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LSDA+U method: A calculation of the U values at the Hartree-Fock level of approximation

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One of the basic problems of the density-functional theory/spin polarized local-density approximation (DFT/LSDA)+U theory is the efficient evaluation of the U term. In the present work, we propose an alternative approach for its calculation which is based on the knowledge of the Hartree-Fock (HF) wave functions of the system under consideration. As a result, the proposed approach is closer to the basic definition of the DFT/LSDA+U scheme and its hybrid-DFT nature. According to our approach, the U value is obtained in a consistent and *ab initio* way using the self-consistently calculated wave functions of the given system at the level of the HF approximation. Our method is applicable for systems which include more than one type of elements with localized d orbitals. Application of the method in the case of the doped Zn(Co)O system is presented.

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I. INTRODUCTION

As part of the first attempts to go beyond the spin polarized local-density approximation (LSDA) or the spin polarized generalized density gradient approximation (SGGA), of the density-functional theory (DFT), the following correction $\Delta E_{cor}[\{n_i\}]$ to the DFT/LSDA (or the DFT/SGGA) functional was considered for systems including d electrons,[1–4]

$$\Delta E_{cor}[\{n_i\}] = -E_{dd}^{\mathrm{LSDA}}[n_d] + E_{\mathrm{HF}}[\{n_i\}], \tag{1}$$

where $E_{dd}^{\mathrm{LSDA}}[n_d]$ is the electron-electron interaction for the localized d states in the LSDA, which depends only on the total number of localized electrons $n_d = \Sigma_i n_i$ with n_i being the orbital occupancies of the localized states, and $E_{\mathrm{HF}}[\{n_i\}]$ is the Hartree-Fock (HF) expression for the d-d (localized electrons) interaction. Thus, by the definition dictated by Eq. (1), the corrected DFT/LSDA is one type of a hybrid DFT with its differentiation from the latter originating from the expression of $E_{\mathrm{HF}}[\{n_i\}]$ which is defined in terms of renormalized orbital dependent Coulomb, U_{ij}, and exchange, J_{ij}, parameters taking the form

$$E_{\mathrm{HF}}[\{n_i\}] = \frac{1}{2}\sum_{i\neq j}(U_{ij} - J_{ij})n_i n_j. \tag{2}$$

This model is known as the DFT/LSDA+U model (although it is mostly implemented within the DFT/SGGA rather than within the DFT/LSDA). Therefore, it can be claimed that, by its definition, this model belongs in one way or the other to the general class of the hybrid-DFT theories which rely on the accurate results of the HF theory. It should be noted, however, that other approximations to $\Delta E_{cor}[\{n_i\}]$ may also be used. These depend on the choice of the functional upon which the U correction is made and, consequently, on the physics underlying such an approximation. For example, Cococcioni and de Gironcoli[5] adopt the U parameter as the (unphysical) curvature of the total-energy curve as a function of the occupation numbers. Interestingly, their correction to the LDA total energy, in fact, amounts to the incorporation of the Hubbard U term. For this type of functional the LDA/GGA type of wave functions are more appropriate.

The realization of the DFT/LSDA+U model depends strongly on the accurate determination of the U_{ij} and J_{ij} parameters which in turn depend on the Slater integrals F^k in terms of which they are calculated.[1,3] Solovyev *et al.*[2] used LSDA-based results to obtain U_{ij} and J_{ij} for the 3d elements arguing that the single electron wave functions derived within the LSDA/SGGA seem to improve the overestimation which is introduced in the calculation of F^2, F^4, and F^6 integrals when these are obtained using atomic functions.

The matrix elements U_{ij} and J_{ij} of the Coulomb and exchange interactions can be obtained by differentiating (second-order derivative) the LSDA energy with respect to the variation in the electron-density matrix and to the variation in the magnetization, respectively.[2,3] These differentiations lead to expressions for U_{ij} and J_{ij}, respectively, in terms of (effective) Slater integrals F^k and integrals over products of three spherical harmonics.[1,3] Such estimations of U_{ij} and J_{ij} are based on the assumption that the LSDA energy is a continuous function of both the electron density and the magnetization. That is, they are based on the well-tested supercell LSDA approach according to which the matrix elements of the electron density have to be constrained locally and the second-order derivative of the LSDA energy with respect to these elements yields the wanted interactions.[3,6]

On the other hand, averaging U_{ij} and $U_{ij}-J_{ij}$ over all possible ij pairs one finds for the average U and J values:

$U=F^0$ and $J=(F^2+F^4)/14$.[1] This is a very useful result because one can make use of the existing tables for F^2 and F^4 for the $3d$ elements and have numerical values for J [$J=(1.625/14)F^2$ as obtained by exploiting the fact that $F^4/F^2 \approx 0.625$].[1–3] This is the most commonly used approach in practical applications of the DFT/LSDA+U method, i.e., obtaining U and J values by using tabulated data of the F^k integrals. This procedure has been applied with success in systems containing single species having localized (d) electrons. For such systems one can employ the averaging of U_{ij} and $U_{ij}-J_{ij}$ and obtain one pair of (U,J) values that will be assigned to the element with the d electrons. However, in many practical applications as, for example, in the case of doped transition-metal oxides, e.g., the Co-doped ZnO [to be denoted as Zn(Co)O], more than one elements with localized electrons coexist, rendering the above averaging scheme inapplicable. One, thus, has to employ the second-order (numerical) differentiations for getting the (U,J) values for each element with localized electrons.

The variety of the proposed implementations of the DFT/LSDA+U method,[1–5,7] despite guaranteeing the self-consistent incorporation of the U and J terms, has not lead to any substantial improvement in the energy gap of the metal oxides if applied only on the d electrons. This has led to semiempirical applications of the DFT/LSDA+U method in which the (U,J) values are treated as parameters which are obtained empirically by fitting to experimental data.[8] As a result, the DFT/LSDA+U approach when applied in this manner looses its *ab initio* character and therefore its predictive power.

In the present work, we propose an alternative approach which is based on the knowledge of the HF wave functions of the system which, as a result, is closer to the basic definition of the DFT/LSDA+U scheme which aims to correct the DFT/LSDA functional so as to be able to recover the correct HF features [as expressed in Eq. (1)]. According to our approach the (U,J) values are obtained in a consistent and *ab initio* way using self-consistently calculated wave functions of the given system at the level of the analytic HF approximation [as stated in Eq. (1)]. In terms of these HF wave functions, we first calculate the U and J values and then incorporate them (as constant parameters) into one of the existing DFT/LSDA+U schemes. The present approach can also be used for s and p electrons as well to generate U and J corrections for them which appear necessary in improving the gap deficiency of the DFT/LSDA theory.[8]

II. PROPOSED NEW APPROACH

Both DFT/LDA+U or the DFT/SGGA+U can be put on a firm *ab initio* footing provided that the determination of the parameters U and J has been achieved in an *ab initio* way. Toward this end, a direct and efficient parametrization of the HF solution is greatly desirable in order to obtain the exact U and J parameters. This is attempted in the following.

In particular, it is assumed that we can run a HF code for a system of interest, obtain the HF energy, E_{HF}, (i.e., its Coulomb, $E_{\mathrm{HF},Cb}$, and the exchange energy, $E_{\mathrm{HF},X}$, contributions and the orbital occupation numbers, n_α^{HF}) and can isolate the contribution E_{HF}^{loc} to the HF energy which is due to the localized orbitals (or more generally to a set of orbitals). Having this E_{HF}^{loc}, and its Coulomb and exchange contributions ($E_{\mathrm{HF},Cb}^{loc}$ and $E_{\mathrm{HF},X}^{loc}$, respectively) the parameters U and J can then be extracted using the following equations:

$$E_{\mathrm{HF},Cb}^{loc} = \sum_{\alpha\neq\beta} U_{\alpha\beta} n_\alpha^{\mathrm{HF}} n_\beta^{\mathrm{HF}} \tag{3}$$

and

$$E_{\mathrm{HF},X}^{loc} = \sum_{\alpha\neq\beta} J_{\alpha\beta} n_\alpha^{\mathrm{HF}} n_\beta^{\mathrm{HF}}. \tag{4}$$

In the spirit of the DFT/GGA+U,[2,5] one needs to apply Eqs. (3) and (4) for the localized orbitals of the system. However, a question remains as to whether this can also be applied for the nonlocalized orbitals by choosing an integration radius around the atom of interest in an appropriate way.

A. Implementation of the present method

We start with the expression of the Hartree-Fock energy assuming atomic orbitals (AOs) Ψ_i of the form

$$\Psi_i = \Psi_i(\mathbf{r_i}) = \Omega_i(\theta_i,\phi_i) R_{n_i\sigma_i}(r_i) = Y_{l_i m_i}(\theta_i,\phi_i) R_{n_i\sigma_i}(r_i) \tag{5}$$

with i representing the set of the quantum numbers $\{n_i l_i m_i \sigma_i\}$ (main, orbital, magnetic, and spin quantum numbers, respectively):

$$E_{\mathrm{HF}} = \sum_{i,j\neq i} n_i^{\mathrm{HF}} n_j^{\mathrm{HF}} (E_{\mathrm{HF},Cb}^{ij} + E_{\mathrm{HF},X}^{ij}), \tag{6}$$

where $E_{\mathrm{HF},Cb}^{ij}$ and $E_{\mathrm{HF},X}^{ij}$ are Coulomb and exchange contributions to E_{HF}, respectively. The Coulomb term

$$E_{\mathrm{HF},Cb}^{ij} = \langle \Psi_i \Psi_j | \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} | \Psi_j \Psi_i \rangle \tag{7}$$

takes the explicit form (suppressing the spin index),

$$E_{\mathrm{HF},Cb}^{ij} = \sum_{L,M} \frac{4\pi\Omega_{ij}^{(0)}}{2L+1} \int \frac{r_<^L}{r_>^{L+1}} R_i R_j R_j R_i r_i^2 dr_i r_j^2 dr_j, \tag{8}$$

where $\Omega_{ij}^{(0)}$ is the output of the integration of the angular terms expressed in terms of a combination of $3j$ symbols

$$\Omega_{ij}^{(0)} = \int \Omega_i^\star \Omega_i \Omega_{LM}(\theta_i,\phi_i) d\omega_i \int \Omega_j \Omega_j^\star \Omega_{LM}^\star(\theta_j,\phi_j) d\omega_j \tag{9}$$

with

$$\int \Omega_{i_1}^\star \Omega_{i_2} \Omega_{i_3}(\theta_i,\phi_i) d\omega = \Lambda \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}, \tag{10}$$

where

$$\Lambda = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \tag{11}$$

and the terms in brackets denote Wigner's $3j$ symbols.

A similar expression is derived in a straightforward way for the exchange contribution $E^{ij}_{\mathrm{HF},X}$ to E_{HF},

$$E^{ij}_{\mathrm{HF},X} = \langle \Psi_i \Psi_j | \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} | \Psi_i \Psi_j \rangle . \tag{12}$$

Our computational approach for evaluating $E^{ij}_{\mathrm{HF},Cb}$ and $E^{ij}_{\mathrm{HF},X}$ makes use of an approach which is commonly used in quantum chemistry calculations. That is, we express the radial functions R_i in terms of Gaussian-type orbitals (GTOs), $\chi_q(r)$, i.e.,

$$R_i(r_i) = C_i \sum_q \chi_{iq}(r_i), \tag{13}$$

where C_i are coefficients obtained from the Hartree-Fock solution as detailed in the following. It is recalled that the wave functions $R_i(r_i)$ of the HF solution include components corresponding to s, p, d, and f orbitals (and correspondingly, GTOs).

As we are interested in the Hartree-Fock energy of the localized orbitals, we locate the components of the HF wave functions which correspond to contributions from these orbitals only (e.g., the d orbitals) extracting thus, the set of the Ψ_i orbitals which we will use in the evaluation of $E^{loc}_{\mathrm{HF},Cb}$ and $E^{loc}_{\mathrm{HF},X}$ using the formalism and the expressions for $E^{ij}_{\mathrm{HF},Cb}$ and $E^{ij}_{\mathrm{HF},X}$ given in the above.

Note that the energy, E^{loc}_{HF}, is calculated by taking the localized electrons to be isolated, i.e., not being in the field of the other electrons of the system. If we want to take into account the interaction of the localized electrons with the rest of the system, then we should repeat the calculation taking in this case the rest of the electrons as the isolated part. From the total E^{loc}_{HF} and its two terms ($E^{loc,1}_{\mathrm{HF}}$ for the localized electrons and one for the remaining ones, $E^{loc,2}_{\mathrm{HF}}$) we can get the $E^{\star,loc}_{\mathrm{HF}}$ for the localized electrons in the field of the rest of the system. Having obtained $E^{loc}_{\mathrm{HF},Cb}$ and $E^{loc}_{\mathrm{HF},X}$, the estimation of U and J can be obtained by fitting the results as given by Eqs. (3) and (4).

B. Example applications: Computational details

We next apply the above described computational scheme in the case of the bulk ZnO approximated by a $\mathrm{Zn}_N\mathrm{O}_N$ cluster exhibiting the wurtzite structure. For the first set of calculations we consider the case $N=22$. Our objective for this system is to calculate the U and J values for the Zn($3d$) orbitals and compare them with other reported results. Thus, the *localized orbitals* are the Zn($3d$) ones and, consequently, we restrict the set of the quantum numbers $\{n_i l_i m_i \sigma_i\}$ to the $\{n_i = 3, l_i = 2, m_i \sigma_i\}$ one.

The symmetry of the system dictates that we choose a set of six basis functions of d character, namely, the set $\{d_{xy}, d_{yz}, d_{xz}, d_{xx}, d_{yy}, d_{zz}\}$. Each of these basis functions is given as a superposition of three GTOs $\chi_{iq}(r)$ of d character with each GTO being localized on each of the Zn ions and specified by its exponent α_{iq} and its coefficient d_{iq} having the form

$$\chi_{iq}(r) = d_{iq} r^2 \exp^{-\alpha_{iq} r^2}. \tag{14}$$

Both the coefficients d_{iq} and the exponents α_{iq} are obtained from reported tables. In the present example we used the results of Ref. 9. Thus, each one of the six basis d functions has the form of Eq. (13). The molecular orbitals (MOs) of the system are a linear superposition of these basis functions taken over the whole system. That is, each MO will consist of $6N$ d components, where N is the number of the d ions of the cluster or the supercell of the system. We obtain the $6N$ C_i d coefficients, which specify the MOs according to Eq. (13), from the HF solution.

It should be understood that in order to get the correct HF solution of the system we include basis functions for the s and p (and sometimes the f) orbitals as well. As a result, the HF wave functions (MOs) have more than just the $6N$ d components. However, it is the $6N$ components of d character that are used in the calculation of U and J.

In the case of the Co-doped ZnO [to be denoted as Zn-(Co)O], U and J values should be found for both Zn($3d$) and Co($3d$) orbitals keeping in mind that these may not be the same for the two materials. In this case one may use for Co the same set of GTOs as used for Zn or specify one set of GTOs for Zn and another one for Co. In either case Zn and Co should be described by the same type of basis functions $\{s; p_x; p_y; p_z; d_{xy}, d_{yz}, d_{xz}, d_{xx}, d_{yy}, d_{zz}\}$.

For the case of the ZnO, we obtained the HF solution of a ZnO cluster consisting of 44 atoms (22 Zn and 22 O atoms) using the GTOs of Ref. 9. We then located those MOs with pronounced d character. That is, those which have significant contribution from the AOs (i.e., basis functions) of d type. From each of the so selected MOs we obtain one set of six coefficients C_i [see Eq. (13)] for the six d orbitals. It is assumed that such a set specifies the localized d orbitals of Zn and use this set to calculate the U and J values according to the procedure described in Sec. II A. This procedure is repeated for all the selected MOs exhibiting d character before finally averaging the U and J values obtained.

Subsequently, the proposed procedure is applied in larger ZnO clusters, namely, the $\mathrm{Zn}_{40}\mathrm{O}_{40}$ and $\mathrm{Zn}_{59}\mathrm{O}_{59}$ clusters, as well as in the case of the Co-doped ZnO approximated by two clusters, namely, the $\mathrm{Zn}_{21}\mathrm{CoO}_{22}$ and the $\mathrm{Zn}_{20}\mathrm{Co}_2\mathrm{O}_{22}$ ones.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the 44-atom ZnO cluster, exhibiting the wurtzite structure, used in our calculations. The lattice sites are numbered and this enumeration is used in Table I in order to indicate the positions of the Zn atoms whose d functions were used in the calculation of the U and J values shown in this table.

The results shown in Table I have been obtained using a selected partial set of the cluster MOs which exhibit a significantly pronounced d character (greater than 70%). Average U and J values of this set of MOs over the Zn atoms of the cluster are shown in Table II. As can be seen in Table I, there is a rather large spread in the obtained U and J values over the Zn atoms. This seems to suggest a strong depen-

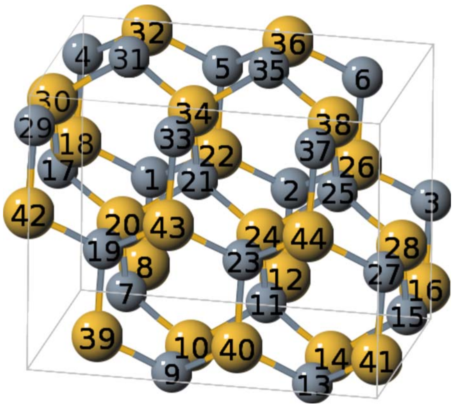

FIG. 1. (Color online) The 44-atom ZnO cluster used in the calculations. Zn atoms are shown in yellow (gray). The numbering of sites corresponds to that referred to in Table I.

dence of the U's and J's on the cluster site while appearing to have a negligible dependence on the MO eigenvalue (shown also in Table I). This observation indicates a dependence of both U and J on the group symmetry of the cluster site which in turn specifies the hybridization associated with this site AOs, their occupancies and their degrees of freedom.

In order to further verify this, we have examined the character of the d MOs which correspond to high (U,J) values and that of the MOs which correspond to low (U,J) values. Surprisingly, we find that MOs with t_{2g} dominant character (i.e., with contributions from XY, XZ, and YZ type orbitals) correspond to low (U,J) values, while MOs with e_g dominant character (e.g., XX, YY, and ZZ type orbitals) correspond to high (U,J) values. This relationship has been checked in a predictive way very successfully.

These conclusions were further verified by extending our methodology to larger ZnO clusters by considering 80- and 118-atom clusters. Results corresponding to partially selected sets of MOs of these clusters are included in the supplementary information.[10] These results provide further confirmation of the conclusions we arrived at by analyzing the results of the 44-atom cluster. This lends strong credence to the predictive character of our conclusion establishing a relationship between the character of the d MO and the (U,J) values associated with it. This in turn naturally leads to the question about the relationship between the point symmetry of the cluster site and the (U,J) values and, therefore, of the site dependence of the (U,J) values. The necessity of introducing such a site dependence of U has been shown in studies of bulk phases as well, as demonstrated in the case of Fe_3O_4 for which different U values were assigned for Fe^{2+} and Fe^{3+} ions (sites).[11] However, our results do not show a clear relationship between the character of the d orbital and the point symmetry of a lattice site.

TABLE I. Calculated values of U, J, and $U-J$ for the ZnO44 cluster according to the proposed computational procedure. The site position shown in column 2 is indicated in Fig. 1. In the first column we indicate the eigenvalue of the corresponding MO relative to the HOMO level.

MO energy (eV)	Site No.	$U-J$ (eV)	U (eV)	J (eV)
−25.287	Zn(39)	1.515	1.848	0.334
−25.219	Zn(39)	3.006	3.671	0.665
−24.922	Zn(41)	2.891	3.388	0.497
−23.130	Zn(8)	4.363	5.263	0.900
−22.358	Zn(16)	1.707	2.068	0.361
−22.067	Zn(28)	4.361	5.218	0.857
−21.845	Zn(42)	4.461	5.228	0.767
−20.104	Zn(20)	2.812	3.372	0.560
−19.975	Zn(20)	3.399	4.091	0.691
−17.392	Zn(36)	2.832	3.515	0.682
−17.051	Zn(32)	5.504	6.528	1.024

In Table II we present the average values of the parameters (U,J) as obtained by averaging over all occupied MOs which exhibit a d character of more than 25%. The number of MOs used for each cluster is also indicated in Table II. It is apparent from this table that there is a rather good convergence of the average values with the cluster size. However, it is quite noticeable that the average values are an isobaric balance of small and large (U,J) values indicating an isobaric distribution of t_{2g} and e_g MOs. As shown in this table, if the averaging process is taken over those MOs which exhibit d contribution greater than 50%, the obtained average values are found to be larger. A further increase in the average (U,J) values is obtained if the d contribution of the MOs is taken to be more than 70%. These results indicate that the level of hybridization of the d states appears to be a crucial factor in specifying the (U,J) values thus making it very

TABLE II. Average values of the U, J, and $U-J$ values over the Zn atoms of the indicated clusters considered in the present investigation. In the fifth column we insert the total number of the cluster MOs exhibiting d contribution greater than that indicated in the last column. The averages were taken over these sets of MOs.

Cluster	$\langle U-J\rangle$ (eV)	$\langle U\rangle$ (eV)	$\langle J\rangle$ (eV)	No. of MOs	MO's d contribution (%)
44-ZnO	1.525	1.722	0.197	111	25
80-ZnO	1.926	1.717	0.209	198	25
118-ZnO	1.593	1.788	0.195	263	25
118-ZnO	1.805	2.014	0.209	97	50
118-ZnO	3.003	3.308	0.305	7	70

clear, as stated in Sec. I, the very crucial nature of the choice of the wave functions used in the estimation of the (U,J) values.

It is also worth noting that the d states obtained from the HF calculation are much deeper [relative to the energy of the highest occupied MO (HOMO)] than the corresponding DFT/LDA findings[12] or the experimentally observed location of the peak of the density of states (DOS) of the Zn($3d$) states with the latter located at $\approx 7-8$ eV below the valence-band maximum.[13–15]

The values of U and J obtained from the wave functions exhibiting e_g character are in rather good agreement with the reported values for ZnO. In fact, the representative U and J values for transition metals reported in the literature are $U = 4.5$ eV and $J = 0.5$ eV.[16] X-ray absorption and emission spectra as well as GW calculations for ZnO are found to be recovered within the DFT/LSDA+U using $U = 6.0$ eV for Zn leading to a Zn($3d$) DOS peak at about -7.0 eV below the valence-band maximum,[14] in close agreement with the experimental value of -7.4 eV.[15] Anisimov *et al.*[7] using table data of the Slater integrals estimate the U and J values in the range (6.8–8.0) eV and (0.78–0.98) eV, respectively. Finally, we find that, in order to fit the experimentally observed peak of the Zn($3d$) DOS with that obtained within the DFT/SGGA+U method for the Zn(Co)O system, the U values for Zn($3d$) and Co($3d$) electrons have to be 6.5 eV and 3.5 eV, respectively. However, these values should be considerably modified if a U value for the O ions is simultaneously incorporated.[8] It is worth noting, however, that a comparison of the U values obtained with different computational schemes is meaningful only if these U corrections are applied to the same DFT functional.

Applying the same procedure to the $Zn_{21}CoO_{22}$ cluster we find that the presence of the Co atom in the cluster site 24 [to be denoted as Co(24)] leads to a 4% and 3% decrease in the partial average (corresponding to the selected set of MOs used in Table I) of U and J values, respectively, over the Zn atoms. On the other hand, in the case of the $Zn_{20}Co_2O_{22}$ cluster (with the two Co atoms located at sites 12 and 43) we find an increase of 4.5% and 6% for the partial average U and J values, respectively (with respect to the undoped cluster).

In the $Zn_{21}CoO_{22}$ cluster, the U and J values for Co were found to be very small, namely, 0.736 eV and 0.210 eV, respectively. In the $Zn_{20}Co_2O_{22}$ cluster, the corresponding U and J values for the two Co atoms were found to be: 5.276 eV and 0.660 eV for Co(12) and 0.878 eV and 0.250 eV for the tetrahedrally bonded Co(43) atom. It should be noted however, that for the Co-doped clusters we did not find MOs with pronounced d character. The contribution of the Co d orbitals to the MOs of the corresponding clusters is approximately 40% indicating a strong delocalization as a result of their hybridization. Furthermore, and in agreement with DFT/SGGA calculations (see, for example, Ref. 8 and references therein), the eigenvalues of the Co(d) dominated MOs are much closer to the HOMO level than that of the Zn($3d$) dominated ones.

In conclusion, we have presented a computational scheme for estimating the parametrization of the DFT/SGGA+U method. Our approach is in consistency with the whole concept (definition) of the SGGA+U correction and is based on the *ab initio* HF theory. Our method was applied to bulk ZnO and the Co-doped ZnO systems both approximated by small clusters. The obtained results indicated a strong dependence of the obtained U and J values on the symmetry of the cluster site. However, on the average, the obtained U and J values are in good agreement with the results obtained by other methods.

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[1] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).

[2] I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov, Phys. Rev. B **50**, 16861 (1994).

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

[4] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57**, 1505 (1998).

[5] M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).

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

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

[8] N. N. Lathiotakis, A. N. Andriotis, and M. Menon, Phys. Rev. B **78**, 193311 (2008).

[9] V. A. Rassolov, J. A. Popple, M. A. Ratner, and T. L. Windus, J. Chem. Phys. **109**, 1223 (1998).

[10] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevB.81.245103 for results corresponding to partially selected sets of MOs of 80- and 118-atom ZnO clusters.

[11] V. N. Antonov, B. N. Harmon, V. P. Antropov, A. Y. Perlov, and A. N. Yaresko, Phys. Rev. B **64**, 134410 (2001).

[12] J. E. Jaffe and A. C. Hess, Phys. Rev. B **48**, 7903 (1993).

[13] B. Sanyal, O. Grånäs, R. Knut, V. A. Coleman, P. Thunström, D. M. Iuşan, O. Karis, O. Eriksson, and G. Westin, J. Appl. Phys. **103**, 07D130 (2008).

[14] S. Z. Karazhanov, P. Ravindran, A. Kjekshus, H. Fjellvag, and B. G. Svensson, Phys. Rev. B **75**, 155104 (2007).

[15] A. R. H. Preston, B. J. Ruck, L. F. J. Piper, A. DeMasi, K. E. Smith, A. Schleife, F. Fuchs, F. Bechstedt, J. Chai, and S. M. Durbin, Phys. Rev. B **78**, 155114 (2008).

[16] P. Gopal and N. A. Spaldin, Phys. Rev. B **74**, 094418 (2006).