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Calculation of the Hubbard U Parameters by the Solid Atom Method

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An effective method, *i.e.*, the solid atom method, is suggested to obtain the Coulomb interaction parameter, U, and the Hund exchange coupling constant, J, for use in the LDA+U calculation. The parameters are obtained self-consistently during the LDA+U calculation. The method is applied to typical transition metal oxides and MnB^{VI} (B^{VI}=S,Se,Te). The U values for the transition metal oxides have similar magnitude to previous calculations although they are obtained by a much simpler method. MnB^{VI}s have been characterized as crossroads materials between charge transfer and band insulators by the LDA+U calculation.

Key words : electronic structure, LDA+U, strong correlation, Hubbard

1. Introduction

Electronic and magnetic properties of a solid can be understood theoretically by electronic structure calculations on the base of the density functional theory [1]. Many body effects due to the Coulomb interaction among electrons are usually considered within the local density approximation (LDA) [2]. LDA is a kind of mean field theory which is adequate for materials without strong correlation effect. However, for materials with the strong correlation such as the transition metal oxides and the high-temperature cuprate superconductors, it is essential to consider the strong correlation effect correctly into theoretical consideration. Well-known examples among transition metal oxides are FeO and CoO that LDA fails to give correct insulating ground states but describe it metallic [3].

Electrons in the *s*- and the *p*- orbitals responsible for the bonding can be described properly by using conventional LDA band calculations. However, the LDA energy bands may not describe correctly the highly correlated transition metal *d*-electrons and excited states. Therefore, it is necessary to treat the highly correlated *d*-electrons separately from the bonding electrons. The LDA+U method [4, 5] is suitable for this kind of calculations, where the strong correlation effect is considered effectively by introducing a Hubbard type interaction in the description of the localized orbitals. LDA+U method is a simple and fast method to include the correlation effect compared to other sophisticated ones like LDA+GW [6] or LDA+DMFT [7].

The LDA+U method requires the Coulomb interaction parameter, U, and the Hund exchange coupling constant, J. Choosing proper values for U and J constitutes another problem in utilizing the LDA+U method. In usual LDA+U calculations, these values are determined from other independent calculations and then they are kept constant in the self-consistent procedure. Several methods have been proposed to calculate the U values such as the cellular method [8] or the supercell methods [4, 9-11]. In the supercell methods, the central atom is treated as an impurity with variable occupation number in the correlated orbitals. Usually, the calculation of U is very involved, since one should consider all possible screening mechanisms as well as the large unit cell. Thus, it is desirable to devise an easy method to obtain the U values.

In this study, we have devised a simple method to calculate U and J, what we call a solid atom method (SAM). In this method, U and J values are evaluated by solving an atomic problem where the charge density in an atomic sphere is taken from the charge density of the solid state calculation. Difference from the usual atomic problem is that the potential obtained from the solid state charge density is used in solving the Schrdinger-like equation. Hence, the potential for the atomic problem has the form of the muffin-tin potential. If U and J values are obtained by SAM, they can be given as input parameters

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for next LDA+U calculations. U and J values are calculated at each iteration during the self-consistent loop until the self-consistency criteria are satisfied. We have tested our method with typical transition metal chalcogens.

This paper is organized as follows: In Sec. 2, we provide a formalism for SAM to obtain the Coulomb interaction parameter, U, and the Hund coupling constant, J, and, in Sec. 3, tested our SAM on typical strongly correlated electron systems, namely, 3*d*-transition metal oxides and MnB^{VI}(B^{VI}=S,Se,Te). Final conclusions follow in Sec. 4.

2. Methodology

In SAM, we make use of the differential definition for U. In the spin polarized case, U is defined as [12]

$$U = E\left(\frac{n}{2}+1;\frac{n}{2}\right)-E\left(\frac{n}{2};\frac{n}{2}\right)-E\left(\frac{n}{2}+1;\frac{n}{2}-1\right)+E\left(\frac{n}{2};\frac{n}{2}-1\right) \tag{1}$$

where $E(n_\uparrow ; n_\downarrow)$ is the total energy of the system with $n_\uparrow$ and $n_\downarrow$ electrons in each localized spin orbital. By using Janak's theorem [13], the LDA eigenvalues are related to the differential of the total energy functional,

$$\varepsilon_i = \frac{\partial E}{\partial n_i} \tag{2}$$

where i is the band index. Then, Eq. (1) reduces to

$$U = \varepsilon_{3d\uparrow}\left(\frac{n}{2}+\frac{1}{2};\frac{n}{2}\right)-\varepsilon_{3d\downarrow}\left(\frac{n}{2}+\frac{1}{2};\frac{n}{2}-1\right) \tag{3}$$

This corresponds to the usual definition of U by Slater's transition-state rule [14]. One can regard this as a finite difference form of

$$U = \frac{\partial \varepsilon_{3d\uparrow}}{\partial n_\downarrow} \tag{4}$$

which allows one to evaluate U by numerical differentiation. Here, the formalism is presented only for 3*d* transition metal compounds while it can be easily extended to 4*f* orbitals [15]. Due to screening by other electrons, the magnitude of the Coulomb interaction in the solid system should be smaller than the atomic value. The Hund exchange constant J is obtained from the relation between the exchange splitting and the magnetic moment of the atom,

$$\varepsilon_{3d\downarrow} - \varepsilon_{3d\uparrow} = mJ \tag{5}$$

where m is the magnetic moment due to the d electrons.

The self-consistent LDA+U procedure is as follows. First, LDA eigen-solutions are obtained for a system self-consistently. Second, an atom is isolated for which the U and the J values are to be extracted. We call this isolated atom as the solid atom, because the atom has the charge density and the potential given by the solution of the solid state Schrödinger-like equation. Then, numerical differentiation of Eq. (4) is performed to obtain the U value. The occupation number of the d-orbital is changed slightly to induce the change of the energy level. In this process, it is assumed that the slight change in d-occupation number is screened by valence s-electrons in the solid atom and that the slight change of charge distribution does not affect the overall charge distribution in the solid atom. During the calculation, the total number of electrons in the solid atom is conserved. One should make the change of occupation number as small as possible to satisfy the above assumptions. Third, with the Coulomb interaction parameter U obtained, the LDA+U Hamiltonian is constructed for the solid. For LDA+U calculation, we have used a rotationally invariant LDA+U code [16, 17] implemented in the first principles linearized muffin-tin orbital method within the atomic sphere approximation (LMTO-ASA) [18, 19]. The rotationally invariant form of LDA+U [20] is convenient since the crystal structure of solid is considered automatically in the formalism although the original one [4] depends on the crystal symmetry. Again, the second and the third procedure are repeated until the self-consistent U value and the electronic structure are obtained.

Eq. (4) can be expressed more generally as

$$U_{\alpha\beta} = \frac{\partial^2 E}{\partial n_\alpha \partial n_\beta} \tag{6}$$

where α and β denote spin indices. However, different values of U are obtained when the order of differentiation in spin indices is changed, that is,

$$\frac{\partial \varepsilon_{3d\downarrow}}{\partial n_{3d\uparrow}} = U_{\uparrow\downarrow} \neq U_{\downarrow\uparrow} = \frac{\partial \varepsilon_{3d\uparrow}}{\partial n_{3d\downarrow}} \tag{7}$$

Hence, in actual calculations, we have used the spin-averaged value for U,

$$U = \frac{1}{2}\left(U_{\uparrow\downarrow} + U_{\downarrow\uparrow} \right) \tag{8}$$

For example, in CoO, the value U=9.8 eV shown in Table 1 is the average of $U_{\uparrow\downarrow} = 9.3$ eV and $U_{\downarrow\uparrow} = 10.3$ eV.

It is well known that the ratio of F^4/F^2 is constant near 0.62 for most atoms, where F^2 and F^4 are the Slater integrals [14]. We have obtained F^4/F^2 by the direct integration of the wave function and we have found that this ratio is nearly constant, around 0.62, for all transition

Table 1. Calculated Coulomb interaction parameter (U), Hund coupling constant (J), energy gap (E_g) and the magnetic moment. Energies are in eV.

	U			J		E_g			M (μ_B)		
	Present	Other	Exp.	Present	Other	Present	Other	Exp.	Present	Other	Exp.
MnO	5.3	6.9[a], 3.6[b]	5.5[c], 4.0[e]	0.88	0.86[a]	2.32	3.5[a]	3.6-3.8[a]	4.78	4.61[a]	4.79[a], 4.58[a]
FeO	8.5	6.8[a], 4.6[b]	6.0[e], 5.7[e]	0.89	0.89[a]	3.60	3.2[a]	2.4[a]	3.75	3.62[a]	3.32[a]
CoO	9.8	7.8[a], 5.0[b]	6.5[e], 5.4[e]	0.89	0.92[a]	3.84	3.2[a]	2.4[a]	2.75	2.63[a]	3.35[a], 3.8[a]
NiO	11.1	6.9[a], 5.1[b], 7.9[c]	7.3[e], 6.9[e]	0.86	0.95[a]	3.36	3.1[a]	4.3, 4.0[a]	1.70	1.59[a]	1.77[a], 1.64[a], 1.90[a]
Fe_3O_4	7.7, 8.3	4.51[d]		0.97, 0.94		0	0.36[d]	0.14[d]	4.36, 4.23		4.1[f]

[a]Ref. 4. [b]Ref. 11. [c]Ref. 9. [d]Ref. 23. [e]A. Tanaka and T. Jo, J. Phys. Soc. Jap. **63**, 2788 (1994). [f]V. C. Rakhecha and N. S. Satya Murthy, J. Phys. C **11**, 4389 (1978).

metal oxides tested in this study. The U and J parameters are related to the Slater integrals by

$$U = F^0, \quad J = \frac{F^2 + F^4}{14}. \tag{9}$$

Thus, if values of U and J are given, the Slater parameters can be calculated directly from them.

3. Results

We have applied SAM to typical binary materials with TB^{VI} type (T = late 3d transition metals, B^{VI} = O,S,Se,Te). First series of materials are late transition metal oxides where the transition metal changes from Mn to Ni. The correlation effect is known to be large for the late transition metals. In the second series of calculations, U and J are obtained for manganese chalcogen compounds, MnB^{VI} (B^{VI} = S, Se, Te). All calculations are performed at experimental lattice constants for observed crystal structures. We have used the LMTO band method to calculate the electronic energy band structures with the von Barth-Hedin form of the exchange-correlation potential [21] and 80 and 160 **k**-points for the NaCl and NiAs structure, respectively, for tetrahedron integration [22] in the irreducible Brillouin zone.

3.1. U and J for transition metal oxides

Metal oxides have the type II antiferromagnetic spin arrangements in the cubic NaCl structure [4]. Table 1 shows calculated results for U, J, magnetic moments, and energy gaps for the transition metal oxides, which are compared with previously reported results. Anisimov *et al.* [4] calculated U and J values, using a rather sophisticated restricted density functional calculation. Pickett *et al.* [11] calculated U by using the differential definition of U. The present procedure gives U values that are a bit larger than previous calculations except for MnO. In the case of MnO, the U value is in-between the above two calculations [4, 11]. The increasing trend in U from MnO to NiO is consistent with other calculations. In transition metal oxides, the J values are nearly constant around 0.9 eV. We have obtained a smaller energy gap for MnO which seems to be due to the smaller value of U.

We have also calculated U and J values of Fe_3O_4 only for the sake of demonstration assuming the ferromagnetic phase, whereas it has a ferrimagnetic spin arrangement in nature. The metallic electronic structure of our result can be ascribed to wrong magnetic configuration. A correct magnetic structure gives rise to a semiconducting electronic structure [23, 24]. Fe_3O_4 has two types of Fe atoms in the spinel structure, one in a tetrahedral environment and the other in an octahedral environment. The LDA calculation yields that Fe at the octahedral site has more *d*-electrons (6.00 vs. 5.86) and a smaller magnetic moment (4.17 μ_B vs. 4.37 μ_B) than Fe at the tetrahedral site. We have obtained a larger U value at the octahedral site (8.3 eV) than at the tetrahedral site (7.7 eV), which is consistent with the tendency that an atom with more *d*-electrons has a larger U value [4, 10, 11, 25]. It is interesting that the U value at the octahedral site is similar to that of FeO which consists of only octahedral sites. Magnetic moments from the LDA+U calculation are 4.23 μ_B and 4.36 μ_B for the octahedral and the tetrahedral sites, respectively. Table 1 indicates that the SAM method gives reasonable values for U and J, and shows a consistent trend in that an atom with more *d*-electrons has a larger U value.

3.2. U and J for MnB^{VI}

We have applied the SAM method to MnB^{VI} (B^{VI} = S,Se,Te). MnB^{VI} are interesting since they are usual band insulators although the correlation effect between *d*-electrons is large [26]. LDA calculation gives a metallic state for antiferromagnetic MnTe in the NiAs structure [27, 28], different from the observed semiconducting state. Both MnS and MnSe have type II antiferromagnetic

Table 2. Calculated Coulomb interaction parameter (U), Hund coupling constant (J), energy gap (E_g), and magnetic moment (M). LDA, LDA+U, and Exp. represent the results of LDA calculation, LDA+U calculation, and experiment, respectively. Energies are in eV.

	U	J	E_g			M (μ_B)		
			LDA	LDA+U	Exp.	LDA	LDA+U	Exp.
MnS	6.0	0.87	0.85	1.24	2.7[a], 2.8[b]	4.29	4.59	4.54[c]
MnSe	6.1	0.86	0.46	0.67	2.0[a], 2.5[b]	4.34	4.64	>4.45[d]
MnTe	6.2	0.86	0.07	0.40	0.9[a], 1.3[b]	4.32	4.66	4.7[e]

[a]H. Sato, T. Mihara, A. Furuda, M. Tamura, K. Mimura, N. Happo, M. Taniguchi, and Y. Ueda, Phys. Rev. B. **56**, 7222 (1997). [b]Ref. 26. [c]Ref. 29. [d]S. J. Pickart, R. Nathans, and G. Shirane, Phys. Rev. **121**, 707 (1961). [e]Ref. 31.

spin arrangements in the cubic NaCl structure [29, 30], whereas MnTe has an antiferromagnetic spin arrangement in the hexagonal NiAs structure [31] in which Mn and Te are located at *2a* and *2c* sites, respectively. We have introduced empty spheres at the *2d* sites to account for the non-isotropic interstitial region around Te. The Mn-*d* electrons in these materials form localized magnetic moments in the high spin state.

In Table 2, the U and J values for MnB^{VI} are presented. The U values are nearly constant but slightly increasing as the anionic atomic number increases. A core x-ray photoemission study on Ni dihalides shows that the on-site Coulomb correlation U is roughly constant but that the charge transfer energy, Δ_{CT}, changes a lot as the halide anion changes [32]. As can be seen in Table 2, LDA+U energy gaps are not improved much from LDA. This is because MnB^{VI} has the crossroads character between charge transfer and band insulators. Since the energy gap is formed between the chalcogen-*p* and the Mn-*s* bands [17], LDA+U correction only at Mn 3*d*-orbital does not help much in enlarging the energy gap.

Table 2 also lists Mn magnetic moments. The resulting magnetic moments from the LDA+U are enhanced as compared to the LDA values, which is in good agreement with experiment. In the case of MnSe, the calculated magnetic moment shows a relatively large discrepancy from experiment because the experimental value is taken from MnSe doped with Li (0.05%). Since the size of magnetic moment varies greatly by doping in MnSe, increasing with reduced doping concentration, the actual magnetic moment may be larger than the values given, 4.45 μ_B, in Table 2.

4. Conclusion

We have devised a simple method, *i.e.*, the solid atom method (SAM), to calculate the Coulomb interaction parameter, U, and the Hund exchange coupling constant, J, for use in the LDA+U calculation. The parameters are calculated self-consistently. SAM is tested for transition metal oxides and MnB^{VI} (B^{VI} = S,Se,Te). U values have similar magnitude to existing values in the literature and show increasing trend with atomic number consistent to other calculations although they are obtained by a much simpler method. LDA+U calculation does not improve much the electronic structure of MnB^{VI} due to its crossroads character between charge transfer and band insulators.

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