Orbital density functional as a means to restore the discontinuities in the total-energy derivative and the exchange–correlation potential

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V I Anisimov[1]**, A V Kozhevnikov**[1]**, M A Korotin**[1]**, A V Lukoyanov**[2] **and D A Khafizullin**[2]

[1] Institute of Metal Physics, Russian Academy of Sciences, Ural Division, 620041 Ekaterinburg GSP-170, Russia
[2] Ural State Technical University-UPI, 620002 Ekaterinburg, Russia

E-mail: via@imp.uran.ru

Abstract
The local density approximation (LDA) to the density functional theory (DFT) has a continuous derivative of the total energy as a function of the number of electrons and continuous exchange–correlation potential, while in *exact* DFT both functions should be discontinuous as the number of electrons goes through an integer value. We propose an ad hoc orbital density functional (ODF) (with orbitals defined as Wannier functions) that by construction obeys this discontinuity condition. Taking its variation, the one-electron equations are obtained with a potential in the form of a projection operator. This operator increases the separation between occupied and empty bands, thus curing an LDA deficiency—systematic underestimation of the energy gap value. The minimization of the ODF gives the ground-state orbital and total electron densities. In addition to that we define the ODF fluctuation Hamiltonian that allows one to treat dynamical correlation effects. The dynamical mean-field theory (DMFT) with the quantum Monte Carlo (QMC) method for an effective impurity problem was used to solve this Hamiltonian. We have applied the ODF method to the problem of the metal–insulator transition in lanthanum trihydride LaH_{3-x}. In the LDA calculations for all values of hydrogen nonstoichiometry x the ground state of this material is metallic, while experimentally the system is insulating for $x < 0.3$. The ODF method gave a paramagnetic insulator solution for LaH_3 and $LaH_{2.75}$ but metallic state for $LaH_{2.5}$.

1. Introduction

Numerical electronic structure calculations are now a well-established branch of solid-state physics. While for the finite systems, such as atoms and molecules, more sophisticated and

rigorous calculation methods exist, for extended systems studied in condensed matter physics the only widely used practical tool is the density functional theory (DFT) in the local density approximation (LDA) [1, 2]. It has so great a predictive power that the charge and spin density, one-electron and total energies obtained in the LDA are generally in very good agreement with experimental data. It was also possible to develop *ab initio* molecular dynamic methods, based on the LDA. Such methods have achieved the level of numerical experiments, because even such complicated effects as reconstruction of the crystal surface can be correctly described by them [3].

However, there are materials where the LDA results do not agree well with experimental data. For band insulators and semiconductors, the LDA gives systematically underestimated values of the energy gap [4]. For Mott insulators, for example transition-metal oxides, the LDA results could be qualitatively wrong, giving a metallic state, while experimentally these systems are wide-gap insulators [5].

There were many attempts to cure this deficiency of the LDA. Among the most widely used one can mention the GW [6], SIC [7], and LDA + U [8, 9] methods. While these approaches have their advantages, there is still no universally accepted calculation scheme which would be as simple and practical as the standard LDA and a search for better methods continues in the scientific community.

The basic problems of the LDA can be traced back to the fact that the exchange–correlation energy functional is defined in a *local* approximation. As a result, its variational derivative, the exchange–correlation potential (that is a *function* of the density value in a particular point **r** instead of being a general *functional* of the density) is a continuous function of a number of electrons. More general approximations, like the GGA [10] method, use in addition to the electron density its gradient, but have a continuous potential as well. However, Perdew *et al* [11] have investigated the properties of the *exact* density functional (EDF) and shown that its potential jumps discontinuously when a number of electrons N goes through an integer value. The proper function of the total energy E versus the number of electrons N should have the form of a series of straight-line segments with derivative discontinuities at integer values of N, while in the LDA this function has continuous derivatives. Any attempts to improve the LDA as an approximation to the exact density functional theory should be done in such a way that a new functional would meet this discontinuity requirement.

In the present work we define an ad hoc functional that by construction has the potential discontinuities required by the exact density functional. To do this, we introduce a concept of *orbital densities* corresponding to one-electron orbitals. The orbital density functional (ODF) depends on a set of *orbital densities* instead of only the total electron density. When the number of electrons goes through an integer value, the variational derivative of the ODF functional jumps discontinuously and the corresponding function of the total energy E_{ODF} versus a number of electrons N has a curve as a series of straight-line segments.

The one-electron equations with a potential in the form of a projection operator were obtained by varying the ODF. This operator decreases the energy of occupied states and increases the energy of empty states. As a result, it widens the gap between the valence and conduction bands compared with the LDA values, thus curing the LDA deficiency that has shown itself in the systematic underestimation of the energy gap value.

The minimization of the ODF results in a set of orbital densities and hence the total electron density corresponding to the ground state of the system. The same functional can be used to calculate energies of the orbital density fluctuations around the ground-state values. From this functional we have derived a *fluctuation Hamiltonian* defined via the orbital density fluctuation operators. This Hamiltonian allows one to treat dynamical correlation effects and hence obtain a better description of the ground-state properties and spectral function for the excitations. To

solve the ODF Hamiltonian problem we used in the present work the dynamical mean-field theory (DMFT) [12–14] with a quantum Monte Carlo (QMC) solver for the effective impurity problem.

The optimal choice for the one-electron orbitals, which are needed to define the orbital densities, can be determined by a condition of fluctuation energy minimum. Below it will be shown that the less extended in space these orbitals are, the lower the energy of orbital density fluctuations around the ground state is. Therefore, to define orbital densities in our ODF method, we used maximally localized Wannier functions (WFs) [15].

Recently, we have developed a 'generalized transition state' (GTS) method [16] to improve the agreement of calculated and experimental spectral properties compared with the LDA. In the present paper we show that the ODF projection operator potential is identical to one in the GTS method equations, and the good results obtained in [16] for semiconductors, band and Mott insulators can be considered as a test for applicability of the ODF method. The GTS method was based on the idea that the one-electron energies corresponding to WFs should have the meaning of the removal (addition) energies for electrons from (to) the corresponding states. This concept was realized by using the 'transition state' scheme [17] generalized on the basis of WFs. It is remarkable that such different approaches as the 'transition state' correction to the one-electron energies and requirement of a discontinuity in the exchange–correlation potential can lead to the same equations.

We have applied the ODF method to the problem of the metal–insulator transition in LaH_{3-x}. The LDA has severe difficulties for this material because it results in a metallic solution for all values of hydrogen deficiency x while experimentally the system is insulating for $x < 0.3$. We have found that the ODF projection operator potential is enough to open a gap for stoichiometric LaH_3, but in order to reproduce the paramagnetic insulator for $LaH_{2.75}$ correlation effects should be taken into account via the DMFT-QMC solution of the ODF fluctuation Hamiltonian.

The paper is structured as follows. In section 2 the ODF functional is defined and in section 3 the fluctuation Hamiltonian is proposed. The problem of orbital choice is discussed in section 4. Section 5 describes the calculation scheme. In section 6 the results of ODF calculations for LaH_{3-x} are presented. Section 7 concludes the paper.

2. Orbital density functional

The exchange–correlation energy in the local density approximation [4] to the density functional theory [1] is calculated via

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r}\, \varepsilon_{xc}(\rho(\mathbf{r}))\rho(\mathbf{r}), \tag{1}$$

where $\varepsilon_{xc}(\rho(\mathbf{r}))$ is an exchange–correlation energy density for a homogeneous electron gas with the electron density equal to $\rho(\mathbf{r})$.

Equation (1) defines an exchange–correlation potential $V_{xc}(\rho(\mathbf{r})) = \delta E_{xc}[\rho]/\delta\rho(\mathbf{r})$ which is a continuous function of the number of electrons N. However, for the *exact* density functional, Perdew *et al* [11] proved that the exchange–correlation potential jumps discontinuously when the number of electrons N goes through an integer value.

The Hohenberg–Kohn theorem [2] was extended in [11] to fractional electron number. It was shown that for the electron density $\rho(\mathbf{r})$ which integrates to $N = M + \omega$, where M is an integer and $0 \leqslant \omega \leqslant 1$, the exact density functional E_{EDF} is

$$E_{EDF}(M + \omega) = (1 - \omega)E_{EDF}(M) + \omega E_{EDF}(M + 1). \tag{2}$$

This means that in general the curve of E_{EDF} versus N is a series of straight-line segments with derivative discontinuities at integer values of N.

It was proven [11] that the chemical potential $\mu = \partial E_{\mathrm{EDF}}/\partial N$ is discontinues when the number of electrons goes through integer value:

$$
\mu = \begin{cases} -I & (M - 1 < N < M) \\ -A & (M < N < M + 1) \end{cases}
\tag{3}
$$

where $I = E_{\mathrm{EDF}}(M - 1) - E_{\mathrm{EDF}}(M)$ and $A = E_{\mathrm{EDF}}(M) - E_{\mathrm{EDF}}(M + 1)$ are removal and addition energies respectively. The functional derivative $\delta E_{\mathrm{EDF}}/\delta \rho(\mathbf{r})$ is also discontinuous: two limits for N approaching M from above and below will differ by constant $I - A$.

The electron density can be expressed as a sum of the 'orbital densities' $\rho_i(\mathbf{r})$ defined in the following way (n_i is the occupancy of an ith orbital wave function, $\psi_i(\mathbf{r})$):

$$
\begin{aligned}
\rho(\mathbf{r}) &= \sum_i \rho_i(\mathbf{r}), \\
\rho_i(\mathbf{r}) &\equiv n_i |\psi_i(\mathbf{r})|^2.
\end{aligned}
\tag{4}
$$

The orbital densities can be varied from zero to the maximum values $\rho_i^{\max}(\mathbf{r}) = |\psi_i(\mathbf{r})|^2$.

The condition of linear dependence of the *exact* density functional on the fractional number of electrons (2) can be expressed via the orbital density $\rho_j(\mathbf{r})$ corresponding to the partially occupied orbital j. This orbital is the lowest unoccupied one for number of electrons $N = M$ and the highest occupied for $N = M + 1$. The variation of the total electron density $\rho(\mathbf{r})$ will be defined only by the variation of $\rho_j(\mathbf{r})$ for the number of electrons changing from M to $M + 1$:

$$
E_{\mathrm{EDF}}[\rho] = E_{\mathrm{EDF}}[\rho_0 + \rho_j] = E_{\mathrm{EDF}}\Big|_{\rho_j(\mathbf{r})=0} + \int d\mathbf{r}\, \rho_j(\mathbf{r}) \Lambda_j(\mathbf{r}),
\tag{5}
$$

where $\rho_0(\mathbf{r})$ is the density for the number of electrons $N = M$. Here $\Lambda_j(\mathbf{r})$ satisfies the equation

$$
\int d\mathbf{r}\, \rho_j^{\max}(\mathbf{r}) \Lambda_j(\mathbf{r}) = E_{\mathrm{EDF}}\Big|_{\rho_j(\mathbf{r})=\rho_j^{\max}(\mathbf{r})} - E_{\mathrm{EDF}}\Big|_{\rho_j(\mathbf{r})=0}.
\tag{6}
$$

The orbital density $\rho_j(\mathbf{r})$ enters (5) in a linear form. However, the LDA functional does not show such a linear dependence on density variation. The equation analogous to (5) for the LDA has a general form (keeping only the first and second variational derivatives in the expansion series):

$$
\begin{aligned}
E_{\mathrm{LDA}}[\rho] = E_{\mathrm{LDA}}[\rho_0 + \rho_j] &\approx E_{\mathrm{LDA}}\Big|_{\rho_j(\mathbf{r})=0} + \int d\mathbf{r}\, \rho_j(\mathbf{r}) \frac{\delta E_{\mathrm{LDA}}}{\delta \rho(\mathbf{r})}\Big|_{\rho_j(\mathbf{r})=0} \\
&\quad + \frac{1}{2} \int d\mathbf{r}\, \rho_j(\mathbf{r}) \int d\mathbf{r}'\, \rho_j(\mathbf{r}') \frac{\delta^2 E_{\mathrm{LDA}}}{\delta \rho(\mathbf{r})\delta \rho(\mathbf{r}')}\Big|_{\rho_j(\mathbf{r})=0}.
\end{aligned}
\tag{7}
$$

The second variational derivative of the LDA functional can be expressed using a response function $\chi(\mathbf{r}, \mathbf{r}')$ [18, 19]:

$$
\frac{\delta^2 E_{\mathrm{LDA}}}{\delta \rho(\mathbf{r})\delta \rho(\mathbf{r}')} = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \delta(\mathbf{r} - \mathbf{r}') \frac{\delta V_{\mathrm{xc}}(\mathbf{r})}{\delta \rho(\mathbf{r}')} - \chi^{-1}(\mathbf{r}, \mathbf{r}') \equiv W(\mathbf{r}, \mathbf{r}');
\tag{8}
$$

$W(\mathbf{r}, \mathbf{r}')$ can be interpreted as an effective interaction strength between density fluctuations $\delta \rho(\mathbf{r})$ and $\delta \rho(\mathbf{r}')$ in the LDA functional. The first variational derivative of the LDA functional is

$$
\frac{\delta E_{\mathrm{LDA}}}{\delta \rho(\mathbf{r})} = -\Phi[\rho](\mathbf{r}),
\tag{9}
$$

where $\Phi[\rho](\mathbf{r})$ is a constraining potential needed to obtain electron density $\rho(\mathbf{r})$ in the self-consistent solution of the Kohn–Sham equations.

Using (8) and (9), expansion (7) can be rewritten via the constrain potential $\Phi(\mathbf{r})$ and effective interaction strength function $W(\mathbf{r}, \mathbf{r}')$:

$$
E_{\text{LDA}}[\rho] = E_{\text{LDA}}[\rho_0 + \rho_j] \approx E_{\text{LDA}}\Big|_{\rho_j(\mathbf{r})=0} + \int d\mathbf{r}\, \rho_j(\mathbf{r})\Phi(\mathbf{r})\Big|_{\rho_j(\mathbf{r})=0}
$$
$$
+ \tfrac{1}{2} \int d\mathbf{r}\, \rho_j(\mathbf{r}) \int d\mathbf{r}'\, \rho_j(\mathbf{r}')W(\mathbf{r}, \mathbf{r}')\Big|_{\rho_j(\mathbf{r})=0}. \tag{10}
$$

If one adds to (7) a correction term

$$
E_{\text{corr}}[\rho_j] \equiv -\tfrac{1}{2} \int d\mathbf{r}\, \rho_j(\mathbf{r}) \int d\mathbf{r}'\, (\rho_j(\mathbf{r}') - \rho_j^{\max}(\mathbf{r}'))W(\mathbf{r}, \mathbf{r}')\Big|_{\rho_j(\mathbf{r})=0}, \tag{11}
$$

then the linear dependence on the density variations (as it is required for the *exact* density functional (5)) will be restored:

$$
E_{\text{LDA}}[\rho_0 + \rho_j] + E_{\text{corr}}[\rho_j] \approx E_{\text{LDA}}\Big|_{\rho_j(\mathbf{r})=0}
$$
$$
+ \int d\mathbf{r}\, \rho_j(\mathbf{r}) \left(\Phi(\mathbf{r})\Big|_{\rho_j(\mathbf{r})=0} + \tfrac{1}{2} \int d\mathbf{r}'\, \rho_j^{\max}(\mathbf{r}')W(\mathbf{r}, \mathbf{r}')\Big|_{\rho_j(\mathbf{r})=0} \right). \tag{12}
$$

Equation (12) is equivalent to (5) with the function $\Lambda_j(\mathbf{r})$ equal to

$$
\Lambda_j(\mathbf{r}) = \Phi(\mathbf{r})\Big|_{\rho_j(\mathbf{r})=0} + \tfrac{1}{2} \int d\mathbf{r}'\, \rho_j^{\max}(\mathbf{r}')W(\mathbf{r}, \mathbf{r}')\Big|_{\rho_j(\mathbf{r})=0}. \tag{13}
$$

Now we are ready to write an ad hoc correction to the LDA functional to imitate the linear form of the functional (5). We define the 'orbital density functional' E_{ODF} as

$$
E_{\text{ODF}}[\{\rho_i\}] \equiv E_{\text{LDA}}[\rho] - \tfrac{1}{2} \sum_i \int d\mathbf{r}\, \rho_i(\mathbf{r}) \int d\mathbf{r}'\, (\rho_i(\mathbf{r}') - \rho_i^{\max}(\mathbf{r}'))W(\mathbf{r}, \mathbf{r}')\Big|_{\rho_i(\mathbf{r})=0}. \tag{14}
$$

Please note that the ODF functional (14) depends both on the total charge density $\rho(\mathbf{r})$ via $E_{\text{LDA}}[\rho]$ and explicitly on a set of orbital densities $\{\rho_i(\mathbf{r})\}$.

Let us investigate the dependence of the functional (14) on the number of electrons N. Note that for the integer values of N corresponding to the integer orbital occupancies n_i the value of the functional (14) coincides with the corresponding value of the LDA functional. For integer n_i values, the orbital density $\rho_i(\mathbf{r})$ is equal either to zero (for an empty state, $n_i = 0$) or $\rho_i^{\max}(\mathbf{r})$ (for an occupied state, $n_i = 1$). In both cases the correction term in (14) vanishes. We will show that according to the properties [11] of the exact density functional E_{EDF} (2) this dependence corresponds to the curve of E_{ODF} versus N as a series of straight-line segments with derivative discontinuities at integer values of N.

The increase of the total number of electrons N occurs via the consequential increase of the orbital occupancies n_i so that when N changes from M to $M + 1$ the value of the n_i corresponding to the highest occupied orbital for the system with $M + 1$ electrons changes from 0 to 1. The corresponding variation $\delta\rho(\mathbf{r})$ of the total charge density $\rho(\mathbf{r})$ will consist exclusively of the variation of the corresponding orbital density $\rho_j(\mathbf{r})$ of particular orbital j. The variational derivative of the functional (14) is equal to

$$
\frac{\delta E_{\text{ODF}}}{\delta\rho(\mathbf{r})}\Big|_{N=M+\omega} = \frac{\delta E_{\text{ODF}}}{\delta\rho_j(\mathbf{r})} = \frac{\delta E_{\text{LDA}}}{\delta\rho(\mathbf{r})} - \int d\mathbf{r}' \left(\rho_j(\mathbf{r}') - \frac{1}{2}\rho_j^{\max}(\mathbf{r}') \right) W(\mathbf{r}, \mathbf{r}')\Big|_{\rho_j(\mathbf{r})=0}. \tag{15}
$$

(Please note that the expression $\frac{\delta E_{\text{ODF}}}{\delta\rho(\mathbf{r})}|_{N=M+\omega}$ does not mean a general variation of the LDA functional but only a variation that happens when the number of electrons N changes from M to $M + 1$ in the limit of ω tending to zero.)

The first term in the right-hand part of (15), $\delta E_{\mathrm{LDA}}/\delta\rho(\mathbf{r})$, is continuous. However, the second term depends on the index j. When the number of electrons N equals $M - \omega$, j corresponds to the highest occupied orbital for the system with M electrons. However, for $N = M + \omega$ the index will change to $j + 1$, corresponding to the lowest unoccupied orbital for the system with M electrons or the highest occupied orbital for the system with $M + 1$ electrons. The value of $\rho_j(\mathbf{r}')$ in the integral in the right-hand part of (15) will jump from $\rho_j^{\max}(\mathbf{r}')$ to zero with N going from $M - \omega$ to $M + \omega$ for infinitesimally small ω. This results in the corresponding jump of the variational derivative $\delta E_{\mathrm{ODF}}/\delta\rho(\mathbf{r})$:

$$\frac{\delta E_{\mathrm{ODF}}}{\delta\rho(\mathbf{r})}\Big|_{N=M+\omega} - \frac{\delta E_{\mathrm{ODF}}}{\delta\rho(\mathbf{r})}\Big|_{N=M-\omega}$$
$$= \tfrac{1}{2}\int \mathrm{d}\mathbf{r}' \left(\rho_j^{\max}(\mathbf{r}')W(\mathbf{r},\mathbf{r}')\Big|_{\rho_j(\mathbf{r})=0} + \rho_{j+1}^{\max}(\mathbf{r}')W(\mathbf{r},\mathbf{r}')\Big|_{\rho_{j+1}(\mathbf{r})=0}\right). \tag{16}$$

In order to show that the variational derivative $\delta E_{\mathrm{ODF}}/\delta\rho(\mathbf{r})$ is constant for the number of electrons varying from M to $M+1$, we need an explicit expression for the variational derivative of the LDA functional $\delta E_{\mathrm{LDA}}/\delta\rho(\mathbf{r})$. The latter can be obtained by using an expansion of (7) and (10):

$$\frac{\delta E_{\mathrm{LDA}}}{\delta\rho(\mathbf{r})}\Big|_{N=M+\omega} = \frac{\delta E_{\mathrm{LDA}}}{\delta\rho_j(\mathbf{r})} \approx \frac{\delta E_{\mathrm{LDA}}}{\delta\rho(\mathbf{r})}\Big|_{\rho_j(\mathbf{r})=0} + \int \mathrm{d}\mathbf{r}'\,\rho_j(\mathbf{r}')\frac{\delta^2 E_{\mathrm{LDA}}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\Big|_{\rho_j(\mathbf{r})=0}$$
$$= \Phi(\mathbf{r})\Big|_{\rho_j(\mathbf{r})=0} + \int \mathrm{d}\mathbf{r}'\,\rho_j(\mathbf{r}')W(\mathbf{r},\mathbf{r}')\Big|_{\rho_j(\mathbf{r})=0}. \tag{17}$$

Equation (15) takes the form

$$\frac{\delta E_{\mathrm{ODF}}}{\delta\rho(\mathbf{r})}\Big|_{N=M+\omega} = \frac{\delta E_{\mathrm{ODF}}}{\delta\rho_j(\mathbf{r})} \approx \frac{\delta E_{\mathrm{LDA}}}{\delta\rho(\mathbf{r})}\Big|_{\rho_j(\mathbf{r})=0} + \frac{1}{2}\int \mathrm{d}\mathbf{r}'\,\rho_j^{\max}(\mathbf{r}')\frac{\delta^2 E_{\mathrm{LDA}}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\Big|_{\rho_j(\mathbf{r})=0}$$
$$= \Phi(\mathbf{r})\Big|_{\rho_j(\mathbf{r})=0} + \frac{1}{2}\int \mathrm{d}\mathbf{r}'\,\rho_j^{\max}(\mathbf{r}')W(\mathbf{r},\mathbf{r}')\Big|_{\rho_j(\mathbf{r})=0}. \tag{18}$$

The right-hand part of (18) does not depend on ρ_j, and hence it is constant for a fractional number of electrons n_j. The jump of $\delta E_{\mathrm{ODF}}/\delta\rho(\mathbf{r})$ in (16) can be assigned to the jump in the variational derivative of the effective exchange–correlation energy term in the ODF functional $\delta E_{\mathrm{xc}}^{\mathrm{ODF}}/\delta\rho(\mathbf{r})$.

The functional (14) can be rewritten in a simpler form that can be used in practical calculations if the set of orbitals $\psi_i(\mathbf{r})$ is fixed. Then variation of the orbital density $\rho_i(\mathbf{r})$ occurs only via variation of the occupancy n_i:

$$\delta\rho_i(\mathbf{r}) = \delta n_i|\psi_i(\mathbf{r})|^2. \tag{19}$$

Then the second variation of the LDA functional is

$$\delta^2 E_{\mathrm{LDA}} = \tfrac{1}{2}\sum_{ij}\int \mathrm{d}\mathbf{r}\,\delta\rho_i(\mathbf{r})\int \mathrm{d}\mathbf{r}'\,\delta\rho_j(\mathbf{r}')W(\mathbf{r},\mathbf{r}')$$
$$= \tfrac{1}{2}\sum_{ij}\delta n_i\delta n_j\int \mathrm{d}\mathbf{r}\,|\psi_i(\mathbf{r})|^2\int \mathrm{d}\mathbf{r}'\,|\psi_j(\mathbf{r}')|^2 W(\mathbf{r},\mathbf{r}'). \tag{20}$$

The second derivative of the LDA functional with respect to the occupancy n_i is

$$\frac{\delta^2 E_{\mathrm{LDA}}}{\delta n_i\delta n_j} = \int \mathrm{d}\mathbf{r}\,|\psi_i(\mathbf{r})|^2\int \mathrm{d}\mathbf{r}'\,|\psi_j(\mathbf{r}')|^2 W(\mathbf{r},\mathbf{r}'). \tag{21}$$

The value of the derivative $\delta^2 E_{\mathrm{LDA}}/\delta n_i\delta n_j$ could be obtained in the constrained LDA calculation either in a direct way or by taking into account that the derivative of the

LDA functional with respect to the orbital occupancy $\delta E_{\mathrm{LDA}}/\delta n_i$ is equal to a one-electron eigenvalue ϵ_i:

$$\frac{\delta^2 E_{\mathrm{LDA}}}{\delta n_i \delta n_j} = \frac{\delta \epsilon_i}{\delta n_j}. \tag{22}$$

Using (19)–(22), the ODF functional (14) could be rewritten via occupancies n_i:

$$E_{\mathrm{ODF}}[\rho(\mathbf{r}), \{n_i\}] = E_{\mathrm{LDA}}[\rho(\mathbf{r})] - \frac{1}{2} \sum_i n_i (n_i - 1) \frac{\delta \epsilon_i}{\delta n_i}. \tag{23}$$

Please note that while the LDA functional depends on n_i only implicitly via the charge density $\rho(\mathbf{r})$, the ODF functional depends not only on $\rho(\mathbf{r})$ but also explicitly on the set of occupancies $\{n_j\}$.

The derivative of the ODF functional (14) with respect to the total number of electrons N can be expressed by using the occupancy n_i of a partially occupied orbital j:

$$\frac{\delta E_{\mathrm{ODF}}}{\delta N}\bigg|_{N=M+\omega} = \frac{\delta E_{\mathrm{ODF}}}{\delta n_j} = \frac{\delta E_{\mathrm{LDA}}}{\delta n_j} + \left(\frac{1}{2} - n_j\right) \frac{\delta \epsilon_j}{\delta n_j} = \epsilon_j + \left(\frac{1}{2} - n_j\right) \frac{\delta \epsilon_j}{\delta n_j}. \tag{24}$$

One can assume a linear dependence of $\epsilon_j(n_j)$ on n_j which is equivalent to keeping only the first and second variational derivatives in (7). Then it is possible to show that the derivative $\delta E_{\mathrm{ODF}}/\delta N$ does not depend on n_j:

$$\frac{\delta E_{\mathrm{ODF}}}{\delta N}\bigg|_{N=M+\omega} \approx \epsilon_j\big|_{n_j=0} + n_j \frac{\delta \epsilon_j}{\delta n_j}\bigg|_{n_j=0} + \left(\frac{1}{2} - n_j\right) \frac{\delta \epsilon_j}{\delta n_j}\bigg|_{n_j=0} = \epsilon_j\big|_{n_j=0} + \frac{1}{2} \frac{\delta \epsilon_j}{\delta n_j}\bigg|_{n_j=0}. \tag{25}$$

The analogue of (16) demonstrates a jump of $\delta E_{\mathrm{ODF}}/\delta N$ when the number of electrons N goes through an integer value M:

$$\frac{\delta E_{\mathrm{ODF}}}{\delta N}\bigg|_{N=M+\omega} - \frac{\delta E_{\mathrm{ODF}}}{\delta N}\bigg|_{N=M-\omega} = (\epsilon_{j+1} - \epsilon_j) + \frac{1}{2} \left(\frac{\delta \epsilon_j}{\delta n_j} + \frac{\delta \epsilon_{j+1}}{\delta n_{j+1}}\right). \tag{26}$$

We have shown that with the accuracy of expansion of (7) the variational derivative of the 'orbital density functional' E_{ODF} (14) conforms to the condition for the *exact* density functional found in [11]: it is constant for a fractional number of electrons and has a discontinuity when the number of electrons goes through an integer value.

One should keep in mind that the 'orbital density functional' (14) was defined as 'ad hoc' formulae and the fact that it obeys exact conditions cannot be considered as a proof of its validity. However, one can hope that an expression with a proper analytical behaviour can give an improvement in the calculation results. Below we will demonstrate that this is indeed the case.

Equations (23) and (24) are directly related to the 'transition state' approach to calculate excitation energies proposed by Slater [17]. In this scheme the LDA eigenvalue (eigenvalue of the Kohn–Sham equations) of the corresponding one-electron state should be calculated with its occupancy equal to 0.5 (half-way between the initial and final states of excitation process). One can identify a derivative of the ODF functional (23) over occupancy n_i as a corresponding one-electron energy $\epsilon_i^{\mathrm{ODF}}$:

$$\epsilon_i^{\mathrm{ODF}} \equiv \frac{\delta E_{\mathrm{ODF}}}{\delta n_i} = \epsilon_i^{\mathrm{LDA}} + \left(\frac{1}{2} - n_i\right) \frac{\delta \epsilon_i}{\delta n_i}. \tag{27}$$

If the LDA eigenvalue $\epsilon_i(n_i)$ is a linear function of the occupancy n_i ($\delta \epsilon_i/\delta n_i = \mathrm{const}$) (which is equivalent to the expansion in (25) leaving only the first two terms in the expansion), then for an empty state ($n_i = 0$)

$$\epsilon_i^{\mathrm{LDA}}(0.5) = \epsilon_i^{\mathrm{LDA}}(0) + \frac{1}{2}\frac{\delta\epsilon_i}{\delta n_i}. \tag{28}$$

For occupied states ($n_i = 1$) the plus sign in (28) will be replaced by minus. One can see that (27) reproduces both these cases:

$$\epsilon_i^{\mathrm{ODF}} = \epsilon_i^{\mathrm{LDA}}(n_i) + \left(\frac{1}{2} - n_i\right)\frac{\delta\epsilon_i}{\delta n_i} = \epsilon_i^{\mathrm{LDA}}(0.5). \tag{29}$$

In [16] we have introduced an auxiliary functional by variation of which (29) giving the 'transition state' correction to one-electron energies can be obtained. That functional is identical to the functional (23). It is interesting to note that the same ad hoc correction to the LDA functional can result in reproducing analytical properties known for the exact density functional [11] and provide 'transition state' eigenvalues.

3. Fluctuation Hamiltonian

The minimization of the ODF functional (14) will give a set of orbital densities $\{\rho_i(\mathbf{r})\}$ and hence the total charge density $\rho(\mathbf{r})$ corresponding to the ground state of the system. It is useful to derive equations for *fluctuations* of the orbital densities $\{\delta\rho_i(\mathbf{r})\}$ around the average ground-state functions $\{\rho_i(\mathbf{r})\}$. This 'ground-state' charge density $\rho(\mathbf{r})$ corresponds to the minimum of the ODF functional (14) but not of the LDA functional, so one must use a constrain potential $\Phi(\mathbf{r})$ in the calculations. Analogous to the expansions (7) and (10) one can write expression for the LDA part of the ODF functional:

$$E_{\mathrm{LDA}}[\{\rho_i + \delta\rho_i\}] \approx E_{\mathrm{LDA}}[\{\rho_i\}] + \sum_i \int d\mathbf{r}\, \delta\rho_i(\mathbf{r})\Phi(\mathbf{r})$$
$$+ \tfrac{1}{2}\sum_i\sum_j \int d\mathbf{r}\, \delta\rho_i(\mathbf{r}) \int d\mathbf{r}'\, \delta\rho_j(\mathbf{r}')W(\mathbf{r},\mathbf{r}'). \tag{30}$$

The corresponding expression for the correction term (11) is

$$E_{\mathrm{corr}}[\{\rho_i + \delta\rho_i\}] \approx E_{\mathrm{corr}}[\{\rho_i\}]$$
$$- \sum_i \int d\mathbf{r}\, \delta\rho_i(\mathbf{r}) \int d\mathbf{r}'\, (\rho_i(\mathbf{r}') - \tfrac{1}{2}\rho_i^{\max}(\mathbf{r}'))W(\mathbf{r},\mathbf{r}')$$
$$- \tfrac{1}{2}\sum_i \int d\mathbf{r}\, \delta\rho_i(\mathbf{r}) \int d\mathbf{r}'\, \delta\rho_i(\mathbf{r}')W(\mathbf{r},\mathbf{r}'). \tag{31}$$

Both (30) and (31) become exact if one supposes that $\frac{\delta^2 E_{\mathrm{LDA}}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} = W(\mathbf{r},\mathbf{r}')$ does not depend on the fluctuations $\delta\rho_i(\mathbf{r})$. As a result, all variational derivatives higher than the second order are equal to zero. In the following we assume that this approximation is valid. Then for the total ODF functional one has

$$E_{\mathrm{ODF}}[\{\rho_i + \delta\rho_i\}] = E_{\mathrm{ODF}}[\{\rho_i\}]$$
$$+ \sum_i \int d\mathbf{r}\, \delta\rho_i(\mathbf{r})\left(\Phi(\mathbf{r}) - \int d\mathbf{r}'\, (\rho_i(\mathbf{r}') - \tfrac{1}{2}\rho_i^{\max}(\mathbf{r}'))W(\mathbf{r},\mathbf{r}')\right)$$
$$+ \tfrac{1}{2}\sum_i\sum_{j\neq i} \int d\mathbf{r}\, \delta\rho_i(\mathbf{r}) \int d\mathbf{r}'\, \delta\rho_j(\mathbf{r}')W(\mathbf{r},\mathbf{r}'). \tag{32}$$

It is convenient to introduce an effective ODF potential $V_i^{\mathrm{ODF}}(\mathbf{r})$:

$$V_i^{\mathrm{ODF}}(\mathbf{r}) \equiv \Phi(\mathbf{r}) - \int d\mathbf{r}'\, (\rho_i(\mathbf{r}') - \tfrac{1}{2}\rho_i^{\max}(\mathbf{r}'))W(\mathbf{r},\mathbf{r}'). \tag{33}$$

Using (32) and (33), one can define a Hamiltonian for the density matrix fluctuation operators $\widehat{\delta\rho}_i(\mathbf{r}) \equiv \widehat{\rho}_i(\mathbf{r}) - \rho_i(\mathbf{r})$ (here a ground-state orbital density can be considered as an average value of a density matrix operator $\rho_i(\mathbf{r}) = \langle\widehat{\rho}_i(\mathbf{r})\rangle$):

$$\widehat{H}_{\mathrm{ODF}} \equiv \sum_i \int d\mathbf{r}\, \widehat{\delta\rho}_i(\mathbf{r}) V_i^{\mathrm{ODF}}(\mathbf{r}) + \tfrac{1}{2}\sum_i \sum_{j\neq i} \int d\mathbf{r}\, \widehat{\delta\rho}_i(\mathbf{r}) \int d\mathbf{r}'\, \widehat{\delta\rho}_j(\mathbf{r}') W(\mathbf{r},\mathbf{r}'). \qquad (34)$$

The orbital density matrix operators $\widehat{\rho}_i(\mathbf{r})$ could be expressed via orbital occupancy operators $\widehat{n}_i$ (if the orbitals $\psi_i(\mathbf{r})$ are fixed and the variation of the orbital density $\rho_i(\mathbf{r})$ occurs only via variation of occupancies n_i):

$$\widehat{\rho}_i(\mathbf{r}) = \widehat{n}_i |\psi_i(\mathbf{r})|^2. \qquad (35)$$

Then fluctuation Hamiltonian (34) can be rewritten (using (19)–(22)) via occupancy operators $\widehat{n}_i$ and their average values $n_i = \langle\widehat{n}_i\rangle$ ($\widehat{\delta n}_i \equiv \widehat{n}_i - \langle\widehat{n}_i\rangle$):

$$\widehat{H}_{\mathrm{ODF}} = \sum_i \left(\epsilon_i + \left(\tfrac{1}{2} - n_i\right) \frac{\partial\epsilon_i}{\partial n_i} \right) \widehat{\delta n}_i + \frac{1}{2}\sum_i \sum_{j\neq i} \frac{\partial\epsilon_i}{\partial n_j} \widehat{\delta n}_i \widehat{\delta n}_j. \qquad (36)$$

4. The choice of the orbitals and Wannier functions

The orbital densities $\rho_i(\mathbf{r})$ are defined by orbitals $\psi_i(\mathbf{r})$ in the expression for the charge density in (4). In the density functional theory it is usually assumed that these orbitals are solutions of the Kohn–Sham equations. However, any unitary transformation (defined by the unitary matrix U) of the set of the occupied functions $\psi_i(\mathbf{r})$ produces a new set of orbitals

$$\widetilde{\psi}_i(\mathbf{r}) \equiv \sum_j U_{ij}\psi_j(\mathbf{r}) \qquad (37)$$

corresponding to the same charge density $\rho(\mathbf{r})$. This new set of orbitals can be used to define the ODF functional in (14) and so this functional is orbital dependent.

In order to remove the uncertainty in choosing the orbital set, one needs to impose an additional condition. We propose the following way to do it: to minimize the energy of orbital density fluctuation defined as the expectation value of the fluctuation Hamiltonian (34):

$$\langle\widehat{H}_{\mathrm{ODF}}\rangle = \tfrac{1}{2}\sum_i \sum_{j\neq i} \int d\mathbf{r} \int d\mathbf{r}'\, \langle\widehat{\delta\rho}_i(\mathbf{r})\widehat{\delta\rho}_j(\mathbf{r}')\rangle W(\mathbf{r},\mathbf{r}'). \qquad (38)$$

(The average value of fluctuations $\langle\widehat{\delta\rho}_i(\mathbf{r})\rangle$ is equal to zero so the first term in (34) does not give a contribution to the fluctuation energy.) Taking into account (30) and (31), one can separate contributions to (38) from the LDA functional, where summation over i and j is performed including terms with $i = j$, and a correction term (31).

The LDA part is

$$\langle\widehat{H}_{\mathrm{LDA}}\rangle = \tfrac{1}{2}\sum_i \sum_j \int d\mathbf{r} \int d\mathbf{r}'\, \langle\widehat{\delta\rho}_i(\mathbf{r})\widehat{\delta\rho}_j(\mathbf{r}')\rangle W(\mathbf{r},\mathbf{r}')$$

$$= \tfrac{1}{2}\int d\mathbf{r} \int d\mathbf{r}' \left\langle \sum_i \widehat{\delta\rho}_i(\mathbf{r}) \sum_j \widehat{\delta\rho}_j(\mathbf{r}') \right\rangle W(\mathbf{r},\mathbf{r}')$$

$$= \tfrac{1}{2}\int d\mathbf{r} \int d\mathbf{r}'\, \langle\widehat{\delta\rho}(\mathbf{r})\widehat{\delta\rho}(\mathbf{r}')\rangle W(\mathbf{r},\mathbf{r}'). \qquad (39)$$

The correction term gives a negative contribution to the total energy equal to

$$\langle\widehat{H}_{\mathrm{corr}}\rangle = -\tfrac{1}{2}\sum_i \int d\mathbf{r} \int d\mathbf{r}'\, \langle\widehat{\delta\rho}_i(\mathbf{r})\widehat{\delta\rho}_i(\mathbf{r}')\rangle W(\mathbf{r},\mathbf{r}'). \qquad (40)$$

From (39) one can see that the LDA contribution to the fluctuation energy is defined by the total charge density fluctuations $\langle \widehat{\delta\rho}(\mathbf{r}) \widehat{\delta\rho}(\mathbf{r}') \rangle$ and hence does not depend on the orbitals' definition. The minimum of the fluctuation energy (38) is achieved when the absolute value of the correction contribution (40) has a maximum.

The correction term contribution in (40) can be calculated by using the expression for the fluctuation Hamiltonian via the fluctuation occupancy operators $\widehat{\delta n_i}$ (36) as

$$\langle \widehat{H}_{\text{corr}} \rangle = -\frac{1}{2} \sum_i \langle \widehat{\delta n_i} \widehat{\delta n_i} \rangle \frac{\partial \epsilon_i}{\partial n_i}. \tag{41}$$

As the average value of square of occupancy fluctuations $\langle \widehat{\delta n_i} \widehat{\delta n_i} \rangle$ depends on the specific properties of the system, the only way to minimize the fluctuation energy $\langle \widehat{H} \rangle$ (38) is to maximize $\partial \epsilon_i / \partial n_i$. Using (21) and (22); this parameter can be expressed via orbitals as

$$\frac{\partial \epsilon_i}{\partial n_i} = \frac{\delta^2 E_{\text{LDA}}}{\delta n_i^2} = \int d\mathbf{r} \, |\psi_i(\mathbf{r})|^2 \int d\mathbf{r}' \, |\psi_i(\mathbf{r}')|^2 W(\mathbf{r}, \mathbf{r}'). \tag{42}$$

For a new set of functions $\widetilde{\psi}_i(\mathbf{r})$ (37), one has

$$\frac{\delta \widetilde{\epsilon}_i}{\delta \widetilde{n}_i} = \sum_{jj'll'} U_{ij} U_{ij'}^* U_{il} U_{il'}^* \int d\mathbf{r} \int d\mathbf{r}' \, \psi_j(\mathbf{r}) \psi_{j'}^*(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') \psi_l(\mathbf{r}') \psi_{l'}^*(\mathbf{r}'). \tag{43}$$

Using (43) and the fact that the derivatives $\delta \epsilon_i / \delta n_i$ are always positive, one can define a functional of the unitary matrix U:

$$F[U] \equiv \sum_i \frac{\delta \widetilde{\epsilon}_i}{\delta \widetilde{n}_i} = \sum_i \sum_{jj'll'} U_{ij} U_{ij'}^* U_{il} U_{il'}^* \int d\mathbf{r} \int d\mathbf{r}' \, \psi_j(\mathbf{r}) \psi_{j'}^*(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') \psi_l(\mathbf{r}') \psi_{l'}^*(\mathbf{r}'), \tag{44}$$

maximization of which one can be used as a condition to determine the matrix U and hence the optimal set of the orbitals $\psi_i(\mathbf{r})$ to define the ODF functional.

The function $W(\mathbf{r}, \mathbf{r}')$ (8) is defined as the screened effective interaction between density fluctuations $\delta\rho(\mathbf{r})$, $\delta\rho(\mathbf{r}')$ and hence should decay with increasing of $|\mathbf{r} - \mathbf{r}'|$ value. Then the more localized in space the orbitals $\psi_i(\mathbf{r})$ are, the larger should be the value of the integral (42). One of the possible choices for these orbitals could be Wannier functions (WFs) [22]. Two orthonormal sets of functions, Wannier and Bloch, are connected via unitary transformation so WFs can be considered as a particular choice of the unitary matrix U in (37). Marzari and Vanderbilt in [15] proposed the condition of maximum localization to determine the procedure to calculate WFs for the multi-band case. The requirement of maximum localization should lead to reasonably maximized values of the parameter $\partial \epsilon_i / \partial n_i$ in (42) and hence to the minimization of the fluctuation energy (38). Then WFs obtained via the procedure proposed in [15, 23] are a good choice for a set of orbitals to define the ODF functional.

In the following we will assume that orbital densities are defined by WFs $W_n(\mathbf{r})$ and their occupancies Q_n calculated via the procedure described in [21] (thus the orbital functions basis set is chosen to be formed by Wannier functions instead of the eigenfunctions ψ_i, and that is emphasized by using notations $W_n(\mathbf{r})$ and Q_n instead of ψ_i and n_i):

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_n \rho_n(\mathbf{r}), \\ \rho_n(\mathbf{r}) &= Q_n |W_n(\mathbf{r})|^2. \end{aligned} \tag{45}$$

Using equations (23)–(35), the ODF functional (14) could be rewritten with the WF occupancy operators

$$\widehat{Q}_n = |W_n\rangle\langle W_n| \tag{46}$$

($|W_n\rangle$ in (46) are Wannier functions) and their average values

$$Q_n = \langle \widehat{Q}_n \rangle = \sum_{i_{\text{occupied}}} \langle \psi_i | \widehat{Q}_n | \psi_i \rangle. \tag{47}$$

The corresponding functional will be similar to (23) but with the WF occupancies Q_n and energies E_n

$$E_{\text{ODF}} = E_{\text{LDA}} - \frac{1}{2} \sum_n \frac{\partial E_n}{\partial Q_n} Q_n (Q_n - 1). \tag{48}$$

The variation of the functional (48) will produce the one-electron Hamiltonian $\widehat{H}^0_{\text{ODF}}$ in the form of the projection operator (see equations (46), (47) and also [16]):

$$\widehat{H}^0_{\text{ODF}} = \widehat{H}_{\text{LDA}} + \sum_n \delta V_n \widehat{Q}_n = \widehat{H}_{\text{LDA}} + \sum_n |W_n\rangle \delta V_n \langle W_n|, \tag{49}$$

δV_n are

$$\delta V_n = \frac{\partial E_n}{\partial Q_n} \left(\frac{1}{2} - Q_n \right). \tag{50}$$

The values of the derivatives $\partial E_n / \partial Q_n$ should be determined in the constrained LDA calculations (see [16]).

The Wannier function analogue of the fluctuation Hamiltonian (36) is

$$\widehat{H}_{\text{ODF}} = \widehat{H}^0_{\text{ODF}} + \frac{1}{2} \sum_n \sum_{n' \neq n} \frac{\partial E_n}{\partial Q_{n'}} (\widehat{Q}_n - \langle \widehat{Q}_n \rangle)(\widehat{Q}_{n'} - \langle \widehat{Q}_{n'} \rangle). \tag{51}$$

5. ODF calculation scheme

Equations (48)–(51) define the ODF calculation scheme. The Hamiltonian $\widehat{H}^0_{\text{ODF}}$ (49) can be considered as a static mean-field approximation to a general problem. It is the analogue of the LDA + U [8, 9] method with Wannier functions used instead of atomic d or f orbitals. For band insulators and Mott–Hubbard insulators with long-range spin ordering $\widehat{H}^0_{\text{ODF}}$ is a good enough approximation and its solution can be considered as a final step in the calculations. However, for strongly correlated metals and paramagnetic Mott insulators, dynamical effects due to the fluctuations play a crucial role, and one should solve the problem defined by the fluctuation Hamiltonian (51). Using this Hamiltonian, we construct a dynamical approximation scheme with the dynamical mean-field theory to solve the arising impurity problem.

Equations (49) and (50) are identical to the equations of 'generalized transition state' (GTS) method that we have developed in [16]. The basis of the GTS method was an idea that one-electron energies corresponding to WFs should have the meaning of the removal (addition) energies for electrons from (to) the corresponding states. That was realized by using a 'transition-state' scheme [17] generalized to WFs instead of eigenfunctions. It is remarkable that the same equations can be obtained by introducing 'ad hoc' correction to the LDA functional restoring the properties of the *exact* density functional theory [11].

The potential correction operator (49) and (50) shifts the energies of Wannier functions by the δV_n values which are negative ($\delta V_n = -\frac{1}{2} \frac{\partial E_n}{\partial Q_n}$) for the occupied states ($Q_n = 1$) and positive ($\delta V_n = \frac{1}{2} \frac{\partial E_n}{\partial Q_n}$) for the empty states ($Q_n = 0$). That makes the valence bands to be pushed down and the conduction bands pushed up compared to the standard LDA, and thus results in a wider energy gap, systematically underestimated in the LDA. In [16] it was shown that calculations with the potential correction (49) and (50) result in a much better agreement with experimental energy gap values for a semiconductor (Si), band insulator (MgO), Mott insulator (NiO), and Peierls insulator $BaBiO_3$.

For metals, Wannier function occupancy values Q_n can be non-integer, and the potential correction δV_n (50) will be much smaller than the insulator values $\pm \frac{1}{2} \frac{\partial E_n}{\partial Q_n}$. For half-filled bands $Q_n = 0.5$ and the potential correction vanishes ($\delta V_n = 0$). For this case only the solution of the fluctuation Hamiltonian (51) can give non-trivial results.

The first and second parts of the Hamiltonian (51) are not (!) a *noninteracting* Hamiltonian and an *interaction* term, as is usually defined in model Hubbard and Anderson Hamiltonians. The first term, $\widehat{H}_{ODF}^0$, is equivalent to the Hartree–Fock approximation Hamiltonian determined by the average values of the WF occupancies $\langle \widehat{Q}_n \rangle$. The second part describes the interaction between fluctuations around $\langle \widehat{Q}_n \rangle$. As these average values are determined from the solution of the full Hamiltonian (51), that defines a self-consistent calculation scheme. In contrast to the LDA + U [8, 9] and LDA + DMFT [20] methods, there is no 'double counting' problem in this Hamiltonian because there is no 'merging' of LDA and Hubbard model concepts, and both terms in (51) were derived from the same functional (48).

The problem defined by the Hamiltonian (51) can be solved by any of the methods developed to treat many-body effects. In the present work we have used dynamical mean-field theory [12–14] which finalizes the dynamical approximation scheme for the ODF method.

The DMFT [12–14] was recently found to be a powerful tool to numerically solve multiband Hubbard models. In order to use this tool, the fluctuation Hamiltonian (51) should be rewritten in the form of a standard multi-orbital Hubbard model. For that one needs to identify the Coulomb parameters $U_{nn'}$ as derivatives $\partial E_n / \partial Q_{n'}$ and rearrange the terms in (51) into noninteracting and interaction terms:

$$\widehat{H}_{ODF} = \widehat{H}^0 + \widehat{H}_{int} \tag{52}$$

with the interaction term

$$\widehat{H}_{int} = \frac{1}{2} \sum_n \sum_{n' \neq n} U_{nn'} \widehat{Q}_n \widehat{Q}_{n'} \tag{53}$$

and the noninteracting Hamiltonian

$$\widehat{H}^0 = \widehat{H}_{ODF}^0 + \frac{1}{2} \sum_n \sum_{n' \neq n} U_{nn'} \langle \widehat{Q}_n \rangle \langle \widehat{Q}_{n'} \rangle - \sum_n \widehat{Q}_n \sum_{n' \neq n} U_{nn'} \langle \widehat{Q}_{n'} \rangle. \tag{54}$$

In the LDA + DMFT method (see [17]) as well as in the LDA + U method, a problem of double counting of the Coulomb interaction appears. Equation (52) together with (49) can be considered as a specific choice of the double counting term. However, one should note that it was not imposed on the formalism using some physical arguments but was derived from the expression for 'orbital density functional' (14) which in its turn was constructed to obey the exact condition of the density functional theory.

Let us briefly summarize the employed formulation of the DMFT method. In DMFT the lattice problem becomes an effective single-site problem which has to be solved self-consistently for the matrix self-energy $\widehat{\Sigma}$ and the local matrix Green function in the WF basis set:

$$G_{nn'}(\varepsilon) = \frac{1}{V_{BZ}} \int d\mathbf{k} \left(\left[(\varepsilon - \mu) \widehat{1} - \widehat{H}^0(\mathbf{k}) - \widehat{\Sigma}(\varepsilon) \right]^{-1} \right)_{nn'}, \tag{55}$$

where μ is a chemical potential, $\widehat{H}^0$ is the noninteracting Hamiltonian (54) and $\widehat{\Sigma}(\varepsilon)$ is the self-energy in the Wannier function basis:

$$\widehat{\Sigma}(\varepsilon) = \sum_{nn'} |W_n \rangle \Sigma_{nn'}(\varepsilon) \langle W_{n'} |. \tag{56}$$

The DMFT single-site problem may be viewed as a self-consistent single-impurity Anderson model [14]. The corresponding local one-particle matrix Green function $\widehat{G}$ can be
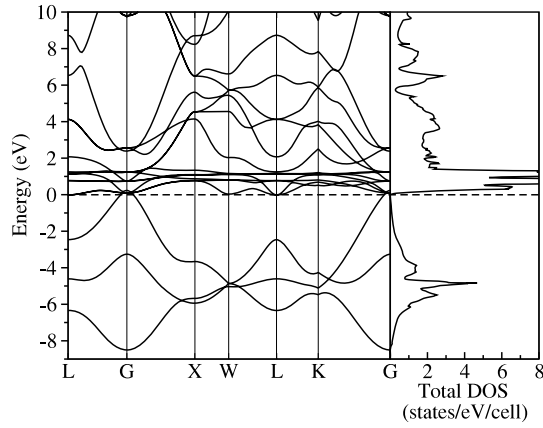
Figure 1. LaH$_3$ band structure and density of states calculated in the standard LDA.

written as a functional integral [14] involving an action where the Hamiltonian of the correlation problem under investigation, including the interaction term with the Hubbard interaction, enters [20]. The action depends on the bath matrix Green function $\widehat{\mathcal{G}}$ through

$$(\widehat{\mathcal{G}})^{-1} = (\widehat{G})^{-1} + \widehat{\Sigma}. \tag{57}$$

To solve the functional integral of the effective single-impurity Anderson problem, various methods can be used: quantum Monte Carlo (QMC), numerical renormalization group (NRG), exact diagonalization (ED), non-crossing approximation (NCA), etc (for a brief overview of the methods see [20]). In the present work the QMC method was used to solve the impurity problem.

The orbital density functional computational scheme described above is *ab initio* (it does not contain any outside parameters) and fully self-consistent. The charge density $\rho(\mathbf{r})$, Wannier functions $W_n(\mathbf{r})$, and derivatives $\partial E_n/\partial Q_{n'}$ (effective fluctuation interaction strengths) are recalculated on each self-consistency loop and hence are modified by correlations compared with the values obtained in the standard LDA calculations. In the present work we used the LMTO basis [24, 25] to construct the Wannier functions. An analogous calculation scheme for the LDA + DMFT method in the Wannier function basis set was developed in [21], where all computational details used in the present work can be found.

One can calculate the charge-density distribution modified by correlation effects using the Green function calculated in (55):

$$\rho(\mathbf{r}) = -\frac{1}{\pi} \, \text{Im} \int_{-\infty}^{E_\text{f}} \mathrm{d}\varepsilon \, G(\mathbf{r}, \mathbf{r}, \varepsilon). \tag{58}$$

With this $\rho(\mathbf{r})$ one can recalculate the LDA potential, which is a functional of electron density. From the Green function one can recalculate new WFs (see [21] for calculation details), which together with the new LDA potential allows one to obtain new parameters for the noninteracting Hamiltonian (49) and (54). With the new set of WFs one performs a series of the constrained LDA calculations to determine the derivatives $\partial E_n/\partial Q_{n'}$ and hence define new values of the Coulomb interaction parameters $U_{nn'}$ in the interaction Hamiltonian (53). The set of new LDA potential, WFs, and Coulomb interaction parameters calculated from the interacting Green function (55) defines the input for the next iteration step and hence closes the self-consistency loop in the computation scheme.
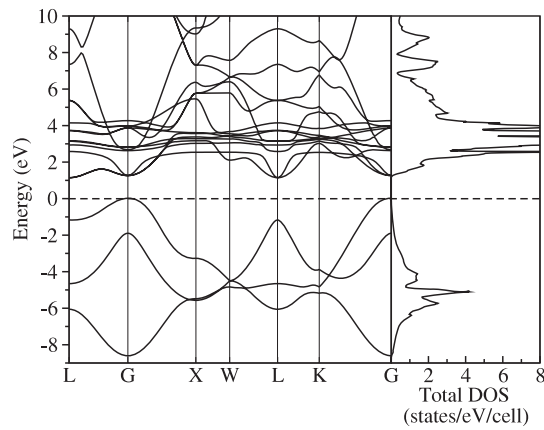
Figure 2. LaH$_3$ band structure and density of states calculated in the orbital density functional (ODF) theory (48). The zero of energy is at the Fermi energy.
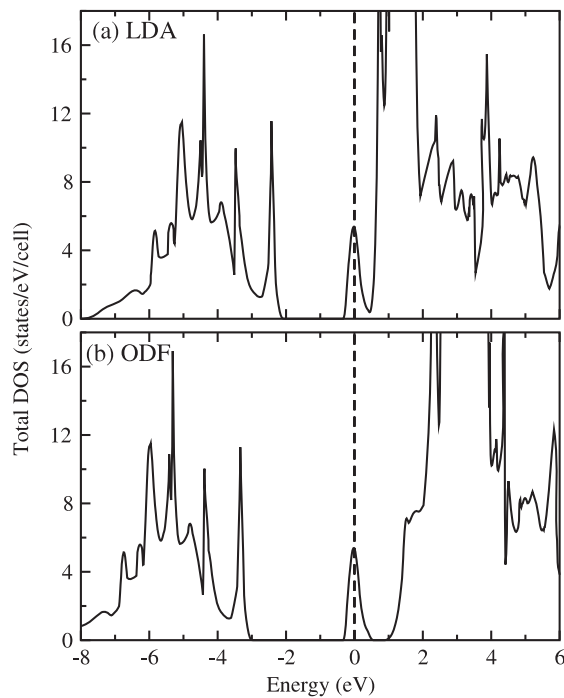

Figure 3. LaH$_{2.75}$ density of states calculated (a) in the standard LDA and (b) in ODF (48).

In the present work, the ODF method was applied to the problem of the metal–insulator transition in nonstoichiometric lanthanum trihydride LaH$_{3-x}$, where both parts of the ODF calculation scheme (static mean-field approximation (48)–(50) and the fluctuation Hamiltonian (51) solved by the DMFT method) were used to describe the experimentally observed dependence of the ground state of the system on the hydrogen concentration parameter x.
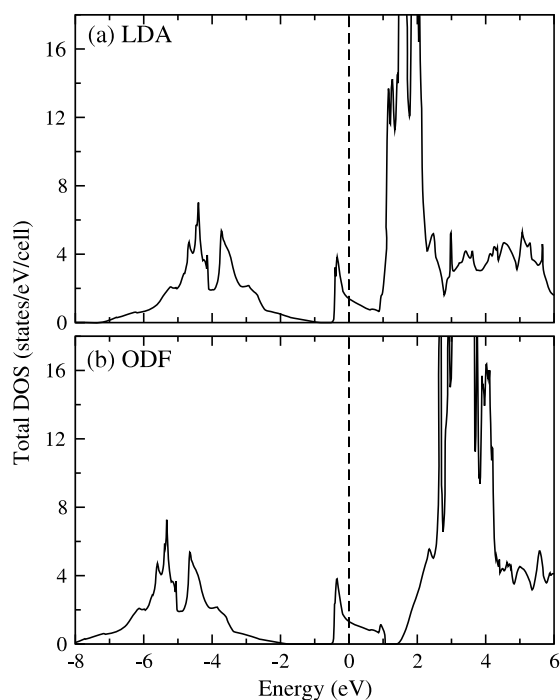
Figure 4. LaH$_{2.5}$ density of states calculated (a) in the standard LDA and (b) in ODF (48).

6. Electronic structure of nonstoichiometric lanthanum trihydride

The lanthanum trihydride LaH$_{3-x}$ shows an interesting metal–insulator transition with increase of the x value [26]. While stoichiometric LaH$_3$ is an insulator, 30% hydrogen deficiency ($x \approx 0.3$) results in a metallic ground state. However, the standard LDA calculations [27] give a metal as a ground state even for the stoichiometric composition LaH$_3$. In this case the well-known problem of the LDA, underestimation of the energy gap value, is so severe that the gap value is negative with valence and conduction bands with overlap of 0.25 eV (see figure 1).

Lanthanum trihydride has a crystal structure derived from the face-centred cubic structure (lattice parameter $a = 10.5946$ au) for La atoms and hydrogen atoms occupying two tetrahedral interstitials and one octahedral interstitial per metallic ion. The band structure of LaH$_3$ (figure 1) is relatively simple: the lower three occupied bands are formed by hydrogen 1s states and the conduction bands correspond to lanthanum 5d, 6s, and 6p states.

Attempts to cure the LDA fault in LaH$_3$ were performed with many methods beyond LDA: among others, GW [28] (the energy gap $E_g = 0.8$–0.9 eV), weighted local density approach [29] ($E_g = 0.7$ eV), and model calculations [30].

The orbital density functional (ODF) theory (48) proposed in the present work adds to the standard Kohn–Sham equations potential correction in the form of the projection operator (49) and (50). This correction is negative for occupied valence bands and positive for empty conduction bands, and hence increases the energy separation between these bands. The ODF calculations for LaH$_3$ result in an insulating ground state with a fundamental gap value of 1.10 eV and direct optical gap 1.25 eV at the G-point (see figure 2). Experimental data for the value of the energy gap $E_g^{\text{expt}} = 0.5$ eV were estimated using the activation energy determined from resistivity measurements in [31]. Optical measurements estimate the direct gap E_g as 1.87 eV, but the fundamental band gap is ~1 eV lower [32].
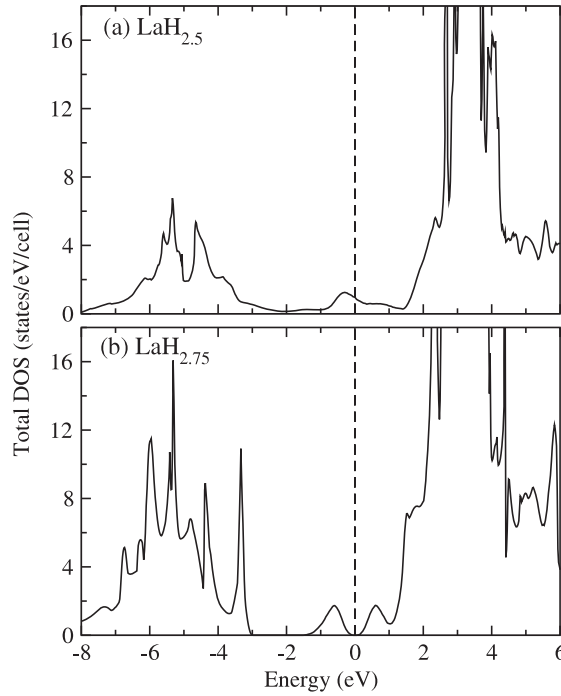
Figure 5. (a) LaH$_{2.5}$ and (b) LaH$_{2.75}$ densities of states calculated with the ODF fluctuation Hamiltonian (51) in DMFT-QMC.

Hydrogen atoms could be removed from lanthanum trihydride, forming nonstoichiometric LaH$_{3-x}$. We have performed LDA and ODF calculations for two compositions: $x = 0.25$ (LaH$_{2.75}$) (see figure 3) and $x = 0.5$ (LaH$_{2.5}$) (see figure 4).

Both LDA and ODF calculations gave a metallic ground state for the two compositions $x = 0.25$ and 0.5. Each hydrogen vacancy leads to the appearance of one vacancy state in the gap split from the conduction band with one electron occupying this state (see figure 3(a)). The static mean-field ODF potential correction (49) and (50) results in separation of the vacancy band from the conduction band and in an increase of the energy gap between the valence and conduction bands compared with the LDA, but the half-filled vacancy band stays metallic (see figures 3(b) and 4(b)). However, experimentally only LaH$_{2.5}$ is metallic while LaH$_{2.75}$ should be an insulator. To treat this problem we have used the ODF fluctuation Hamiltonian (51) and have solved it using the DMFT-QMC method. The inverse temperature parameter was $\beta = 15$ eV^{-1}. We obtained a paramagnetic insulator ground state for LaH$_{2.75}$ with a typical Mott insulator pattern of lower and upper Hubbard bands around the chemical potential with an energy gap of 0.1 eV (see figure 5(b)) in agreement with experiment. However, for LaH$_{2.5}$ the width of the vacancy band is significantly larger than for LaH$_{2.75}$ (see figures 3(b) and 4(b)) and the DMFT calculations resulted in a well-defined metallic state (see figure 5(a)).

7. Conclusion

We have proposed an 'ad hoc' orbital density functional that by construction has discontinuous exchange–correlation potential imitating the properties of *exact* density functional theory. The one-electron potential obtained by variation of this functional produces lower energies

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for valence bands and higher energies for conduction bands compared with the LDA, thus overcoming the systematic underestimation of the energy gap value in the LDA. In addition to that, we have defined the Hamiltonian corresponding to the fluctuations of the orbital densities around the ground-state values to treat correlation effects. Combining this Hamiltonian with the dynamical mean-field theory, we have developed an *ab initio* and fully self-consistent scheme for electronic structure calculations. This scheme was applied to the problem of the metal–insulator transition in LaH_{3-x} and resulted in a qualitatively better agreement with experimental data.

Acknowledgments

References

[1] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133–8
[2] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864–71
[3] Gygi G and Galli G 2005 *Mater. Today* **8** 26–32
[4] Jones R O and Gunnarsson O 1989 *Rev. Mod. Phys.* **61** 689–746
[5] Pickett W E 1989 *Rev. Mod. Phys.* **61** 433–512
[6] Hedin L 1965 *Phys. Rev.* **139** A796–823
[7] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048–79
[8] Anisimov V I, Zaanen J and Andersen O K 1991 *Phys. Rev.* B **44** 943–54
[9] Anisimov V I, Aryasetiawan F and Lichtenstein A 1997 *J. Phys.: Condens. Matter* **9** 767–808
[10] Becke A D 1988 *Phys. Rev.* A **38** 3098–100
     Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13244–54
     Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865–8
[11] Perdew J P, Parr R G, Levy M and Balduz J L 1982 *Phys. Rev. Lett.* **49** 1691–4
[12] Vollhardt D 1993 *Correlated Electron Systems* ed V J Emery (Singapore: World Scientific) p 57
[13] Pruschke Th, Jarrell M and Freericks J K 1995 *Adv. Phys.* **44** 187–210
[14] Georges A, Kotliar G, Krauth W and Rozenberg M J 1996 *Rev. Mod. Phys.* **68** 13–125
[15] Marzari N and Vanderbilt D 1997 *Phys. Rev.* B **56** 12847–65
     Marzari N, Souza I and Vanderbilt D 2003 *Psi-k Newslett.* **57** 112–60 (psi-k.dl.ac.uk/newsletters/News_57/Highlight_57.pdf)
[16] Anisimov V I and Kozhevnikov A V 2005 *Phys. Rev.* B **72** 075125
[17] Slater J C 1974 *Quantum Theory of Molecules and Solids* vol IV (New York: McGraw-Hill)
[18] Grabo T, Kreibich T, Kurth S and Gross E K U 2000 *Strong Coulomb Correlations in Electronic Structure Calculations* ed V I Anisimov (Amsterdam: Gordon and Breach) p 203
[19] Görling A and Levy M 1994 *Phys. Rev.* A **50** 196–204
[20] Held K, Nekrasov I A, Blümer N, Anisimov V I and Vollhardt D 2001 *Int. J. Mod. Phys.* B **15** 2611
     Held K, Nekrasov I A, Keller G, Eyert V, Blümer N, McMahan A K, Scalettar R T, Pruschke T, Anisimov V I and Vollhardt D 2002 *Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms* (*NIC Series* No. 10) ed J Grotendorst, D Marks and A Muramatsu (Jülich: NIC Directors Forschunszentrum Jülich) pp 175–209
     Held K, Nekrasov I A, Keller G, Eyert V, Blümer N, McMahan A K, Scalettar R T, Pruschke Th, Anisimov V I and Vollhardt D 2006 *Phys. Status Solidi* b **243** 2599–631
     Lichtenstein A I, Katsnelson M I and Kotliar G 2002 *Electron Correlations and Materials Properties* 2nd edn, ed A Gonis, N Kioussis and M Ciftan (New York: Kluwer–Academic/Plenum) p 428
[21] Anisimov V I *et al* 2005 *Phys. Rev.* B **71** 125119

[22] Wannier G H 1937 *Phys. Rev.* **52** 191–7
[23] Ku W, Rosner H, Pickett W E and Scalettar R T 2002 *Phys. Rev. Lett.* **89** 167204
[24] Andersen O K 1975 *Phys. Rev.* B **12** 3060–83
        Gunnarsson O, Jepsen O and Andersen O K 1983 *Phys. Rev.* B **27** 7144–68
[25] Skriver H L 1984 *The LMTO Method* (*Springer Series on Solid State Science* No. 41) (New York: Springer)
[26] Huiberts J N, Griessen R, Rector J H, Wijngaarden R J, Dekker J P, de Groot D G and Koeman N J 1996 *Nature*
        380 231
[27] Dekker J P, van Ek J, Lodder A and Huiberts J N 1993 *J. Phys.: Condens. Matter* **5** 4805–16
        Wang Y and Chou M Y 1993 *Phys. Rev. Lett.* **71** 1226–9
        Gupta M and Burger J P 1980 *Phys. Rev.* B **22** 6074–84
[28] Alford J A, Chou M Y, Chang E K and Louie S G 2003 *Phys. Rev.* B **67** 125110
        Chang E K, Blase X and Louie S G 2001 *Phys. Rev.* B **64** 155108
[29] Wu Z, Cohen R E, Singh D J, Gupta R and Gupta M 2004 *Phys. Rev.* B **69** 085104
[30] Ng K K, Zhang F C, Anisimov V I and Rice T M 1997 *Phys. Rev. Lett.* **78** 1311–4
        Ng K K, Zhang F C, Anisimov V I and Rice T M 1999 *Phys. Rev.* B **59** 5398–413
[31] Shinar J, Dehner B, Barnes R G and Beaudry B J 1990 *Phys. Rev. Lett.* **64** 563–6
        Peterman D J, Weaver J H and Peterson D T 1981 *Phys. Rev.* B **23** 3903–13
[32] van Gogh A T M, Nagengast D G, Kooij E S, Koeman N J, Rector J H, Griessen R, Flipse C F L and
        Smeets R J J G A M 2001 *Phys. Rev.* B **63** 195105