Coulomb interaction in oxygen $p$-shell in LDA+U method and its influence on calculated spectral and magnetic properties of transition metal oxides.

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Abstract

Coulomb interaction between electrons on $p$-orbitals of oxygen atom in strongly correlated compounds is not negligible, since its value ($U_p$) has comparable order of magnitude with the value of Coulomb interaction on $d$-orbitals of transition metal atom ($U_d$). We investigate the effect of taking into account Coulomb correlations in oxygen $p$-shell in addition to the correlations in the transition metal $d$-shell in frame of the LDA+U method. Our calculations for NiO, MnO and La$_2$CuO$_4$ show that this additional correction in general improves the agreement with experimental data for the spectral (energy gap values, relative position of the main peaks in X-ray photoemission spectroscopy (XPS) and Bremsstrahlung isohromate spectroscopy (BIS)) and magnetic properties (magnetic moment values and intersite exchange interaction parameters values).

71.27.+a Strongly correlated electron systems; heavy fermions - 74.25.Jb Electronic structure - 79.60.-i Photoemission and photoelectron spectra

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I. INTRODUCTION

During last several decades the electronic structure calculations from first principles became an important part of the solid state theory. The solution of such essentially many-particle problem as calculation of band structure of real materials is impossible without rather severe approximations. The most famous and commonly used approximation in \textit{ab initio} electronic structure calculations is density functional theory (DFT) \cite{1} within the local spin density approximation (LSDA). But, as an approximation based on the homogeneous electron gas theory \cite{2}, the LSDA is valid only for compounds with slow varying through the crystal charge density. In other words, the LSDA must describe well only the delocalized electronic states (broad bands). Nevertheless the LSDA is sometimes able to give correct ground state properties for the systems with rather narrow bands (see for example \cite{3}).

The most unusual physical properties were found in the systems with strong electron-electron Coulomb correlations (such as Mott insulators, high-$T_c$ superconductors, \textit{etc.}). These systems have been intensively investigated during last 20 years both by experimentalist and theoretician communities. All intriguing features of these systems come from the existence of nearly localized electronic states (narrow bands) such as $d$ or $f$ states of transition metals ions or rare-earth metals ions, respectively. To mark out the localized state one can apply the following criteria: kinetic energy of localized states is of the same or even smaller order of magnitude as the energy of Coulomb interactions. It is known that for strongly-correlated systems the LSDA often fails (high-$T_c$ related compound La$_2$CuO$_4$; insulating, antiferromagnetic transition metal oxides). However constrained LSDA calculations \cite{4} give Coulomb interaction parameter values in surprisingly good agreement with the experimental estimations \cite{4–11}.

Several approaches were built on the LSDA basis repairing its deficiency in describing Coulomb interaction between localized states. The most popular methods are the self-interaction correction method (SIC) \cite{12,13} and the LDA+U method \cite{14}. 

2
The basic problem of the LSDA is the orbital-independent potential which does not allow to reproduce Coulomb interaction derived energy splitting between occupied and empty subbands. The SIC method solves this problem by introducing the orbital-dependent potential correction which explicitly substracts the self-interaction present in the LSDA. This method restores correct electronic properties of the transition metal oxides where the LSDA fails. However the self-interaction correction for the $d$ states is so strong, that when one implements SIC potential only to the $d$-orbitals of transition metal then the oxygen $p$-orbitals do not shift from the LSDA obtained positions and the occupied $d$-band lies much lower in energy than oxygen valence band, which does not agree with the spectroscopy data. However the values of energy gaps and the spin magnetic moments are in rather good agreement with experiment [13]. To improve this situation one can treat all valence states (namely the transition metal ions $d$-orbitals and oxygen $p$-orbitals) as localized and apply SIC potential to all of them [16]. In this case structure of occupied bands is well reproduced, but the value of energy gaps will be overestimated [17].

Another way to overcome the well known disadvantages of the LSDA is the LDA+U method, which gives better agreement with experimental spectra [14]. The LDA+U method corresponds to the static limit of recently developed new many-body approach — the dynamical mean-field theory (DMFT) [18]. In its standard form the LDA+U takes into account only Coulomb interaction between $d$ (or $f$) electrons of transition metal ions. In the present paper we investigate the problem of Coulomb interaction between oxygen $p$ electrons and show that the inclusion of the corresponding term in LDA+U equations leads to significant improvement of agreement between calculated and experimental spectral and magnetic properties.

II. METHOD OF CALCULATION

The main idea of the LDA+U method is to add to the LSDA functional the term $E^U$ corresponding to the mean-field approximation of the Coulomb interaction in multiband
Hubbard model.

\[
E^{LDA+U}[\rho^\sigma(r), \{n^\sigma\}] = E^{LSDA}[\rho^\sigma(r)] + E^U[\{n^\sigma\}] - E_{dc}[\{n^\sigma\}],
\]  

(1)

where \( \rho^\sigma(r) \) is the charge density for spin-\( \sigma \) electrons and \( E^{LSDA}[\rho^\sigma(r)] \) is the standard LSDA (Local Spin-Density Approximation) functional. Eq. (1) asserts that the LSDA is sufficient in the absence of orbital polarizations, while the latter are driven by,

\[
E^U[\{n^\sigma\}] = \frac{1}{2} \sum_{\{m\}, \sigma} \{\langle m, m'' | V_{ee} | m', m''' \rangle n_{mm'}^\sigma n_{m'm'''\sigma} - \}
\]

\[
(\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m'''', m' \rangle)n_{mm'}^\sigma n_{m'''m'''\sigma},
\]

(2)

where \( V_{ee} \) are the screened Coulomb interactions among the \( d \) electrons. Finally, the last term in Eq. (1) corrects for double counting (in the absence of orbital polarizations, Eq. (1) should reduce to \( E^{LSDA} \)) and is given by

\[
E_{dc}[\{n^\sigma\}] = \frac{1}{2} UN(N - 1) - \frac{1}{2} J[N^\uparrow(N^\uparrow - 1) + N^\downarrow(N^\downarrow - 1)],
\]

(3)

were \( N^\sigma = \text{Tr}(n_{mm'}^\sigma) \) and \( N = N^\uparrow + N^\downarrow \). \( U \) and \( J \) are screened Coulomb and exchange parameters \([8,10]\).

In addition to the usual LSDA potential, an effective single-particle potential to be used in the effective single-particle Hamiltonian has the form:

\[
\hat{H} = \hat{H}_{LSDA} + \sum_{mm'} |inlm\sigma\rangle V_{mm'}^\sigma \langle inlm'\sigma| \]

(4)

\[
V_{mm'}^\sigma = \sum_{m''m'''\sigma} \{\langle m, m'' | V_{ee} | m', m''' \rangle n_{m'm''\sigma} - \}
\]

\[
(\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m'''', m' \rangle)n_{m'm'''\sigma} - \}
\]

\[
U(N - \frac{1}{2}) + J(N^\sigma - \frac{1}{2}).
\]

(5)

The matrix elements of Coulomb interaction can be expressed in terms of complex spherical harmonics and effective Slater integrals \( F^k \) \([19]\) as
\[ \langle m, m'' | V_{ee} | m', m'' \rangle = \sum_k a_k(m, m', m'', m''') F^k, \] (6)

where \( 0 \leq k \leq 2l \) and

\[ a_k(m, m', m'', m''') = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} \langle lm | Y_{kq} | lm' \rangle \langle lm'' | Y_{kq}^{*} | lm''' \rangle \]

For \( d \) electrons one needs \( F^0, F^2 \) and \( F^4 \) and these can be linked to the Coulomb- and Stoner parameters \( U \) and \( J \) obtained from the LSDA-supercell procedures via \( U = F^0 \) and \( J = (F^2 + F^4)/14 \), while the ratio \( F^2/F^4 \) is to a good accuracy a constant \( \sim 0.625 \) for the 3\( d \) elements \(^{20,21}\). (For \( f \) electrons the corresponding expression is \( J = (286F^2 + 195F^4 + 250F^6)/6435 \)). The Coulomb parameter \( U \) is calculated as a second derivative of the total energy (or the first derivative of the corresponding eigenvalue) in respect to the occupancy of localized orbitals of the central atom in a supercell with fixed occupancies on all other atoms \(^{3}\).

If one neglects the exchange and non-sphericity of the Coulomb interaction (which is exact in the case of the fully occupied or empty band) the potential correction will have the more simple form:

\[ V_i = U(\frac{1}{2} - n_i) \] (7)

where \( n_i \) is the occupancy of \( i \)-orbital. Then for fully occupied state LDA+U potential correction would be the shift to the lower energies on \( U/2 \), while for empty states it gives an upward shift on the same value. So the LDA+U gives correct splitting between occupied and empty subbands equal to the Coulomb interaction parameter \( U \).

In the LDA+U approach the Coulomb interactions are taken into account conventionally only on \( d \)-orbitals of transition metals. However it is known that Coulomb interactions between electrons on \( p \)-orbitals of oxygen have comparable order of magnitude \(^{3,4}\) with the corresponding \( d-d \) Coulomb interactions and so must be taken into consideration on the same footing as for \( d \)-orbitals. The usual justification for omitting of \( U \) on oxygen \( p \)-shell is that the oxygen shell is fully occupied and the correlation effects between electrons (or rather
holes) in it can be neglected due to the small number of holes in ground state. However the LDA+U equations \( \text{(4)} \) will give nonzero correction for the fully occupied oxygen band:

\[
V_p = -\frac{U_p}{2}
\]

This potential correction must be applied to the orbitals forming oxygen band, however corresponding Wannier functions (in contrast to \( d \) states) are far from being of pure \( O(2p) \) character because they have very strong admixture of \( s \) and \( p \) states of transition metal ions and other extended orbitals. Since the main influence on the electronic structure is the change of the energy separation between the oxygen \( p \)-band and the transition metal \( d \)-band, the upward shift in energy of the transition metal \( d \)-band on \( U_p/2 \) will be equivalent to the shifting down of the oxygen \( p \)-band on the same value. Thus in our calculations we added \( U_p/2 \) term to the diagonal matrix elements of the LDA+U potential correction \( \text{(5)} \). We call this extension of the LDA+U method in the paper as the LDA+U \( (d+p) \).

Recently the modified LDA+U \( (d+p) \) method was used by Korotin et al. for investigation of charge and orbital ordering effects in \( \text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3 \) compound \[22\]. The inclusion of Coulomb interactions in the oxygen \( p \)-shell was found to be crucial in that calculation, since it controls the value of charge transfer energy between \( \text{Mn}(3d) \) and \( \text{O}(2p) \) valence states and significantly enhances the tendency of localization in this system.

In the present paper we report the results with the use of the modified LDA+U \( (d+p) \) method for the typical strongly correlated transition metal oxides \( \text{NiO}, \text{MnO} \) and \( \text{La}_2\text{CuO}_4 \). We show that inclusion of the correlations in oxygen \( p \)-shell leads to the better agreement with the experimental data for the main peaks position in X-ray photoemission spectroscopy (XPS) and Bremsstrahlung isohromate spectroscopy (BIS) spectra in comparison with conventional LDA+U calculated spectra. Not only spectral properties, but both spin magnetic moments and intersite exchange interaction parameters \( J_{ex} \) for \( \text{NiO}, \text{MnO} \) and \( \text{La}_2\text{CuO}_4 \) are in better agreement with the corresponding experimental data.
III. RESULTS AND DISCUSSION

The important part of the LDA+U calculation scheme is the determination of Coulomb interaction parameters $U$ and $J$ in equations (3): Coulomb parameter $U_p$ for $p$-orbitals of oxygen, $U_d$ for transition metals ion and Hund’s parameter $J$ for $d$-orbitals of transition metals. To get $U_d$ and $J$ one can use the supercell procedure [10,11] or the constrained LSDA method [8], which are based on calculation of the variation of the total energy as a function of the local occupation of the $d$-shell. We took the values of $U_d$ and $J$ parameters listed in Table I previously calculated in [14]. The problem is how to determine the Coulomb parameter $U_p$.

Due to more extended nature of the O(2p) Wannier states in comparison with transition metal $d$ states, the constrained occupation calculations can not be implemented as easy as for the $d$-shell of transition metals. Nevertheless several independent and different techniques were used for this purpose previously by different authors. McMahen et al. estimated the value of $U_p$ in high-$T_c$ related compound La$_2$CuO$_4$ using the constrained LDA calculation where only atomic-like O(2p)-orbitals within oxygen atomic spheres were considered instead of the more extended Wannier functions. The corresponding value of Coulomb interaction parameter $U_p$ was obtained as 7.3 eV. This value can be considered as the upper limit of the exact $U_p$. The LDA calculations gave the estimation that only 75% of Wannier function density lies in the oxygen atomic sphere so that renormalized value of Coulomb interaction parameter for oxygen Wannier functions is $U_p = (7.3) \times (0.75)^2 = 4.1$ eV [6].

Later Hybertsen et al. suggested the scheme to calculate $U_p$, which consists of two steps: (i) via constrained-density-functional approach one can obtain the energy surface $E(N_d, N_p)$ as a function of local charge states and (ii) simultaneously extended Hubbard model was solved in mean-field approximation as a function of local charge states $N_d$ and $N_p$. Corresponding Coulomb interaction parameters were extracted as those which give the energy surface matching the microscopic density-functional calculations results [7]. The obtained values for $U_p$ are $3 \div 8$ eV depending on the parameters of calculations.
Another way to estimate $U_p$ is to use Auger spectroscopy data, where two holes in O($2p$)-shell are created in the excitation process. Such fitting to the experimental spectra gave the value of $U_p = 5.9 \; eV$ \cite{23}. In our LDA+$U^{(d+p)}$ calculations we used $U_p = 6 \; eV$.

To solve the LDA+$U$ hamiltonian we implemented the self-consistent tight-binding (TB) linear muffin-tin orbitals method (LMTO) in the atomic sphere approximation (ASA) \cite{24–26}. For the calculations we choose the classical strongly correlated transition metal oxides NiO, MnO and La$_2$CuO$_4$, which were well investigated by experimental and theoretical methods.

Comparison between the LDA+$U$ (left column) and the LDA+$U^{(d+p)}$ (right column) calculated density of states (DOS) of NiO, MnO and La$_2$CuO$_4$ is presented in figures 1, 2 and 3. For all compounds one can see that the main difference between the LDA+$U^{(d+p)}$ and the LDA+$U$ calculated densities of states is the increased energy separation between the oxygen 2$p$ and transition metal 3$d$ bands. The larger value of "charge transfer" energy ($O(2p)$-$Me(3d)$) ($Me=\text{Ni,Mn,Cu}$) leads to the enhanced ionicity and decreased covalency nature of the electronic structure: the unoccupied bands have more pronounced 3$d$ character and the admixture of oxygen states to those bands becomes weaker.

The ground state is correctly described both by LDA+$U$ and LDA+$U^{(d+p)}$ calculations as antiferromagnetic insulator for all compounds. The values of energy gaps \cite{27} and spin magnetic moments are presented in tables II and III. One can see that the values obtained in the LDA+$U^{(d+p)}$ calculations are in general in better agreement with experiment than the LDA+$U$ calculated values. While the increasing of the energy gap values with applying $U_p$ correction was obviously expected with the increasing of "charge transfer" energy in the compounds belonging to the class of "charge transfer" insulators \cite{28}, the increasing of the magnetic moments values is more complicated self-consistency effect due to the increased ionicity in the LDA+$U^{(d+p)}$ calculations comparing with the LDA+$U$ results.

In Fig. 4 the DOS obtained by LDA+$U^{(d+p)}$ and LDA+$U$ calculations for MnO and NiO compounds are compared with the superimposed XPS and BIS spectra corresponding to the removal of an electron (the occupied bands) and addition of an electron (the empty bands),
respectively. The better agreement with the experimental data of position of the main peaks of unoccupied band relative to the occupied one is the direct confirmation of the importance of taking into account Coulomb interactions in oxygen 2p-shell.

The values of the intersite exchange interaction parameters $J_{ex}$ depend on the parameters of the electronic structure in a rather indirect implicit way. The developing of the good calculating scheme for exchange parameters is very important because the \textit{ab-initio} calculation is often the only way to describe the magnetic properties of complicated compounds such as for example “spin-gap” systems \cite{29}. Recently Solovyev \textit{et al.} \cite{30} did very through analysis of the exchange interaction parameters for MnO calculated using different methods of electronic structure calculations. They used the positions of the Mn(3d)-spin-up and Mn(3d)-spin-down bands relative to the oxygen 2p states as adjustable parameters to fit the values of exchange interaction for the nearest and second Mn-Mn neighbors. Their results gave nearly the same splitting between Mn(3d)-spin-up and Mn(3d)-spin-down states as in standard LDA+U calculations (10.6 eV) but the position of those states relative to the oxygen band was shifted approximately on 3 eV up relative to the LDA+U case. It is practically the same as we have in our LDA+U$^{(d+p)}$ calculations, because with $U_p = 6$ eV the shift of the position Me(3d)-band relative to the oxygen O(2p)-band is equal to $U_p/2 = 3$ eV.

Comparison between LDA+U and LDA+U$^{(d+p)}$ calculated $J_{ex}$ parameters and experimental data is presented in table IV. $J_{ex}$ were calculated from Greens function method as second derivatives of the ground state energy with respect to the magnetic moment rotation angle \cite{31,32}. Again one can see that in general the LDA+U$^{(d+p)}$ gives better results than the LDA+U, especially for MnO compound.

\textbf{IV. CONCLUSION}

The method for inclusion of Coulomb interactions between oxygen $p$ electrons in the calculation scheme of the LDA+U method was proposed. The main effect was found to be the increasing of ”charge transfer” energy parameter (the separation of O(2p) and Me(3d)
states). As the result, the spectral and magnetic properties of the typical strongly correlated transition metal oxides NiO, MnO and La$_2$CuO$_4$ were found in better agreement with experimental data than in the conventional LDA+U method where only correlations between Me(3$d$) state are taken into account.

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[27] One should say that we look at the energy gap between the highest edge of occupied and the lowest edge of empty part of Me(3d)-band (Me=Ni,Mn,Cu), because in total DOS the value of energy gap is $\sim 1$ eV due to very low intensive O(3s)-band.

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[32] To calculate $J_{ex}$ in MnO and NiO we used the 8-fold enlarged supercell in order to get the exchange parameters between nearest and second order neighbors. For La$_2$CuO$_4$ the 2-fold enlarged supercell was used.
FIG. 1. \( \text{La}_2\text{CuO}_4 \) DOS calculated by the LDA+U (left column) and the LDA+U\(^{(d+p)}\) (right column) methods. (On all figures the total DOS is presented per formula unit, the DOS of particular states are per atom. Fermi energy corresponds to zero.)
FIG. 2. MnO DOS calculated by the LDA+U (left column) and the LDA+U\(^{(d+p)}\) (right column) methods.

FIG. 3. NiO DOS calculated by the LDA+U (left column) and the LDA+U\(^{(d+p)}\) (right column) methods.

FIG. 4. DOS calculated by the LDA+U (dashed line) and the LDA+U\(^{(d+p)}\) (solid line) Ni(3\(d\)) and Mn(3\(d\)) in comparison with superimposed XPS and BIS spectra.
Spectroscopic data:

MnO: G.A. Sawatzky and J.W. Allen, Phys. Rev. Lett. 53, 2339 (1984).

NiO: J. van Elp, R. H. Potze, H. Eskes, R. Berger, and G. A. Sawatzky, Phys.Rev.B 44, 1530 (1991).
### TABLE I. Coulomb parameters $U_d$ and Hund’s parameters $J$ (eV) used in calculations.

|       | La$_2$CuO$_4$ | MnO | NiO |
|-------|---------------|-----|-----|
| $U_d$ | 8.0           | 6.9 | 8.0 |
| $J$   | 1.0           | 0.86| 0.95|

### TABLE II. Calculated and experimental values of energy gaps (eV).

|       | LDA+U   | LDA+U$^{(d+p)}$ | Experiment |
|-------|---------|----------------|------------|
| La$_2$CuO$_4$ | 0.7     | 2.0            | 2.0$^a$    |
| MnO   | 3.8     | 4.5            | 3.6 – 3.8$^b$ |
| NiO   | 1.8     | 2.8            | 4.3$^c$, 4.0$^d$ |

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### TABLE III. Calculated and experimental values of spin magnetic moments ($\mu_B$).

|          | LDA+U | LDA+U\((d+p)\) | Experiment |
|----------|-------|----------------|------------|
| La$_2$CuO$_4$ | 0.45  | 0.68           | 0.60$^a$   |
| MnO      | 4.51  | 4.59           | 4.79$^b$, 4.58$^c$ |
| NiO      | 1.50  | 1.64           | 1.77$^d$, 1.64$^e$, 1.90$^f$ |

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### TABLE IV. Calculated and experimental values of intersite exchange interaction parameters $J_{ex}$ (meV).

|          | LDA+U | LDA+U\((d+p)\) | Experiment |
|----------|-------|----------------|------------|
| \(^1\)La$_2$CuO$_4$ | 82.9  | 100.9          | 136 $\pm$ 5$^a$ |
| \(^2\)MnO   | 5.4   | 9.3            | 5.4, 5.1, 4.8$^b$, 5.4$^c$ |
| \(^2\)NiO  | 0.8   | 23.2           | 0.2, 19.4, 1.4$^d$, 19.0$^d$ |

$^1$Cu-Cu exchange parameter between nearest Cu atoms in plane.

$^2$Me-Me exchange parameters between nearest and second neighbors.

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