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Consistent LDA′+DMFT – an unambiguous way to avoid double counting problem: NiO test

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We present a consistent way of treating a double counting problem unavoidably arising within the LDA+DMFT combined approach to realistic calculations of electronic structure of strongly correlated systems. The main obstacle here is the absence of systematic (e.g. diagrammatic) way to express LDA (local density approximation) contribution to exchange correlation energy appearing in the density functional theory. It is not clear then, which part of interaction entering DMFT (dynamical mean-field theory) is already taken into account through LDA calculations. Because of that, up to now there is no accepted unique expression for the double counting correction in LDA+DMFT. To avoid this problem we propose here the consistent LDA′+DMFT approach, where LDA exchange correlation contribution is explicitly excluded for correlated states (bands) during self-consistent band structure calculations. What is left out of Coulomb interaction for those strongly correlated states (bands) is its non-local part, which is not included in DMFT, and the local Hartree like contribution. Then the double counting correction is uniquely reduced to the local Hartree contribution. Correlations for strongly correlated states are then directly accounted for via the standard DMFT. We further test the consistent LDA′+DMFT scheme and compare it with conventional LDA+DMFT calculating the electronic structure of NiO. Opposite to the conventional LDA+DMFT our consistent LDA′+DMFT approach unambiguously produces the insulating band structure in agreement with experiments.

1. Introduction. During the last 15 years the so called LDA+DMFT approach (local density approximation + dynamical mean-field theory) became a common tool to describe band structure of real strongly correlated materials [1–6]. In this approach the results of LDA band structure calculations are supplemented with local Coulomb (Hubbard) interaction term for those states which are counted as strongly correlated. Formally the LDA+DMFT Hamiltonian can be written as

$$\hat{H} = \hat{H}_{\rm LDA} - \hat{H}^{DC} + \\ + \frac{1}{2}\sum_{i=i_d,l=l_d}\sum_{m\sigma,m'\sigma'}{}' U^{\sigma\sigma'}_{mm'}\hat{n}_{ilm\sigma}\hat{n}_{ilm'\sigma'} - \\ - \frac{1}{2}\sum_{i=i_d,l=l_d}\sum_{m\sigma,m'\bar{\sigma}}{}' J_{mm'}\hat{c}^{\dagger}_{ilm\sigma}\hat{c}^{\dagger}_{ilm'\bar{\sigma}}\hat{c}_{ilm'\sigma}\hat{c}_{ilm\bar{\sigma}}. \quad (1)$$

Here $U^{\sigma\sigma'}_{mm'}$ are the most important matrix elements of Coulomb matrix (Coulomb repulsion and z-component of Hund's rule coupling) and $J_{mm'}$ are spin-flip terms of Hund's rule couplings between the strongly correlated electrons (assumed here to be d-states, enumerated by $i = i_d$ and $l = l_d$). The prime on the sum indicates that at least two of the indices of operators have to be different, and $\bar{\sigma} = \downarrow(\uparrow)$ for $\sigma = \uparrow(\downarrow)$.

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The LDA part of the Hamiltonian (1) is given by:

$$\hat{H}_{\rm LDA} = -\frac{\hbar^2}{2m_e}\Delta + V_{\rm ion}(\mathbf{r}) + \int d^3r'\,\rho(\mathbf{r}')V_{ee}(\mathbf{r}-\mathbf{r}') + \\ + \frac{\delta E^{\rm LDA}_{xc}(\rho)}{\delta\rho(\mathbf{r})}, \quad (2)$$

where Δ is the Laplace operator, m_e the electron mass, e the electron charge, and

$$V_{\rm ion}(\mathbf{r}) = -e^2\sum_i\frac{Z_i}{|\mathbf{r}-\mathbf{R_i}|},\; V_{ee}(\mathbf{r}-\mathbf{r}') = \frac{e^2}{2}\sum_{\mathbf{r}\neq\mathbf{r}'}\frac{1}{|\mathbf{r}-\mathbf{r}'|} \quad (3)$$

denote the one-particle potential due to all ions i with charge eZ_i at given positions $\mathbf{R_i}$, and the electron-electron interaction, respectively.

The $E^{\rm LDA}_{xc}[\rho(\mathbf{r})]$ in (2) is a function of local charge density which approximates true exchange correlation functional $E_{xc}[\rho]$ of density functional theory in the framework of local density approximation [7]. The form of the function $E^{\rm LDA}_{xc}[\rho(\mathbf{r})]$ is usually calculated from perturbation theory [8] or numerical simulations [9] of the "jellium" model with $V_{\rm ion}(\mathbf{r})$ = const. Once we choose some basis set of one-particle wave functions φ_i (e.g. to do practical calculations and explicitly express matrix elements of the Hamiltonian (2)), we can obtain ρ as:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2. \tag{4}$$

Finally a term $\hat{H}^{DC}$ is subtracted in Eq. (1) to avoid double-counting of those contributions of the *local* Coulomb interaction already contained in $\hat{H}_{\mathrm{LDA}}$ via Hartree term and $E_{xc}^{\mathrm{LDA}}[\rho(\mathbf{r})]$. Since there does not exist a direct microscopic or diagrammatic link between the model (Hubbard like) Hamiltonian approach and LDA it is not possible to express $\hat{H}^{DC}$ rigorously in terms of U, J and ρ. Thus there is no unique and accepted expression for $\hat{H}^{DC}$ (see e.g. Ref. [10]).

One popular expression for $\hat{H}^{DC}$ is the Hartree like (fully localized limit) expression [11]:

$$H^{DC} = \frac{1}{2}Un_d(n_d-1) - \frac{1}{2}J\sum_{\sigma} n_{d\sigma}(n_{d\sigma}-1). \tag{5}$$

Here, $n_{d\sigma} = \sum_m n_{il_d m\sigma} = \sum_m \langle \hat{n}_{il_d m\sigma}\rangle$ is total number of electrons on interacting orbitals per spin, $n_d = \sum_\sigma n_{d\sigma}$, U is Coulomb (Hubbard) repulsion and J is the exchange or Hund's rule coupling obtained usually from constrained LDA procedure [12]. The n_d value can be obtained either from LDA calculations or can be recalculated during the DMFT loop. Practically, the values obtained are pretty close to each other.

Below we introduce the consistent LDA′+DMFT approach, which allows one to avoid the double counting problem unambiguously. To illustrate the advantages of this new approach we shall apply it to calculations of the band structure of the well known prototype of charge transfer insulating system NiO.

2. Consistent LDA′+DMFT approach. One of the possible ways to solve the double counting problem is to perform Hartree+DMFT or Hartree–Fock+DMFT calculations (see for the overview of the concept Ref. [13]). This approach uses the advantage of knowledge of diagrammatic expression for Hartree or Hartree–Fock terms. Thus, performing Hartree–Fock band structure calculations for real materials we do know exactly what portion of interaction is, in fact, explicitly included. Then obviously, the double counting term should be chosen in the form of Eq. (5). However, up to now we are unaware of any Hartree+DMFT or Hartree–Fock+DMFT calculations for real materials.

In fact, Hartree–Fock band structure calculations are in some sense a large step backwards from DFT/LDA approach, which was so successful in description of many real materials. Even in the case of strongly correlated systems DFT/LDA is recognized as a best starting point for further model Hamiltonian treatments, such as e.g. LDA+DMFT method.

In view of this we suggest a kind of compromise between Hartree–Fock and DFT/LDA starting points to be followed by DMFT calculations. As described above main obstacle to express double counting term exactly is exchange correlation $E_{xc}^{\mathrm{LDA}}[\rho(\mathbf{r})]$ portion of interaction within LDA. It seems somehow inconsistent to use it to describe correlation effects in narrow (strongly correlated) bands from the very beginning, as these should be treated via more elaborate schemes like DMFT. To overcome this difficulty for these states, we propose to redefine charge density (4) in E_{xc}^{LDA} as follows:

$$\rho'(\mathbf{r}) = \sum_{i\neq i_d} |\varphi_i(\mathbf{r})|^2 \tag{6}$$

excluding the contribution of the density of strongly correlated electrons. Then this redefined $\rho'(\mathbf{r})$ is used to obtain E_{xc}^{LDA} and perform the self-consistent LDA band structure calculations for correlated bands at the initial stage of LDA+DMFT, while correlations of d-electrons are left to be treated via DMFT. This means that what is left for correlated states out of interaction on the LDA stage would be just the Hartree contribution of Eq. (2). At the same time all other states (not counted as strongly correlated) are to be treated with the full power of DFT/LDA and *full* ρ in E_{xc}^{LDA}. Now, the problem of double counting correction is uniquely defined – it should be taken in the form of the Hartree like term, given by Eq. (5).

This approach to describe realistic strongly correlated systems we shall call the consistent LDA′+DMFT. It is in precise correspondence with the standard definition of correlations, as interaction corrections "above" Hartree–Fock. We explicitly exclude contributions to E_{xc}^{LDA} from (strongly) correlated bands, where correlations are treated via DMFT, while we take all electrons into account in LDA calculations for all other (non correlated) bands.

3. Results. Following many recent works [10, 14, 15] (and references therein) we choose as a testing system the prototype charge transfer insulator NiO. LDA band structure calculations for NiO were performed within the linearized muffin-tin orbitals (LMTO) basis set [16]. In the corresponding program package TB-LMTO v. 47 the E_{xc}^{LDA} was taken in von Barth–Hedin form [8].

In the Fig. 1 we present LDA densities of states (left panel) and band dispersions (right panel) of NiO. Band dispersions consist of two separate sets of bands: the O-2p bands (from -3 to -9 eV) and Ni-3d bands, crossing the Fermi level (from 1.5 to -3 eV). Dashed lines

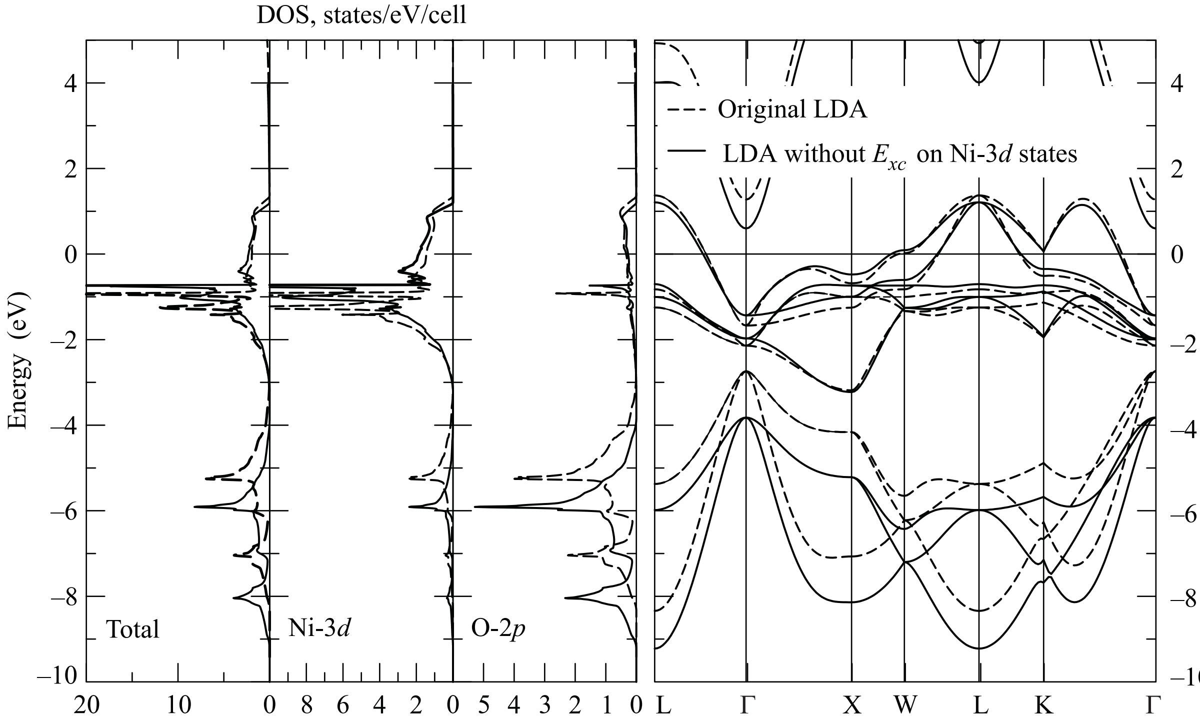

Fig. 1. LDA (dashed line) and LDA′ (full line) calculated band dispersions and densities of states of NiO. The Fermi level E_F is at zero energy

in Fig. 1 show conventional LDA results. Full lines correspond to LDA′ calculations without $E_{xc}^{\rm LDA}$ on Ni-3d states, namely, with redefined charge density (6) in $E_{xc}^{\rm LDA}$. Overall changes can be characterized as an almost rigid shift of oxygen states down in energy by about 1 eV for LDA′ calculations, while Ni-3d states are only slightly modified due to change of Ni-O hybridization. In other words LDA′ calculations lead to the change of charge transfer energy $\Delta = |\varepsilon_d - \varepsilon_p|$ by about 1 eV. Rather small influence of $E_{xc}^{\rm LDA}$ on Ni-3d states is not surprising, since $E_{xc}^{\rm LDA}$ for metallic (LDA produces metallic state for NiO) electron densities $r_s = 2{-}6$ are known to be of the order of 1 eV [9]. Further we perform DMFT calculations using LDA and LDA′ Hamiltonians, which include all states (without any projecting). DMFT impurity solver used was Hirsh–Fye quantum Monte-Carlo algorithm [17]. Inverse temperature was taken $\beta = 5\,\mathrm{eV}^{-1}$ (2321 K) and 80 time slices were used, with 10^6 Monte-Carlo sweeps. The use of very high temperature does not lead to any qualitative effects in the results, allowing us to avoid unnecessary computational efforts. Parameters of Coulomb interaction were chosen as typical for NiO [10, 15]: $U = 8$ eV and $J = 1$ eV. To obtain DMFT(QMC) densities of states at real energies, we employed the maximum entropy method [18].

In the Fig. 2 we compare the conventional LDA + + DMFT (upper panel) and consistent LDA′+DMFT (lower panel) results for NiO. Different lines represent partial Ni-3$d(t_{2g})$ (solid line), Ni-3$d(e_g)$ (dashed line) and oxygen O-2p (dash-dot line) contributions to density of states. To obtain O-2p states DMFT(QMC) self-energy was analytically continued to real frequencies by Pade approximant method. For both conventional LDA+DMFT and consistent LDA′+DMFT calculations we used H^{DC} of Eq. (5) with n_d recalculated on each DMFT iteration step. Corresponding values of H^{DC} are 62 eV ($n_d = 8.7$) and 58.13 eV ($n_d = 8.2$) for conventional LDA+DMFT and consistent LDA′+DMFT respectively. The total occupancies of Ni-3d states within LDA and LDA′ calculations were 8.5 and 8.3.

Within conventional LDA+DMFT we obtain the metallic solution, which contradicts experiments. This fact can be explained as follows. We already mentioned that LDA and LDA′ calculations results differ mainly by the values of charge transfer energy $\Delta = |\varepsilon_d - \varepsilon_p|$. In fact, we observed [19] that double counting correction essentially affects Δ, or the other way around, the different values of Δ require the different values of double counting corrections to obtain the same results. In its turn, the different values of double counting correction can lead either to metallic or insulating solutions for the same set of other parameters [10, 19].

Once we employ the consistent LDA′+DMFT approach, we obtain the charge transfer *insulating* solution

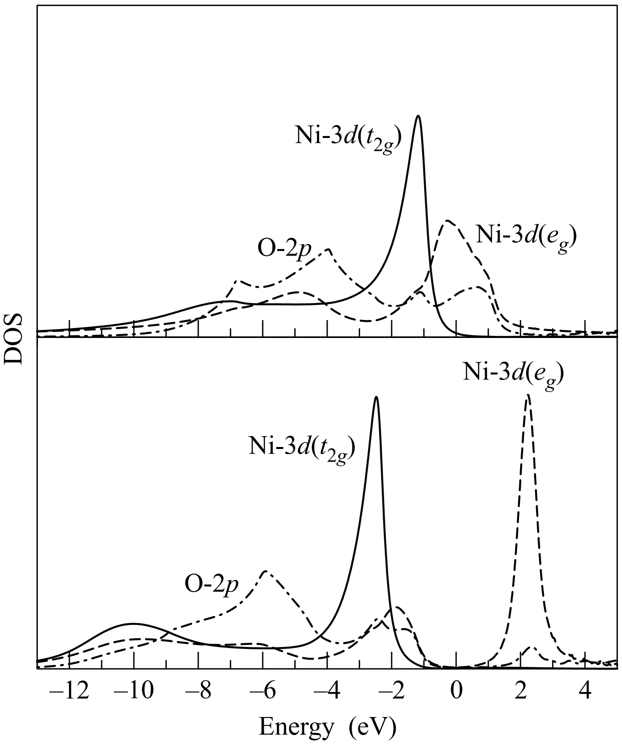

Fig. 2. Consistent LDA′+DMFT (lower panel) and LDA+DMFT (upper panel) partial densities of states for NiO: solid line – Ni-3$d(t_{2g})$, dashed line – Ni-3$d(e_g)$, dot-dashed line – O-2p. The Fermi level is at zero energy

for NiO, which agrees well with other LDA+DMFT calculations for NiO [10, 15] and experiment [20], confirming the effectiveness of our approach. Namely, the peak at -2 eV which consists almost in equal parts from Ni-3d and O-2p states is nothing else but Zhang–Rice bound state (in agreement with Ref. [15]). Lower Hubbard band formed mainly from Ni-3d states is located lower in energy than Zhang–Rice band. Conducting band is just the upper Hubbard band dominated by Ni-3d states.

As an additional check of consistency of our approach we also performed LDA′+DMFT calculations for $SrVO_3$. The results obtained are in good agreement with those obtained in Ref. [21], further validating our proposed LDA′+DMFT approach as an effective and unambiguous method of band structure calculations for strongly correlated systems.

4. Conclusion. In this work we proposed the consistent LDA′+DMFT approach, which solves the problem of non-uniqueness of the double counting correction. By excluding LDA exchange correlation contribution for correlated states within the self-consistent LDA calculations (e.g. for Ni-3d states) we end up with just Hartree like portion of interaction for (strongly) correlated states. Then we know exactly, what should be subtracted as a double counting correction term, while merging LDA′ and DMFT. We tested our consistent LDA′+DMFT approach, calculating the band structure of NiO. We obtained the insulating solution without any additional fitting parameters and in general agreement with experimental data [20], while in other LDA+DMFT works for NiO the double counting correction was either treated as an adjustable parameter [10], or the special form of double counting term was introduced [15] to achieve agreement with experiment.

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