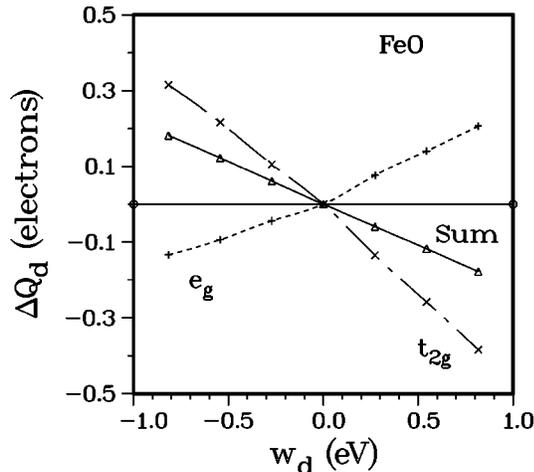


FIG. 2. Change in the d charge in FeO, plotted as in Fig. 1.

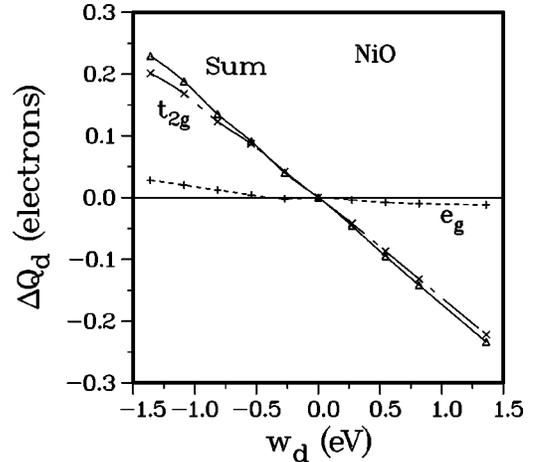


FIG. 3. Change in the d charge in NiO, plotted as in Fig. 1.

Empirically determined values (obtained by comparing to excited state data) lie in nearly all cases between our values and those of AZA.

The values of U in Table I are obtained as the first derivative of polynomial fits to the w_d vs Q_d curve Eq. (12). Figures 1–3 indicate the ΔQ_d vs w_d curve for shifts w_d up to ± 0.8 eV for MnO, FeO, and NiO. The change in total d charge is linear up to this size of shift (≈ 20 – 30 % of U). Even for this size shift, however, the individual t_{2g} and e_g contributions are beginning to become nonlinear, as seen most clearly for MnO in Fig. 1.

On-site charges and Mulliken charges within the LDA, for our basis set, are compared in Table II. The charges are less ionic than their formal (dipositive) charge, as experience would suggest. (Although atomic charge within a crystal cannot be defined uniquely, it is widely accepted that “effective” ionic charges are nearly always reduced by hybridization from their formal, full ionic values.) Although VO is somewhat of an exception, the Mulliken charge does not differ more than 4% from the on-site charge for these examples. The response of Mulliken and on-site charges are very different, however, with Mulliken charges varying more slowly. If one uses Mulliken charges rather than on-site charges to obtain U , the resulting values are much larger: 3.8 eV for VO, 6.2 eV for MnO, and 11.1 eV for NiO.

B. Suborbital dependent U

We have studied FeO charge redistribution when e_g and t_{2g} subshells are treated separately. In Fig. 4, we present the change in subshell charge when a shift in potential is applied individually to the subshells. In both cases, charge forced out of one subshell by an upward shift in potential goes prima-

TABLE II. d -shell charges, according to various definitions, for transition-metal monoxides from VO to NiO.

Type	VO	MnO	FeO	CoO	NiO
Formal	3	5	6	7	8
On-site	3.67	5.45	6.22	7.41	8.22
Mulliken	3.09	5.48	6.44	7.20	8.40

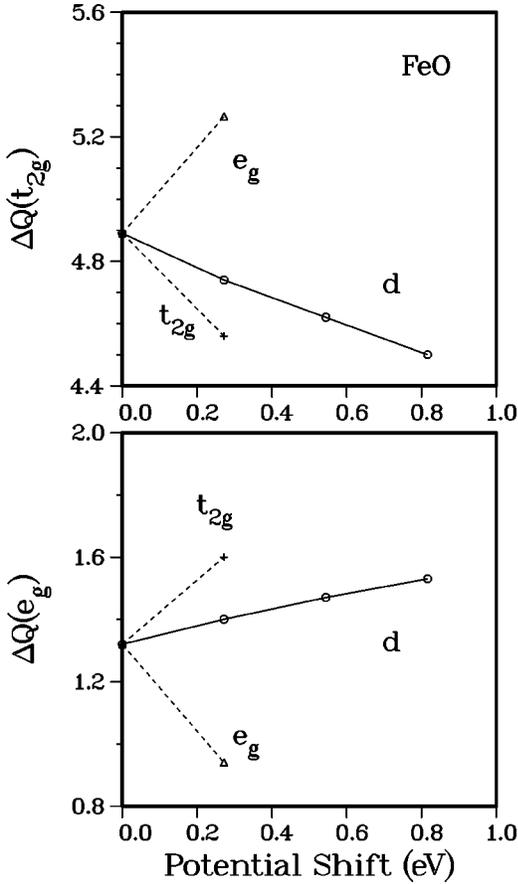


FIG. 4. Change in the subshell (e_g and t_{2g}) charge in FeO, resulting from a potential shift of only one of the subshells. Top panel: change in t_{2g} charge; bottom panel: change in e_g charge. The label indicates the type of applied potential shift w : d indicates shifts of all d states; t_{2g} (e_g) indicates a shift of only t_{2g} (e_g) states. Only positive energy shifts are shown.

rily into the other subshell, amounting to very strong intra- d -shell screening in these cases. Using Eq. (21), we obtain, in eV^{-1} ,

$$\begin{pmatrix} U_{t_{2g},t_{2g}}^{-1} & U_{t_{2g},e_g}^{-1} \\ U_{e_g,t_{2g}}^{-1} & U_{e_g,e_g}^{-1} \end{pmatrix} = \begin{pmatrix} 1.18 & -1.00 \\ -1.39 & 1.41 \end{pmatrix}, \quad (23)$$

which satisfies the sum rule of Eq. (22). The inverse is, in eV ,

$$\begin{pmatrix} U_{t_{2g},t_{2g}} & U_{t_{2g},e_g} \\ U_{e_g,t_{2g}} & U_{e_g,e_g} \end{pmatrix} = \begin{pmatrix} 5.15 & 3.65 \\ 5.08 & 4.31 \end{pmatrix}. \quad (24)$$

Recall that $U_{dd}=4.6 \text{ eV}$, so in the usual orbital-independent treatment the corresponding matrix would be

$$\begin{pmatrix} U_{t_{2g},t_{2g}} & U_{t_{2g},e_g} \\ U_{e_g,t_{2g}} & U_{e_g,e_g} \end{pmatrix} = \begin{pmatrix} 4.6 & 4.6 \\ 4.6 & 4.6 \end{pmatrix}. \quad (25)$$

Thus the behavior that looks rather peculiar in Fig. 4, and the negative off-diagonal elements in Eq. (21), do not lead to pathological behavior in the direct matrix \mathbf{U} .

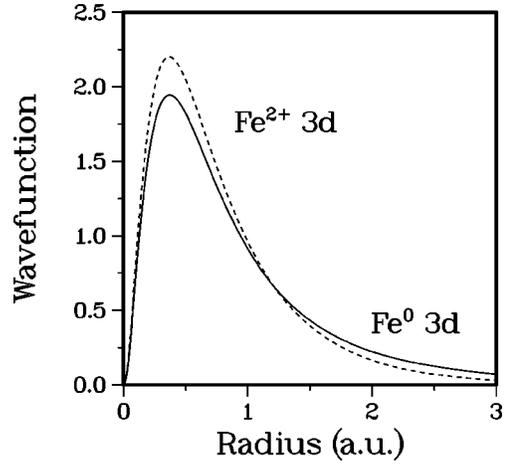


FIG. 5. Comparison of the $3d$ radial functions used in the LCAO basis set as the Fe $3d$ orbital to calculate the two values of U reported in the text. The functions are radial wave functions from neutral and doubly ionized Fe atomic calculations, fit to a set of 11 Gaussians.

C. Dependence of local orbital shape

The LDA+ U procedure is built around some choice of local orbital. In a LCAO basis, this orbital is specified at the beginning, and we have used neutral atom d orbitals from atomic LDA calculations. Another possible choice might be, say, the d orbital from a positive ion. For FeO we have checked the effect of using the Fe^{2+} d orbital obtained from an atomic calculation on an isolated ion. The difference in radial density is shown in Fig. 5. For the FeO (paramagnetic) solid, the on-site charge of 6.22 electrons (Table II) changes to the rather peculiar value of 4.85 electrons, and the calculated value of U increases from 4.6 to 7.8 eV. The total energy, however, changes only by +0.12 eV/FeO, which is a very modest change (adding f functions in a LCAO or LMTO calculation, or increasing the number of basis functions in a LAPW calculation, can result even larger changes, which are unimportant for most purposes).

This result makes it clear that the choice of d orbital can affect the calculated value of U , certainly in the LCAO method but most likely in any calculational approach. In our calculation it is the result of the density being represented in a different fashion, that is, the separation between local orbital charges and the overlap (Mulliken) contributions is a rather sensitive function of the basis set choice. As a result the values of n_{ms} that arise in the LDA+ U functional depend on the choice of d orbital. We are investigating methods of minimizing this effect, by normalizing the sum of the “ d occupation numbers” over the full d band region to ten.

VI. DISCUSSION

The results presented in Sec. V reflect a strong difference in response of the e_g and t_{2g} electrons, at least to potentials of moderate strength. Such differences have been noted several times in the literature. In the context of the LDA+ U method, Solovyev, Hamada, and Terakura¹⁵ have advocated using separate values of U for the two subshells in perovskite structure transition-metal oxides. Their method of obtaining U_α was a generalization of the standard method

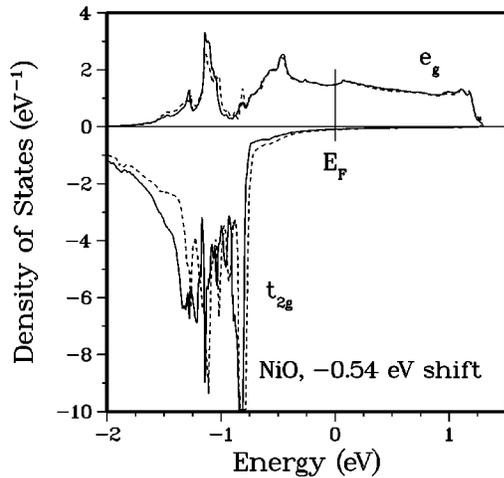


FIG. 6. Ni d density of states in NiO, before (dashed lines) and after a shift of the d states by -0.54 eV. The e_g (t_{2g}) density is plotted upward (downward). The Fermi levels have been aligned.

described in Sec. II. We, on the other hand, have adopted the differential definition of U that leads to a matrix $U_{\alpha\beta}$.

To begin to understand the response of the separate subshells, in Fig. 6 we show the on-site e_g and t_{2g} densities of states (DOS) on a Ni atom in an eight-atom supercell of NiO, both before and after a downward shift of all d states by -0.54 eV. The t_{2g} states in the rocksalt structure are weakly $dp\pi$ bonding and form a narrow band, whereas the e_g states form $dp\sigma$ bonds that produce wider e_g bands. From Fig. 3 it is seen that such shifts produce negligible change in the on-site e_g charge, with all the difference coming entirely from the on-site t_{2g} subshell. This result is counterintuitive, since the t_{2g} DOS is full, and pulling it down seemingly cannot increase its occupation. The e_g DOS is open shell and could accept charge, but does not do so.

The resolution of this paradox lies in the change in the representation of charge of the system by the LCAO basis functions as a shift in potential is applied. By looking at other local DOS's, for both on-site and Mulliken charge decompositions, we have found that a downward shift of d states, which changes the degree and character of hybridization as well as the probability of occupation, results in a more active participation of the virtual orbitals in representing the charge density. To some extent this is a real effect: d - p hybridization increases as the d states are pulled down nearer the p bands, and what one calls the d function, or the d charge, becomes less well defined. (The definition becomes clear for well-separated atoms, and perhaps for states well separated in energy from any other states.) The effect is

present with other basis sets as well, but is more difficult to identify.

It is important to understand clearly the source of this paradox. It arises because the “ d charge density” is not a precisely and objectively defined quantity. Although we are accustomed to thinking in terms of five d bands in a transition-metal oxide that can be identified and whose DOS integrates to five electrons per spin, this is a fiction that becomes apparent as soon as orbital overlap becomes appreciable. This difficulty has the same origin as the difficulty in defining the “ d orbital” to be used in the LDA+ U method. These ambiguities are problems that must be lived with until a better prescription can be formulated.

VII. SUMMARY

We have presented a reformulation of the method of obtaining U for a LDA+ U calculation. The approach is based on a local-orbital expansion, which is a natural one considering that the d orbital is to be singled out and specified in any case. We aim specifically to improve ground-state properties rather than to account for spectroscopic data.

Values of U using this approach are found to be only 40–65 % of the values of Anisimov and co-workers. Most of this difference is understood in terms of the definitions and procedures that are used in each case. A generalization presented here is the identification of an interaction matrix that describes interactions that are nondiagonal in the suborbital index, e.g., the change in energy of t_{2g} states due to a change in e_g charge. The off-diagonal parts of this interaction are expected to be strongly dependent on the environment of the ion, and this expectation is borne out in our study of FeO.

There are important aspects of our approach that require further work. The contribution to U from the kinetic energy, and how it should be dealt with, is one loose end. The most appropriate choice of d orbital is another question that may require some experience to answer. Carrying out LDA+ U studies to compare with results using the previous LDA+ U method, and ascertaining the effect of off-diagonal interactions, are, however, the main priority, and this work is in progress.

ACKNOWLEDGMENTS

We have benefited from discussions with V. I. Anisimov, G. E. Engel, and I. I. Mazin. E.C.E gratefully acknowledges support from the National Research Council. This work was supported by the Office of Naval Research. Calculations were carried out at the Arctic Region Supercomputer Center and at the DoD Shared Resource Center at NAVO.

*Permanent address: Department of Physics, University of California, Davis CA 95616. Electronic address: pickett@physics.ucdavis.edu

¹T. C. Leung, X. W. Wang, and B. N. Harmon, Phys. Rev. B **37**, 384 (1988).

²W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

³J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963); **277**, 237 (1964); **281**, 401 (1964).

⁴F. Aryasetiawan and O. Gunnarsson, Phys. Rev. Lett. **74**, 3221 (1995).

⁵V. I. Anisimov and O. Gunnarsson, Phys. Rev. B **43**, 7570 (1991).

⁶V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

⁷V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyżyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16 929 (1993).

⁸A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).

⁹M. T. Czyżyk and G. A. Sawatzky, Phys. Rev. B **49**, 14 211 (1994).

- ¹⁰P. H. Dederichs, S. Blugel, R. Zeller, and H. Akai, Phys. Rev. Lett. **53**, 2512 (1984).
- ¹¹B. N. Cox, M. A. Coulthard, and P. Lloyd, J. Phys. F **4**, 807 (1974).
- ¹²S. C. Erwin, M. R. Pederson, and W. E. Pickett, Phys. Rev. B **41**, 10 437 (1990).
- ¹³R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).
- ¹⁴I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov, Phys. Rev. B **50**, 16 861 (1994).
- ¹⁵I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B **53**, 7158 (1996).
- ¹⁶M. S. Hybertsen, M. Schlüter, and N. E. Christensen, Phys. Rev. B **39**, 9028 (1989); See also A. K. McMahon, r. M. Martin, and S. Satpathy, *ibid.* **38**, 6650 (1988); G. Vielsack and W. Weber, *ibid.* **54**, 6614 (1996).
- ¹⁷One could try making use of the relation $\mathcal{E}_K = -[d\mathcal{E}/d \ln m]_{m=m_o}$, which makes use of the variational nature of the total energy \mathcal{E} (m_o is the electron mass).
- ¹⁸W. E. Pickett and S. C. Erwin, Phys. Rev. B **41**, 9756 (1990).
- ¹⁹M. R. Norman and A. J. Freeman, Phys. Rev. B **33**, 8896 (1986).
- ²⁰J. Zaanen and G. A. Sawatzky, J. Solid State Chem. **88**, 8 (1990).
- ²¹A. E. Bocquet *et al.*, Phys. Rev. B **46**, 3771 (1992).