Orbital densities functional

V. I. Anisimov, A. V. Kozhevnikov, M. A. Korotin, A. V. Lukoyanov, and D. A. Khafizullin

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

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Abstract

Local density approximation (LDA) to the density functional theory (DFT) has continuous derivative of total energy as a number of electrons function and continuous exchange-correlation potential, while in exact DFT both should be discontinuous as number of electrons goes through an integer value. We propose orbital densities functional (ODF) (with orbitals defined as Wannier functions) that by construction obeys this discontinuity condition. By its variation one-electron equations are obtained with potential in the form of projection operator. The operator increases a separation between occupied and empty bands thus curing LDA deficiency of energy gap value systematic underestimation. Orbital densities functional minimization gives ground state orbital and total electron densities. The ODF expression for the energy of orbital densities fluctuations around the ground state values defines ODF fluctuation Hamiltonian that allows to treat correlation effects. Dynamical mean-field theory (DMFT) was used to solve this Hamiltonian with quantum Monte Carlo (QMC) method for effective impurity problem. We have applied ODF method to the problem of metal-insulator transition in lanthanum trihydride LaH$_{3-x}$. In LDA calculations ground state of this material is metallic for all values of hydrogen nonstoichiometry $x$ while experimentally the system is insulating for $x < 0.3$. ODF method gave paramagnetic insulator solution for LaH$_3$ and LaH$_{2.75}$ but metallic state for LaH$_{2.5}$.

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I. INTRODUCTION

Numerical electronic structure calculations are now 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 up to now density functional theory (DFT) in the local density approximation (LDA).\textsuperscript{1,2} It has so great predictive power, that not only charge and spin density, one-electron and total energies obtained in LDA are in general in a very good agreement with experimental data, but it was possible to develop \textit{ab initio} molecular dynamic methods, based on LDA. Such methods achieved the level of numerical experiment, because even so complicated effects, such as reconstruction of the crystal surface can be correctly described by them.\textsuperscript{3}

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

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

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

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

Varying this functional one-electron equations were obtained with potential in the form of projection operator. For occupied states the effect of this operator on the energy is negative and positive for empty states. As a the result it increases separation between valence and conduction bands comparing with LDA values thus curing LDA deficiency of energy gap value systematic underestimation.

The minimization of ODF functional gives a set of orbital densities and hence the total electron density corresponding to ground state of the system. The same functional can be used to calculate energies of orbital densities fluctuations around the ground state values. From this we have derived fluctuation Hamiltonian defined via orbital density fluctuation operators. This Hamiltonian allows to treat correlation effects and hence obtain better description of ground state properties and spectral function for the excitations. In the present work we have used for ODF Hamiltonian dynamical mean-filed theory (DMFT)\textsuperscript{12,13,14} with quantum Monte Carlo (QMC) method to solve the effective impurity problem.

The optimal choice for one-electron orbitals needed to define orbital densities can be determined by condition of fluctuation energy minimum. We have shown that the less extended in space these orbitals are, the lower the energy of orbital densities fluctuations around ground state is. Therefore in our ODF method we have used maximally localized Wannier functions for orbital densities definition.\textsuperscript{15}

Recently we have developed “generalized transition state” (GTS) method\textsuperscript{16} to improve agreement of calculated and experimental spectral properties comparing with LDA. We have found that ODF projection operator is identical to the one in equations of GTS method. The basis of GTS method was an idea that one-electron energies corresponding to Wannier
functions should have a meaning of the removal (addition) energies for electrons from (to) the corresponding states. That was realized by using “transition state” scheme\textsuperscript{17} generalized to Wannier functions. It is remarkable that so different approaches as “transition state” correction to excitation energies and requirement of exchange-correlation potential discontinuity can lead to the same equations.

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

The paper is structured as follows. In Sec. II the derivations of ODF functional and fluctuation Hamiltonian are presented. In Sec. III and IV we describe the construction of Wannier functions. Sec. V gives a short account of DMFT method and Sec. VI describes the self-consistency issues. In Sec. VII results of ODF calculations for LaH\textsubscript{3−x} are presented. Sec. VIII concludes the paper.

II. ORBITAL DENSITIES FUNCTIONAL AND FLUCTUATION HAMILTONIAN

In the local density approximation (LDA)\textsuperscript{4} to the density functional theory\textsuperscript{1} (see Appendix A) exchange-correlation energy is calculated via:

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

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

Equation II 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, Perdew \textit{et al.}\textsuperscript{11} proved that for the \textit{exact} density functional exchange-correlation potential must jump discontinuously when number of electrons \(N\) goes through an integer value.

The Hohenberg-Kohn theorem\textsuperscript{2} was extended in Ref.\textsuperscript{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 $0 \leq \omega \leq 1$ the exact density functional $E_{EDF}$ is equal to:

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

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\cite{footnote} that the chemical potential $\mu = \partial E_{EDF}/\partial N$ is discontinuous when the number of electrons goes through integer value:

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

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

Electron density [Eq. (A1)] can be expressed as a sum of the “orbital densities” $\rho_i(r)$ defined in the following way ($\psi_i(r)$ is $i$-th orbital wave function):

$$\rho(r) = \sum_i \rho_i(r), \quad (4)$$

$$\rho_i(r) \equiv n_i|\psi_i(r)|^2.$$  

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

The condition of linear dependence of the exact density functional on the fractional number of electrons [Eq. (2)] can be expressed via orbital density $\rho_j(r)$ 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 $\rho(r)$ will be defined only by the variation of $\rho_j(r)$ for number of electrons changing from $M$ to $M + 1$

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

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

$$\int d\mathbf{r} \rho_j^{\text{max}}(r) \Lambda_j(r) = E_{EDF}\bigg|_{\rho_j(r)=\rho_j^{\text{max}}(r)} - E_{EDF}\bigg|_{\rho_j(r)=0}. \quad (6)$$
Orbital density $\rho_j(r)$ enters Eq. (5) in a linear form. However LDA functional [Eqs. (A2) and (11)] does not show such a linear dependence on density variations. Equation analogous to Eq. (5) for LDA has a general form (keeping only first and second variational derivatives in expansion series):

$$E_{LDA}[\rho] = E_{LDA}[\rho_0 + \rho_j] \approx E_{LDA}\left|_{\rho_j(r)=0}\right. + \int d\mathbf{r}\rho_j(r) \frac{\delta E_{LDA}}{\delta \rho(r)} \bigg|_{\rho_j(r)=0} + \frac{1}{2} \int d\mathbf{r}\rho_j(r) \int d\mathbf{r}'\rho_j(r') \frac{\delta^2 E_{LDA}}{\delta \rho(r) \delta \rho(r')} \bigg|_{\rho_j(r)=0}. \quad (7)$$

Using Eqs. (A24) and (A26) this expansion can be rewritten via constrain potential $\Phi(r)$ and effective interaction strength function $W(r, r')$:

$$E_{LDA}[\rho] = E_{LDA}[\rho_0 + \rho_j] \approx E_{LDA}\left|_{\rho_j(r)=0}\right. + \int d\mathbf{r}\rho_j(r) \Phi(r) \bigg|_{\rho_j(r)=0} + \frac{1}{2} \int d\mathbf{r}\rho_j(r) \int d\mathbf{r}'\rho_j(r') W(r, r') \bigg|_{\rho_j(r)=0}. \quad (8)$$

If one will add to Eq. (7) a correction term:

$$E_{corr}[\rho_j] \equiv -\frac{1}{2} \int d\mathbf{r}\rho_j(r) \int d\mathbf{r}'(\rho_j(r') - \rho_j^{\text{max}}(r')) W(r, r') \bigg|_{\rho_j(r)=0} \quad (9)$$

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

$$E_{LDA}[\rho_0 + \rho_j] + E_{corr}[\rho_j] \approx E_{LDA}\left|_{\rho_j(r)=0}\right. + \int d\mathbf{r}\rho_j(r) \Phi(r) \bigg|_{\rho_j(r)=0} + \frac{1}{2} \int d\mathbf{r}\rho_j^{\text{max}}(r') W(r, r') \bigg|_{\rho_j(r)=0}. \quad (10)$$

Equation (10) is equivalent to Eq. (5) with the function $\Lambda_j(r)$ equal to:

$$\Lambda_j(r) = \Phi(r) \bigg|_{\rho_j(r)=0} + \frac{1}{2} \int d\mathbf{r}'\rho_j^{\text{max}}(r') W(r, r') \bigg|_{\rho_j(r)=0}. \quad (11)$$

We define the “orbital densities functional” $E_{ODF}$ as:

$$E_{ODF}[\{\rho_i\}] \equiv E_{LDA}[\rho] - \frac{1}{2} \sum_i \int d\mathbf{r}\rho_i(r) \int d\mathbf{r}'(\rho_i(r') - \rho_i^{\text{max}}(r')) W(r, r') \bigg|_{\rho_i(r)=0}. \quad (12)$$

Please note that the ODF functional [Eq. (12)] depends not only on the total charge density $\rho(r)$ that is a sum of orbital densities but also explicitly on a set of orbital densities $\{\rho_i(r)\}$.

Let us investigate the dependence of the functional [Eq. (12)] on the number of electrons $N$. At first please note that for the integer values of $N$ corresponding to the integer orbital
occupancies $n_i$ the value of the functional [Eq. (12)] coincides with the corresponding value of the LDA functional. For integer $n_i$ values orbital density $\rho_i(r)$ is equal either zero for empty state ($n_i = 0$) or $\rho_i^{\text{max}}(r)$ for occupied state ($n_i = 1$). In both cases correction term in Eq. (12) vanishes. We will show that in accordance with the properties of the exact density functional $E_{EDF}$ [Eq. (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 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 $\delta \rho(r)$ of the total charge density $\rho(r)$ will consist exclusively of the variation of corresponding orbital density $\rho_j(r)$ of particular orbital $j$.

Then variational derivative of the functional [Eq. (12)] is equal to:

$$\frac{\delta E_{ODF}}{\delta \rho(r)} = \frac{\delta E_{ODF}}{\delta \rho_j(r)} = \frac{\delta E_{LDA}}{\delta \rho_j(r)} - \int dr' (\rho_j(r') - \frac{1}{2} \rho_j^{\text{max}}(r')) W(r, r') \bigg| _{\rho_j(r) = 0}. \quad (13)$$

The first term in the right part of Eq. (13) $\delta E_{LDA}/\delta \rho(r)$ is continuous. However, the second term depends on the index $j$. When number of electrons $N$ is equal to $M - \omega$ then $j$ 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 $\rho_j(r')$ in the integral in the right part of Eq. (13) will jump from $\rho_j^{\text{max}}(r')$ to zero with $N$ going $M - \omega$ to $M + \omega$ for infinitesimally small $\omega$. That results in the corresponding jump of variational derivative $\delta E_{ODF}/\delta \rho(r)$:

$$\frac{\delta E_{ODF}}{\delta \rho(r)} \bigg| _{M + \omega} - \frac{\delta E_{ODF}}{\delta \rho(r)} \bigg| _{M - \omega} = \frac{1}{2} \int dr' (\rho_j^{\text{max}}(r') W(r, r') \bigg| _{\rho_j(r) = 0} + \rho_j^{\text{max}}(r') W(r, r’) \bigg| _{\rho_j+1(r) = 0}). \quad (14)$$

In order to show that the variational derivative $\delta E_{ODF}/\delta \rho(r)$ is constant for number of electrons varying from $M$ to $M + 1$ we need explicit expression for the variational derivative of LDA functional $\delta E_{LDA}/\delta \rho(r)$. That could be obtained using expansion of Eqs. (7) and (8):

$$\frac{\delta E_{LDA}}{\delta \rho(r)} = \frac{\delta E_{LDA}}{\delta \rho_j(r)} \approx \frac{\delta E_{LDA}}{\delta \rho_j(r)} \bigg| _{\rho_j(r) = 0} + \int dr' \rho_j(r') \frac{\delta^2 E_{LDA}}{\delta \rho(r) \delta \rho(r')} \bigg| _{\rho_j(r) = 0} \quad (15)$$

$$= \Phi(r) \bigg| _{\rho_j(r) = 0} + \int dr' \rho_j(r') W(r, r') \bigg| _{\rho_j(r) = 0}.$$
Then Eq. (13) takes the form:

\[
\frac{\delta E_{ODF}}{\delta \rho(r)} = \frac{\delta E_{ODF}}{\delta \rho_j(r)} \approx \frac{\delta E_{LDA}}{\delta \rho(r)} \bigg|_{\rho_j(r) = 0} + \frac{1}{2} \int dr' \rho_j^{max}(r') \frac{\delta^2 E_{LDA}}{\delta \rho(r) \delta \rho(r')} \bigg|_{\rho_j(r) = 0} \\
= \Phi(r) \bigg|_{\rho_j(r) = 0} + \frac{1}{2} \int dr' \rho_j^{max}(r') W(r, r') \bigg|_{\rho_j(r) = 0}.
\]  

(16)

The right part of Eq. (16) does not depend on \( \rho_j \) and hence it is constant for fractional number of electrons \( n_j \). As derivatives of all terms in LDA functional are continuous the jump of \( \delta E_{ODF}/\delta \rho(r) \) in Eq. (14) can be assigned to the jump in the variational derivative of the effective exchange-correlation energy term in ODF functional \( \delta E_{xc}^{ODF}/\delta \rho(r) \). This term can be derived from ODF functional [Eq. (12)] similarly to the LDA case Eq. (A2).

If orbital \( \psi_i(r) \) is fixed then variation of orbital density \( \rho_i(r) \) occurs only via variation of occupancy \( n_i \):

\[
\delta \rho_i(r) = n_i |\psi_i(r)|^2.
\]  

(17)

Then the second variation of LDA functional is:

\[
\delta^2 E_{LDA} = \frac{1}{2} \sum_{ij} \int dr \delta \rho_i(r) \int dr' \delta \rho_j(r') W(r, r')
\]  

\[
= \frac{1}{2} \sum_{ij} \delta n_i \delta n_j \int dr |\psi_i(r)|^2 \int dr' |\psi_j(r')|^2 W(r, r').
\]  

(18)

The second derivative of LDA functional with respect to the occupancy \( n_i \) is:

\[
\frac{\delta^2 E_{LDA}}{\delta n_i \delta n_j} = \int dr |\psi_i(r)|^2 \int dr' |\psi_j(r')|^2 W(r, r').
\]  

(19)

The value of the derivative \( \delta^2 E_{LDA}/\delta n_i \delta n_j \) could be obtained in constrained LDA calculation either in a direct way or by taking into account that derivative of LDA functional over orbital occupancy \( \delta E_{LDA}/\delta n_i \) is equal to one-electron eigenvalue \( \epsilon_i \) [see Eqs. (A26)-(A31)]:

\[
\frac{\delta^2 E_{LDA}}{\delta n_i \delta n_j} = \frac{\delta \epsilon_i}{\delta n_j}.
\]  

(20)

Using Eqs. (17)-(20) ODF functional [Eq. (12)] could be rewritten via occupancies \( n_i \):

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

(21)

The derivative of ODF functional [Eq. (12)] with respect to the total number of electrons \( N \) can be expressed via occupancies \( n_i \) of partially occupied orbital \( j \):

\[
\frac{\delta E_{ODF}}{\delta N} = \frac{\delta E_{ODF}}{\delta n_j} = \frac{\delta E_{LDA}}{\delta n_j} + \left( \frac{1}{2} - n_j \right) \frac{\delta \epsilon_j}{\delta n_j} = \epsilon_j + \left( \frac{1}{2} - n_j \right) \frac{\delta \epsilon_j}{\delta n_j}.
\]  

(22)
Expanding $\epsilon_j(n_j)$ as a function of $n_j$ and keeping only the first term (which is equivalent to keeping only first and second variational derivatives in Eq. (7)) one can show that derivative $\delta E_{ODF}/\delta N$ does not depend on $n_j$:

$$
\frac{\delta E_{ODF}}{\delta N} \approx \epsilon_j \Big|_{n_j=0} + n_j \frac{\delta \epsilon_j}{\delta n_j} \Big|_{n_j=0} + \left( \frac{1}{2} - n_j \right) \frac{\delta \epsilon_j}{\delta n_j} \Big|_{n_j=0} = \epsilon_j \Big|_{n_j=0} + \frac{1}{2} \frac{\delta \epsilon_j}{\delta n_j} \Big|_{n_j=0}. 
$$

(23)

Analogue of Eq. (14) demonstrates a jump of $\delta E_{ODF}/\delta N$ when number of electrons $N$ is going through an integer value $M$:

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

(24)

We have shown that with the accuracy of expansion of Eq. (7) the variational derivative of the “orbital densities functional” $E_{ODF}$ [Eq. (12)] conforms to the conditions for the exact density functional found in Ref. 11: it is a constant for fractional number of electrons and has a discontinuity when number of electrons is going through an integer value.

Equations (21) and (22) are directly related to “transition state” approach proposed by Slater17 to calculate excitation energies. In this scheme LDA eigenvalue (Kohn-Sham equations eigenvalue) of the corresponding one-electron state should be calculated with its occupancy equal 0.5 (half way between initial and final states of excitation process). One can identify a derivative of the ODF functional [Eq. (21)] over occupancy $n_i$ as a corresponding one-electron energy $\epsilon_{i_{ODF}}$:

$$
\epsilon_{i_{ODF}} \equiv \frac{\delta E_{ODF}}{\delta n_i} = \epsilon_{i_{LDA}} + \left( \frac{1}{2} - n_i \right) \frac{\delta \epsilon_i}{\delta n_i}. 
$$

(25)

If LDA eigenvalue $\epsilon_i(n_i)$ is a linear function of occupancy $n_i$ ($\delta \epsilon_i/\delta n_i = const$) (which is equivalent to expansion Eq. 24) then for an empty state ($n_i = 0$):

$$
\epsilon_{i_{LDA}}(0.5) = \epsilon_{i_{LDA}}(0) + \frac{1}{2} \frac{\delta \epsilon_i}{\delta n_i}. 
$$

(26)

For occupied states ($n_i = 1$) a sign plus in Eq. (26) will be replaced by minus. One can see that Eq. (26) can reproduce both those cases:

$$
\epsilon_{i_{ODF}} = \epsilon_{i_{LDA}}(n_i) + \left( \frac{1}{2} - n_i \right) \frac{\delta \epsilon_i}{\delta n_i} = \epsilon_{i_{LDA}}(0.5). 
$$

(27)

In Ref. 16 we have introduced an auxiliary functional by variation of which Eq. (27) giving “transition state” correction to one-electron energies can be obtained. That functional is identical to the functional [Eq. (21)]. Keeping in mind that we have defined functional
In order to reproduce properties of the exact density functional one can arrive to conclusion that eigenvalues calculated in “transition state” method are a good approximation to the eigenvalues of the exact functional.

The minimization of the functional Eq. (12) will give a set of orbital densities \( \{ \rho_i(r) \} \) and hence the total charge density \( \rho(r) \) corresponding to the ground state of the system. It is useful to derive equations for fluctuations of the orbital densities \( \{ \delta \rho_i(r) \} \) around the average ground state functions \( \{ \rho_i(r) \} \). This “ground state” charge density \( \rho(r) \) corresponds to the minimum of ODF functional [Eq. (12)] but not of the LDA functional so that one must use in the calculations constrain potential \( \Phi(r) \) (see Appendix A Eq. (A25)). Analogous to the expansion Eqs. (7) and (8) one can write for the LDA part of ODF functional:

\[
E_{LDA}[\{ \rho_i + \delta \rho_i \}] \approx E_{LDA}[\{ \rho_i \}] + \frac{1}{2} \sum_i \int d r \delta \rho_i(r) \int d r' \delta \rho_j(r') W(r, r').
\]

For the correction term Eq. (9) the corresponding expression is:

\[
E_{corr}[\{ \rho_i + \delta \rho_i \}] \approx E_{corr}[\{ \rho_i \}] - \frac{1}{2} \sum_i \int d r \delta \rho_i(r) \int d r' \left( \rho_i(r') - \frac{1}{2} \rho_{i, \text{max}}(r') \right) W(r, r')
\]

Both Eqs. (28) and (29) become exact if one supposes that \( \frac{\partial^2 E_{LDA}}{\partial \rho(r) \partial \rho'(r')} = W(r, r') \) does not depend on fluctuations \( \delta \rho_i(r) \) so that 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:

\[
E_{ODF}[\{ \rho_i + \delta \rho_i \}] = E_{ODF}[\{ \rho_i \}] + \frac{1}{2} \sum_i \int d r \delta \rho_i(r) \int d r' \left( \Phi(r) - \int d r' \rho_i(r') - \frac{1}{2} \rho_{i, \text{max}}(r') \right) W(r, r')
\]

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

\[
V_i^{ODF}(r) \equiv \Phi(r) - \int d r' \rho_i(r') - \frac{1}{2} \rho_{i, \text{max}}(r') W(r, r').
\]
Using Eqs. (30) and (31) one can define a Hamiltonian for the density matrix fluctuation operators
\[ \hat{\delta}\hat{\rho}_i(r) \equiv \hat{\rho}_i(r) - \rho_i(r) \] (here ground state orbital density can be considered as an average value of density matrix operator \( \rho_i(r) = \langle \hat{\rho}_i(r) \rangle \):

\[ \hat{H} \equiv \sum_i \int dr \hat{\delta}\rho_i(r) V_i^{ODF}(r) + \frac{1}{2} \sum_i \sum_{j \neq i} \int dr \hat{\delta}\rho_i(r) \int dr' \hat{\delta}\rho_j(r') W(r, r'). \] (32)

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

\[ \hat{\rho}_i(r) = \hat{n}_i |\psi_i(r)|^2. \] (33)

The fluctuation Hamiltonian Eq. (32) can be expressed using Eqs. (17)-(20) via occupancy operators \( \hat{n}_i \) and their average values \( n_i = \langle \hat{n}_i \rangle \) (\( \delta\hat{n}_i \equiv \hat{n}_i - \langle \hat{n}_i \rangle \))

\[ \hat{H} = \sum_i (\epsilon_i + \frac{1}{2} - n_i) \frac{\partial \epsilon_i}{\partial n_i} \delta\hat{n}_i + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{\partial \epsilon_i}{\partial n_j} \delta\hat{n}_i \delta\hat{n}_j. \] (34)

The orbital densities \( \rho_i(r) \) are defined by orbitals \( \psi_i(r) \) in expression for charge density in Eq. (4). In the density functional theory it is usually assumed that those orbitals are solutions of Kohn-Sham equations [Eqs. (A3) and (A15)] and so minimize functional Eq. (A2). However, any unitary transformation (defined by unitary matrix \( U \)) of the set of the functions \( \psi_i(r) \) produces a new set of orbitals:

\[ \tilde{\psi}_i(r) \equiv \sum_j U_{ij} \psi_j(r) \] (35)

corresponding to the same charge density \( \rho(r) \). This new set of orbitals can be used to define ODF functional in Eq. (12) an so this functional is orbital-dependent.

In order to remove uncertainty in choosing the orbital set one needs to impose an additional condition. We propose the following way to do it. The Hamiltonian Eq. (32) can be used to calculate the contribution to the energy from fluctuations:

\[ \langle \hat{H} \rangle = \frac{1}{2} \sum_i \sum_{j \neq i} \int dr \int dr' \langle \hat{\delta}\rho_i(r) \hat{\delta}\rho_j(r') \rangle W(r, r'). \] (36)

(The average value of fluctuations \( \langle \hat{\delta}\rho_i(r) \rangle \) is equal to zero so the first term in Eq. (32) does not give contribution to the fluctuation energy.) Taking into account Eqs. (28) and (29) one
can separate contributions to Eq. (36) from LDA functional where summation over $i$ and $j$ is performed including terms with $i = j$ and a correction term Eq. (29).

The LDA part is:

$$\langle \hat{H}_{LDA} \rangle = \frac{1}{2} \sum_i \sum_j \int \, d\mathbf{r} \int \, d\mathbf{r}' \langle \hat{\delta} \rho_i(\mathbf{r}) \hat{\delta} \rho_j(\mathbf{r}') \rangle W(\mathbf{r}, \mathbf{r}')$$

$$= \frac{1}{2} \int \, d\mathbf{r} \int \, d\mathbf{r}' \langle \sum_i \hat{\delta} \rho_i(\mathbf{r}) \sum_j \hat{\delta} \rho_j(\mathbf{r}') \rangle W(\mathbf{r}, \mathbf{r}')$$

$$= \frac{1}{2} \int \, d\mathbf{r} \int \, d\mathbf{r}' \langle \hat{\delta} \rho(\mathbf{r}) \hat{\delta} \rho(\mathbf{r}') \rangle W(\mathbf{r}, \mathbf{r}') .$$

Correction term gives a negative contribution equal to:

$$\langle \hat{H}_{\text{corr}} \rangle = -\frac{1}{2} \sum_i \int \, d\mathbf{r} \int \, d\mathbf{r}' \langle \hat{\delta} \rho_i(\mathbf{r}) \hat{\delta} \rho_i(\mathbf{r}') \rangle W(\mathbf{r}, \mathbf{r}') .$$

From Eq. (37) one can see that LDA contribution to fluctuation energy is defined by the total charge density fluctuations $\langle \hat{\delta} \rho(\mathbf{r}) \hat{\delta} \rho(\mathbf{r}') \rangle$ and so does not depend on the orbitals definition. Then the minimum of the fluctuation energy Eq. (36) is achieved when the absolute value of correction contribution Eq. (38) has a maximum.

The correction term contribution in Eq. (38) can be calculated using expression of fluctuations Hamiltonian via fluctuation occupancy operators $\hat{\delta} n_i$ [Eq. (34)]:

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

As the average value of square of occupancy fluctuations $\langle \hat{\delta} n_i \hat{\delta} n_i \rangle$ depends on the specific properties of the system, the only way to minimize fluctuation energy $\langle \hat{H} \rangle$ [Eq. (36)] is to maximize $\partial \epsilon_i/\partial n_i$. Using Eqs. (19) and (20) this parameter can be expressed via orbitals as:

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

For new set of the functions $\tilde{\psi}_i(\mathbf{r})$ [Eq. (35)] one has:

$$\frac{\delta \epsilon_i}{\delta n_i} = \sum_{jj'll'} U_{ij} U_{il}^* U_{ij'}^* U_{il'} \int \, d\mathbf{r} \int \, d\mathbf{r}' \psi_j(\mathbf{r}) \psi_{j'}^*(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') \psi_l(\mathbf{r}') \psi_{l'}^*(\mathbf{r}') .$$

Using Eq. (41) and the fact that the derivatives $\delta \epsilon_i/\delta n_i$ are always positive one can define a functional of unitary matrix $U$:

$$F[U] \equiv \sum_i \frac{\delta \epsilon_i}{\delta n_i} = \sum_i \sum_{jj'll'} U_{ij} U_{il}^* U_{ij'}^* U_{il'} \int \, d\mathbf{r} \int \, d\mathbf{r}' \psi_j(\mathbf{r}) \psi_{j'}^*(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') \psi_l(\mathbf{r}') \psi_{l'}^*(\mathbf{r}') .$$
maximization of which one can use as a condition to determine the matrix $U$ and hence the optimal set of orbitals $\psi_i(r)$ to define ODF functional.

The function $W(r, r')$ [Eq. [A24]] is defined as screened effective interaction between density fluctuations $\delta \rho(r), \delta \rho(r')$ and so should decay with increasing of $|r - r'|$ value. Then the more localized in space orbitals $\psi_i(r)$ are, the larger should be the integral Eq. [A10] value. One of possible choices for these orbitals could be Wannier functions. Marzari and Vanderbilt in Ref. 15 proposed the condition of maximum localization to determine the procedure to calculate Wannier functions for multi-band case (two orthonormal sets of functions, Wannier and Bloch, are connected via unitary transformation so Wannier functions can be considered as a particular choice of unitary matrix $U$ in Eq. [35]). The requirement of maximum localization should lead to the reasonably maximized values of parameter $\partial \epsilon_i/\partial n_i$ in Eq. [10] and hence to minimization the fluctuations energy Eq. [36]. Then Wannier functions obtained via procedure proposed in Ref. 15 are a good choice for a set of orbitals to define ODF functional.

In the following we will assume that orbital densities are defined not by one-electron eigenfunctions $\psi_i(r)$ as in Eq. [4] but by Wannier functions $W_n(r)$ and their occupancies $Q_n$ calculated via procedure described in Sec. [11]:

$$\rho(r) = \sum_n \rho_n(r),$$

$$\rho_n(r) = Q_n |W_n(r)|^2.$$  \hspace{1cm} (43)

Using Eqs. [21]-[33] ODF functional [Eq. [12]] could be rewritten with Wannier functions occupancy operators $\hat{Q}_n$ [Eq. [31]] and their average values $Q_n = \langle \hat{Q}_n \rangle$. The corresponding functional will be analogous to Eq. [21] but with occupancies $Q_n$ [Eq. [31]] and energies $E_n$ [Eq. [60]] corresponding to Wannier functions:

$$E_{ODF} = E_{LDA} - \frac{1}{2} \sum_n \frac{\partial E_n}{\partial Q_n} Q_n (Q_n - 1).$$  \hspace{1cm} (44)

The variation of the functional Eq. [44] will produce (see Appendix B) one-electron Hamiltonian $\hat{H}_{ODF}^0$ in the form of projection operator:

$$\hat{H}_{ODF}^0 = \hat{H}_{LDA} + \sum_n \delta V_n \hat{Q}_n = \hat{H}_{LDA} + \sum_{nT} |W_n^T\rangle \delta V_n \langle W_n^T|,$$  \hspace{1cm} (45)

$|W_n^T\rangle$ in Eq. [45] are Wannier functions [Eq. [63]] and $\delta V_n$ are:

$$\delta V_n = \frac{\partial E_n}{\partial Q_n} \left( \frac{1}{2} - Q_n \right).$$  \hspace{1cm} (46)
The values of derivatives $\partial E_n/\partial Q_n$ should be determined in constrained LDA calculations (see Sec. III).

Equations (44)-(46) are identical to the equations of “generalized transition state” (GTS) method that we have developed in Ref. 16. The basis of GTS method was an idea that one-electron energies corresponding to Wannier functions should have a meaning of the removal (addition) energies for electrons from (to) the corresponding states. That was realized by using “transition state” scheme\(^\text{17}\) generalized to Wannier functions instead of eigenfunctions. It is remarkable that the same equations can be obtained by introducing correction to the LDA functional restoring the properties of the exact density functional theory.\(^\text{11}\)

The potential correction operator \([\text{Eqs. (45) and (46)}]\) shifts the energies of Wannier functions on $\delta V_n$ 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 gives valence bands pushed down and conduction bands pushed up comparing with standard LDA results increasing energy separation between them (energy gap value) which is systematically underestimated in LDA. It was shown in Ref. 16 that calculations with potential correction \([\text{Eqs. (45) and (46)}]\) result in a much better agreement with experimental energy gap values for semiconductor (Si), band insulator (MgO), Mott insulator (NiO), and Peierls insulator BaBiO$_3$.

The Hamiltonian $\hat{H}_{ODF}^0$ \([\text{Eq. (45)}]\) can be considered as a static mean-field approximation to a general problem. Wannier functions analogue of the fluctuation Hamiltonian Eq. \([\text{45}]\) is:

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

(47)

The first and second parts of Hamiltonian Eq. \([\text{47}]\) are not (!) noninteracting Hamiltonian and interaction term as it is usually defined in model Hubbard and Anderson Hamiltonians. The first part $\hat{H}_{ODF}^0$ is equivalent to the Hartree-Fock approximation Hamiltonian determined by the average values of Wannier functions occupancies $\langle \hat{Q}_n \rangle$ and the second part describes interaction between fluctuations around $\langle \hat{Q}_n \rangle$. As these average values are determined from the solution of the full Hamiltonian Eq. \([\text{47}]\), that defines a self-consistent calculation scheme. In contrast to LDA+$U$\(^\text{8,9}\) and LDA+DMFT\(^\text{18}\) methods there is no “double counting” problem in this Hamiltonian because there were no “merging” of LDA and Hubbard model concepts here and both terms in Eq. \([\text{47}]\) were derived from the same functional Eq. \([\text{44}]\).
The problem defined by the Hamiltonian Eq. (47) 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 (DMFT)\textsuperscript{12,13,14} (see Sec. V).

III. DEFINITION AND CONSTRUCTION OF WANNIER FUNCTIONS

The orbital projection calculation scheme for Wannier functions (WFs) used in the present work was described in details in the earlier paper\textsuperscript{19} where the LDA+DMFT (DMFT – dynamical mean-field theory) method in the Wannier function basis set was proposed. Below we present the main formulas of this scheme.

The concept of WFs has a very important place in the electron theory in solids since its first introduction in 1937 by Wannier.\textsuperscript{20} WFs are the Fourier transformation of Bloch states $|\psi_{ik}\rangle$.

$$|W^T_i\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-ikT} |\psi_{ik}\rangle,$$

(48)

where $N$ is the number of discrete $k$ points in the first Brillouin zone (or, the number of cells in the crystal) and $T$ is lattice translation vector.

Wannier functions are not uniquely defined for a many-band case because for a certain set of bands any orthogonal linear combination of Bloch functions $|\psi_{ik}\rangle$ can be used in Eq. (48). In general it means the freedom to choose the of unitary transformation matrix $U_{ji}^{(k)}$ for Bloch functions: \textsuperscript{15}

$$|\tilde{\psi}_{ik}\rangle = \sum_j U_{ji}^{(k)} |\psi_{jk}\rangle.$$

(49)

There is no rigorous way to define $U_{ji}^{(k)}$. This calls for an additional restriction on the properties of WFs. Among others, Marzari and Vanderbilt\textsuperscript{15} used the condition of maximum localization for WFs, resulting in a variational procedure to calculate $U_{ji}^{(k)}$. To get a good initial guess the authors of Ref. 15 proposed choosing a set of localized trial orbitals $|\phi_n\rangle$ and projecting them onto the Bloch functions $|\psi_{ik}\rangle$. It was found that this starting guess is usually quite good. This fact later led to the simplified calculating scheme in Ref. 21 where the variational procedure was abandoned and the result of the aforementioned projection was considered as the final step.
For the projection procedure used in the present work one needs to identify the set of bands and corresponding set of localized trial orbitals \( |\phi_n\rangle \). The choice of bands and orbitals is determined by the physics of the system under consideration.

The set of bands can be defined either by the band indices of the corresponding Bloch functions \( (N_1, ..., N_2) \), or by choosing the energy interval \( (E_1, E_2) \) in which the bands are located. Nonorthogonalized WFs in reciprocal space \( \tilde{W}_{nk} \) are then the projection of the set of site-centered atomiclike trial orbitals \( |\phi_n\rangle \) on the Bloch functions \( |\psi_{ik}\rangle \) of the chosen bands defined by band indices \( (N_1 \text{ to } N_2) \) or by energy interval \( (E_1, E_2) \):

\[
|\tilde{W}_{nk}\rangle \equiv \sum_{i=N_1}^{N_2} |\psi_{ik}\rangle \langle \psi_{ik}|\phi_n\rangle = \sum_{i(E_1 \leq \varepsilon_i(k) \leq E_2)} |\psi_{ik}\rangle \langle \psi_{ik}|\phi_n\rangle. \tag{50}
\]

In the present work we have used LMTO method\textsuperscript{22} to solve a band structure problem and the trial orbitals \( |\phi_n\rangle \) were LMTOs. The coefficients \( \langle \psi_{ik}|\phi_n\rangle \) in Eq. \textsuperscript{50} define (after orthonormalization) the unitary transformation matrix \( U^{(k)}_{ji} \) in Eq. \textsuperscript{19}.

In any DFT method the Kohn-Sham orbitals are expanded through the certain basis:

\[
|\psi_{ik}\rangle = \sum_{\mu} c_{\mu i}^{k} |\phi_{\mu}^{k}\rangle. \tag{51}
\]

The basis functions of the LMTO method are Bloch sums of the site-centered orbitals:

\[
\phi_{\mu}^{k}(r) = \frac{1}{\sqrt{N}} \sum_{T} e^{i k T} \phi_{\mu}(r - R_q - T), \tag{52}
\]

where \( \mu \) is the combined index representing \( qlm \) (\( q \) is the atomic number index in the unit cell, \( lm \) are orbital and magnetic quantum numbers), \( R_q \) is the position of atom in the unit cell.

For the orthogonal LMTO basis \( c_{\mu i}^{k} = \langle \phi_{\mu}|\psi_{ik}\rangle \) and hence

\[
|\tilde{W}_{nk}\rangle = \sum_{i=N_1}^{N_2} |\psi_{ik}\rangle c_{\mu i}^{k*} = \sum_{i=N_1}^{N_2} \sum_{\mu} c_{\mu i}^{k} c_{\mu i}^{k*} |\phi_{\mu}^{k}\rangle = \sum_{\mu} \tilde{b}_{\mu i}^{k} |\phi_{\mu}^{k}\rangle, \tag{53}
\]

with

\[
\tilde{b}_{\mu i}^{k} \equiv \sum_{i=N_1}^{N_2} c_{\mu i}^{k} c_{\mu i}^{k*}. \tag{54}
\]

For a nonorthogonal basis set orthogonalization of the Hamiltonian must be done before using Eq. \textsuperscript{54}.

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In order to orthonormalize the WFs [Eq. (53)] one needs to calculate the overlap matrix

\[ O_{nn'}(k) \equiv \langle \tilde{W}_{n'k} | \tilde{W}_{nk} \rangle = \sum_{i=N_1}^{N_2} c^k_{ni} c^{k*}_{n'i}, \quad (55) \]

and its inverse square root \( S_{nn'}(k) \)

\[ S_{nn'}(k) \equiv O^{-1/2}_{nn'}(k). \quad (56) \]

From Eqs. (53) and (56) the orthonormalized WFs in \( k \) space \( |W_{nk}⟩ \) can be obtained as

\[ |W_{nk}⟩ = \sum_{n'} S_{nn'}(k) |\tilde{W}_{n'k}⟩ = \sum_{n'} \sum_{i=N_1}^{N_2} |ψ_{ik}⟩ c^k_{ni} c^{k*}_{n'i}, \quad (57) \]

with

\[ c^k_{ni} \equiv ⟨ψ_{ik} | W_{nk}⟩ = \sum_{n'} S_{nn'}(k) c_{n'i}, \quad (58) \]

\[ b^k_{\mu n} \equiv ⟨ϕ_{\mu k} | W_{nk}⟩ = \sum_{i=N_1}^{N_2} c^k_{\mu i} c^{k*}_{ni}. \quad (59) \]

Using Eqs. (57)-(59) one can find energies of WFs:

\[ E_n = \langle W^T_n | \hat{H} | W^T_n \rangle = \langle W^T_n | \left( \sum_{i,k} |ψ_{ik}⟩ \epsilon_i(k) ⟨ψ_{ik}| \right) |W^T_n \rangle \]

\[ = \frac{1}{N} \sum_{k} \sum_{i=N_1}^{N_2} c^k_{ni} c^{k*}_{n'i} \epsilon_i(k) \quad \text{(60)} \]

and their occupancies:

\[ Q_n = \langle W^T_n | \left( \sum_{i,k} |ψ_{ik}⟩ \theta(E_f - \epsilon_i(k))⟩ ⟨ψ_{ik}| \right) |W^T_n \rangle \]

\[ = \frac{1}{N} \sum_{k} \sum_{i=N_1}^{N_2} c^k_{ni} c^{k*}_{n'i} \theta(E_f - \epsilon_i(k)), \quad \text{(61)} \]

where \( \epsilon_i(k) \) is the eigenvalue for a particular band, \( \theta(x) \) is the step function, \( E_f \) is the Fermi energy.

The transformation from LMTO to the WF basis set is defined by the explicit form of WFs Eqs. (57) and (59), and by the expressions for matrix elements of the Hamiltonian.
and density matrix operators in WF basis [Eqs. (60) and (61)]. The transformation from WF to LMTO basis can also be defined using Eq. (57). Such transformation is necessary in calculations using ODF correction potential in the form of projection operator Eq. (45). It will also be used for constrained LDA calculations needed to determine the values of WFs energy derivatives with respect to their occupancies $\partial E_n / \partial Q_n'$ which define potential correction parameters $\delta V_n$ in Eqs. (45) and (46) and effective Coulomb parameters $U_{nn'}$ in ODF fluctuation Hamiltonian in the Hubbard form Eqs. (76)-(78). For example if constrain potential operator is diagonal in WF basis ($H_{nn'}^{\text{constr}} = \Lambda_n \delta_{nn'}$), then in LMTO basis its matrix elements can be calculated via:

$$\hat{H}_{nn'}^{\text{constr}} = \sum_{n,T} |W_n^T\rangle \Lambda_n \langle W_n^T|,$$

$$|W_n^T\rangle = \sum_{j,k} e^{-i k T^j} b_k^j |\phi_k^j\rangle,$$

$$H_{\mu\nu}^{\text{constr}}(k) = \langle \phi_k^\mu | \hat{H}_{nn'}^{\text{constr}} | \phi_k^\nu \rangle = \sum_n b_k^\mu \Lambda_n b_k^\nu*.$$

IV. WANNIER FUNCTIONS IN THE GREEN-FUNCTION FORMALISM

In many-body theory the system is usually described not by Bloch functions $|\psi_ik\rangle$ [Eq. (51)] and their energies $\epsilon_i(k)$ but by the Green function

$$G(r, r', \epsilon) = \frac{1}{N} \sum_k G_k(r, r', \epsilon) = \frac{1}{N} \sum_k \sum_{\mu\nu} \phi_k^\mu(r) G_{\mu\nu}(\epsilon) \phi_k^\nu(r').$$

The matrix Green function $G_{\mu\nu}(\epsilon)$ is defined via the noninteracting Hamiltonian matrix $H_{0\mu\nu}(k)$ [Eq. (78) and (81)] and the matrix self-energy $\Sigma_{\mu\nu}(\epsilon)$ [Eq. (82)] as

$$G_{\mu\nu}(\epsilon) = [\epsilon - \hat{H}_0(k) - \hat{\Sigma}(\epsilon, k) + i\eta]_{\mu\nu}^{-1}.$$

We define the nonorthonormalized WF obtained by projecting the trial orbital $\phi_n(r)$ on the Hilbert subspace determined by the Green function [Eq. (65)] in the energy interval $(E_1, E_2)$, namely,

$$\tilde{W}_{nk}(r) = -\frac{1}{\pi} \text{Im} \int_{E_1}^{E_2} d\epsilon \int dr' G_k(r, r', \epsilon) \phi_n(r') = \sum_{\mu} b_k^\mu \phi_n^\mu(r).$$
and

\[ \tilde{b}_{\mu n}^k \equiv -\frac{1}{\pi} \text{Im} \int_{E_1}^{E_2} d\varepsilon G_{\mu n}^k (\varepsilon). \]  

(68)

In the noninteracting case, the self-energy \( \hat{\Sigma}(\varepsilon, \mathbf{k}) \) is absent and hence we have

\[ G_{\mu \nu}^k (\varepsilon) = \sum_i \frac{c_{\mu i}^k c_{\nu i}^k}{\varepsilon - \varepsilon_i (\mathbf{k}) + i\eta}, \]

(69)

where \( c_{\mu i}^k \) are the eigenvectors, and \( \varepsilon_i (\mathbf{k}) \) are the eigenvalues of \( \hat{H}^0 (\mathbf{k}) \). Thus \( \tilde{b}_{\mu n}^k \) in Eq. (68) becomes

\[ \tilde{b}_{\mu n}^k = N_2 \sum_{i=N_1}^{N_2} c_{\mu i}^k c_{\nu i}^k, \]

(70)

where \( N_1, N_2 \) are the band numbers corresponding to the energy interval \( (E_1, E_2) \). Since this recovers the result of Eq. (54), we demonstrated that our general definition of WFs [Eq. (67)] via Green function reduces to that in terms of Bloch functions [Eq. (53)] in Sec. III.

To orthonormalize \( \tilde{W}_{nk} (\mathbf{r}) \) defined in Eq. (67), one can just follow the orthonormalizing procedure made in Sec. III [Eqs. (55)-(59)] with the overlap matrix \( O_{nn'} (k) \) is defined as

\[ O_{nn'} (T) = \frac{1}{N} \sum_{k} \sum_{\mu \nu} b_{\mu n}^k b_{\nu n'}^* G_{\mu \nu}^k (\varepsilon) e^{-i k T}. \]

(71)

By using Eq. (65) and orthogonalized Wannier functions [Eq. (67)], one finds

\[ Q_{nn'} (T) = \frac{1}{N} \sum_{k} \sum_{\mu \nu} b_{\mu n}^k b_{\nu n'}^* Q_{\mu \nu}^k e^{-i k T}, \]

(72)

with

\[ Q_{\mu \nu}^k = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_f} d\varepsilon G_{\mu \nu}^k (\varepsilon). \]

(73)

The energy matrix can be defined similarly (except that the integral over energy is calculated in the \( (E_1, E_2) \) interval where the corresponding WFs are determined) as

\[ E_{nn'} (T) = \frac{1}{N} \sum_{k} \sum_{\mu \nu} b_{\mu n}^k b_{\nu n'}^* E_{\mu \nu}^k e^{-i k T}, \]

(74)

where

\[ E_{\mu \nu}^k = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_f} d\varepsilon G_{\mu \nu}^k (\varepsilon). \]
with
\[ E_{\mu\nu}^k = -\frac{1}{\pi} \text{Im} \int_{E_1}^{E_2} \varepsilon d\varepsilon G_{\mu\nu}^k(\varepsilon). \] (75)

V. DMFT FOR ODF FLUCTUATION HAMILTONIAN

The DMFT\textsuperscript{12,13,14} was recently found to be a powerful tool to numerically solve multiband Hubbard models. In order to use this tool the fluctuation Hamiltonian [Eq. (47)] should be rewritten in the form of standard multi-orbital Hubbard model. For that one needs to identify Coulomb parameters \( U_{nn'} \) as derivatives \( \partial E_n / \partial Q_{n'} \) and rearrange terms in Eq. (47) into noninteracting and interaction parts:

\[ \hat{H}_{ODF} = \hat{H}^0 + \hat{H}_{int} \] (76)

with interaction term:

\[ \hat{H}_{int} = \frac{1}{2} \sum_n \sum_{n' \neq n} U_{nn'} \hat{Q}_n \hat{Q}_{n'} \] (77)

and noninteracting Hamiltonian:

\[ \hat{H}^0 = \hat{H}_{ODF}^0 + \frac{1}{2} \sum_n \sum_{n' \neq n} U_{nn'} \langle \hat{Q}_n \rangle \langle \hat{Q}_{n'} \rangle - \sum_n \hat{Q}_n \sum_{n' \neq n} U_{nn'} \langle \hat{Q}_{n'} \rangle. \] (78)

In DMFT the lattice problem becomes an effective single-site problem which has to be solved self-consistently for the matrix self energy \( \hat{\Sigma} \) and the local matrix Green function in Wannier functions basis set:

\[ G_{nn'}(\varepsilon) = \frac{1}{V_{BZ}} \int d\mathbf{k} \left( \left( \varepsilon - \mu \right) \hat{1} - \hat{H}^0(\mathbf{k}) - \hat{\Sigma}(\varepsilon) \right)^{-1}_{nn'}, \] (79)

where \( \mu \) is a chemical potential, \( \hat{H}^0 \) is noninteracting Hamiltonian [Eq. (78)] and \( \hat{\Sigma}(\varepsilon) \) is self-energy in Wannier functions basis:

\[ \hat{\Sigma}(\varepsilon) = \sum_{nn'} |W_n\rangle \Sigma_{nn'}(\varepsilon) \langle W_{n'}|. \] (80)

The DMFT single-site problem may be viewed as a self-consistent single-impurity Anderson model.\textsuperscript{14} The corresponding local one-particle matrix Green function \( \hat{G} \) can be written as a functional integral\textsuperscript{14} involving an action where the Hamiltonian of the correlation problem
under investigation, including the interaction term with the Hubbard interaction, enters.\[^{18}\]

The action depends on the bath matrix Green function \(\mathcal{G}\) through

\[
(\mathcal{G})^{-1} = (\hat{G})^{-1} + \hat{\Sigma}.
\] (81)

To solve the functional integral of the effective single-impurity Anderson problem, several 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 Ref. [18].)

In the present work the QMC method was used to solve the impurity problem.

VI. SELF-CONSISTENCY

The matrix self-energy \(\mathcal{\Sigma}(\varepsilon)\) obtained as a solution of DMFT is defined in the WF basis set [Eq. (80)]. In order to compute the interacting Green function in the full-orbital Hilbert space [Eqs. (65) and (66)] one has to transform self-energy to the LMTO basis set. This can be easily done by using the linear-expansion form of the WFs in terms of the LMTO basis set [Eqs. (57) and (59)],

\[
\mathcal{\Sigma}_{\mu\nu}^k(\varepsilon) \equiv \langle \phi_{\mu}^k | \mathcal{\Sigma}(\varepsilon) | \phi_{\nu}^k \rangle = \sum_{nn'} \langle \phi_{\mu}^k | W_{nk} \rangle \Sigma_{nn'}(\varepsilon) \langle W_{n'k} | \phi_{\nu}^k \rangle = \sum_{nn'} b_{\mu n}^k \Sigma_{nn'}(\varepsilon) b_{\nu n'}^k. \] (82)

The matrix elements of the self-energy \(\mathcal{\Sigma}_{\mu\nu}^k(\varepsilon)\) [Eq. (82)] together with the noninteracting Hamiltonian matrix \(H^0_{\mu\nu}(k)\) [Eqs. (78) and (64)] allow one to calculate the matrix Green function \(G_{\mu\nu}^k(\varepsilon)\) [Eq. (66)] and thus the interacting Green function \(G(r, r', \varepsilon)\) [Eq. (65)]. \(G(r, r', \varepsilon)\) contains the full information about the system, and various electronic, magnetic, and spectral properties can be obtained from it.

One can also calculate the charge-density distribution modified by correlation effects via

\[
\rho(r) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_f} d\varepsilon G(r, r, \varepsilon). \] (83)

With this \(\rho(r)\) one can recalculate the LDA potential which is a functional of electron density [Eq. (A7)]. From the Green function [Eq. (65)] one can recalculate new WFs [Eqs. (67) and (68)] which together with the new LDA Hamiltonian allows one to obtain new parameters for the noninteracting Hamiltonian [Eqs. (64) and (78)]. With the new set of Wannier functions one performs a series of constrain LDA calculation to determine derivatives \(\partial E_n / \partial Q_n\).
and hence define a new Coulomb interaction parameters $U_{nn'}$ in the interaction Hamiltonian [Eq. (77)]. The set of new LDA potential, WFs, and Coulomb interaction parameters calculated from the interacting Green function [Eq. (65)] defines the input for the next iteration step and hence closes the self-consistency loop in the computation scheme. For the feedback from DMFT to LDA in the particular case of the LMTO method\textsuperscript{22} one needs a set of moments for the partial densities of states $M_{ql}^{(p)}$ for every atomic sphere $q$ and the orbital moment $l$ (Ref. 23) in order to calculate the new charge density and hence the new LDA potential:

$$
M_{ql}^{(p)} = \int_{-\infty}^{E_f} d\varepsilon \varepsilon^p N_{ql}(\varepsilon), \quad (84)
$$

$$
N_{ql}(\varepsilon) = -\frac{1}{\pi N} \text{Im} \sum_k \sum_m G^k_{qlm,qlm}(\varepsilon).
$$

The orbital densities functional computational scheme described above is \textit{ab initio} (does not contain any outside parameters) and fully self-consistent. The charge density $\rho(r)$, Wannier functions $W_n(r)$, and derivatives $\partial E_n/\partial Q_{n'}$ (effective fluctuations interaction strength) are recalculated on every self-consistency loop and hence modified by correlations comparing with the values obtained in standard LDA calculations. Analogous calculation scheme was proposed in Fig. 1 in Ref. 19.

In the present work ODF method was applied to the problem of metal-insulator transition in nonstoichiometric lanthanum trihydride LaH$_{3-x}$, where both parts of the calculation scheme, static mean-field approximation [Eqs. 44]-[46] and fluctuation Hamiltonian [Eq. (47)] in DMFT (Sec. V) were needed to describe experimentally observed dependence of the system ground state on the hydrogen deficiency parameter $x$.

**VII. ELECTRONIC STRUCTURE OF NONSTOICHIOMETRIC LANTHANUM TRIHYDRIDE**

Lanthanum trihydride LaH$_{3-x}$ shows an interesting metal-insulator transition with increasing of $x$ value\textsuperscript{24} While stoichiometric LaH$_3$ is an insulator, 30% hydrogen deficiency ($x \approx 0.3$) results in a metallic ground state. However, standard LDA calculations\textsuperscript{25} give a metal as a ground state even for stoichiometric composition LaH$_3$. In this case well-known problem of LDA, underestimation of the energy gap value, is so severe that the gap value is negative with valence and conduction bands overlapping on 0.25 eV (see Fig. 1).
The lanthanum trihydride has a crystal structure derived from the face-centered cubic structure (lattice parameter \(a = 10.5946\) a.u.) for La atoms and hydrogen atoms occupying two tetrahedral and one octahedral interstitials per every metallic ion. The band structure of LaH\(_3\) (Fig. 1) is relatively simple: 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, the GW method\(^{26}\) (the energy gap \(E_g=0.8-0.9\) eV), the weighted local density approach\(^{27}\) (\(E_g=0.7\) eV), and model calculations\(^{28}\).

The orbital densities functional (ODF) theory [Eq. (44)] proposed in the present work adds to standard Kohn-Sham equations potential correction in the form of projection operator [Eqs. (45) and (46)]. This correction is negative for occupied valence bands and positive for empty conduction bands and hence increases energy separation between those bands. ODF calculations for LaH\(_3\) results in insulating ground state with a fundamental gap value of 1.10 eV and direct optical gap 1.25 eV at G-point (see Fig. 2). Experimental data for the value of energy gap \(E_g=0.5\) eV was estimated using activation energy determined from resistivity measurements in Ref. 29. Optical measurements estimate the direct gap \(E_g\) as 1.87 eV but the fundamental band gap \(\sim 1\) eV lower\(^{30}\).

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

Both LDA and ODF calculations gave metallic ground state for two compositions \(x=0.25\) and \(x=0.5\). Every hydrogen vacancy leads to appearance of one vacancy state in the gap split from the conduction band with one electron occupying this state (see Fig. 3(a)). Static mean-field ODF potential correction [Eqs. (45) and (46)] results in separation of the vacancy band from the conduction band and in increasing of energy gap between valence and conduction bands comparing with LDA but half-filled vacancy band stays metallic (see Figs. 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 ODF fluctuation Hamiltonian [Eq. (47)] and have solved it using DMFT-QMC (see Sec. V). Inverse temperature parameter was \(\beta=10\) eV\(^{-1}\). In the result we have obtained in agreement with experiment paramagnetic insulator ground state for LaH\(_{2.75}\) with a typical Mott insulator pattern of lower and upper Hubbard bands around chemical potential with the energy gap of 0.1 eV (see Fig. 5(b)). However, for LaH\(_{2.5}\)
a width of the vacancy band is significantly larger than for LaH\textsubscript{2.75} (see Figs. 3(b) and 4(b)) and DMFT calculations resulted in well defined metallic state (see Fig. 5(a)).

VIII. CONCLUSION

We have proposed orbital densities functional that by construction has discontinuous exchange-correlation potential in agreement with exact density functional theory. The one-electron potential obtained by variation of this functional produces comparing with LDA lower energies for valence bands and higher energies for conduction bands thus overcoming systematic underestimation of energy gap value in LDA. To treat correlation effects we have derived from orbital densities functional the Hamiltonian corresponding to the fluctuations of orbital densities around the ground state values. Combining this Hamiltonian with dynamical mean-filed theory and quantum Monte Carlo method for effective impurity problem we have developed \textit{ab initio} and fully self-consistent scheme for electronic structure calculations. The scheme was applied to the problem of metal-insulator transition in LaH\textsubscript{3−x} and gave a qualitative improvement for agreement with experimental data.

IX. ACKNOWLEDGMENTS

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APPENDIX A: CONSTRAIN LDA FUNCTIONAL AND ITS DERIVATIVES

LDA functional $E_{LDA}[\rho]$ depends on the electron density $\rho(\mathbf{r})$ defined by one-electron functions $\psi_i(\mathbf{r})$ and their occupancies $n_i$:

$$\rho(\mathbf{r}) = \sum_i n_i |\psi_i(\mathbf{r})|^2,$$  \hfill (A1)
\[ E_{LDA}[\rho] = T[\rho] + \frac{1}{2} \int dr \int dr' \frac{\rho(r)\rho(r')}{|r-r'|} \]
\[ + \int dr V_Z(r)\rho(r) + E_{xc}[\rho], \]  
where \( V_Z(r) \) is external potential, \( E_{xc}[\rho] \) is exchange-correlation energy functional [see Eq. (1)] and \( T[\rho] \) is kinetic energy term.

Kinetic energy is a functional of electron density \( T[\rho] \) via single particle orbitals \( \psi_i(r) \) which are functionals of density themselves. To prove that the following reasoning can be used\(^3\) Hohenberg-Kohn theorem\(^2\) states that external potential is uniquely defined by the ground state electron density of the system. That is also true for a noninteracting system with potential \( V_S[\rho](r) \). This potential defines a Schrödinger equation for the orbitals \( \psi_i(r) \):
\[ (-\nabla^2 + V_S[\rho](r))\psi_i(r) = \epsilon_i \psi_i(r). \]

As potential \( V_S[\rho](r) \) is a functional of density then solutions of the Eq. (A3) are also functionals of density:
\[ \psi_i(r) = \psi_i[\rho](r). \]

Kinetic energy is defined by a set of orbitals \( \psi_i[\rho](r) \) and hence it is also a functional of density:
\[ T[\rho] = \sum_i n_i \int dr \psi_i^*[\rho](r)(-\nabla^2)\psi_i[\rho](r). \]

Minimization of the functional Eq. (A2) gives:
\[ \frac{\delta E_{LDA}[\rho]}{\delta \rho(r)} = \frac{\delta T[\rho]}{\delta \rho(r)} + V_{LDA}(r) = 0 \]

where one-electron LDA potential is:
\[ V_{LDA}(r) = \int dr' \frac{\rho(r')}{|r-r'|} + V_Z(r) + V_{xc}(r) \]

\( (V_{xc}(r) = \delta E_{xc}[\rho]/\delta \rho(r) \) is exchange-correlation potential).

Variation of kinetic energy functional is:
\[ \delta T[\rho] = \delta \left( \sum_i n_i \int dr \psi_i^*[\rho](r)(-\nabla^2)\psi_i[\rho](r) \right) \]
\[ = \delta \left( \sum_i n_i \int dr \psi_i^*[\rho](r)(\epsilon_i[\rho] - V_S[\rho](r))\psi_i[\rho](r) \right) \]
\[ = \delta \left( \sum_i n_i \epsilon_i[\rho] - \int dr V_S[\rho](r)\rho(r) \right). \]
First order perturbation theory for one-electron energies $\epsilon_i[\rho]$ gives:

$$\delta \epsilon_i[\rho] = \int d\mathbf{r} \psi_i^*[\rho](\mathbf{r})(\delta V_S[\rho](\mathbf{r}))\psi_i[\rho](\mathbf{r}) \tag{A9}$$

Then Eq. (A8) is:

$$\delta T[\rho] = -\int d\mathbf{r}' V_S[\rho](\mathbf{r})\delta \rho(\mathbf{r}) \tag{A10}$$

and variational derivative of kinetic energy functional is:

$$\frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} = -V_S[\rho](\mathbf{r}). \tag{A11}$$

The minimization condition [Eq. (A6)] becomes:

$$\frac{\delta E_{LDA}[\rho]}{\delta \rho(\mathbf{r})} = -V_S[\rho](\mathbf{r}) + V_{LDA}(\mathbf{r}) = 0. \tag{A12}$$

A set of Kohn-Sham equations (A3) with $V_S[\rho](\mathbf{r}) = V_{LDA}(\mathbf{r})$ defines one-electron orbitals $\psi_i[\rho](\mathbf{r})$ and hence a new electron density $\rho(\mathbf{r})$ via Eq. (A1). The problem should be solved self-consistently till electron density used to calculate $V_{LDA}(\mathbf{r})$ will coincide with the density obtained using Kohn-Sham equations solutions $\psi_i[\rho](\mathbf{r})$.

In order to define functional [Eq. (A2)] for charge density $\tilde{\rho}(\mathbf{r})$ different from the density minimizing $E_{LDA}[\rho]$ one needs to introduce constrain potential $\Phi(\mathbf{r})$ and minimize auxiliary functional:

$$F[\rho] = E_{LDA}[\rho] + \int d\mathbf{r} \Phi(\mathbf{r})(\rho(\mathbf{r}) - \tilde{\rho}(\mathbf{r})), \tag{A13}$$

$$\frac{\delta F}{\delta \rho(\mathbf{r})} = \frac{\delta E_{LDA}}{\delta \rho(\mathbf{r})} + \Phi(\mathbf{r}) = -V_S[\rho](\mathbf{r}) + V_{LDA}(\mathbf{r}) + \Phi(\mathbf{r}) = 0. \tag{A14}$$

Then potential in Kohn-Sham equations (A3) is:

$$V_S[\rho](\mathbf{r}) = V_{LDA}(\mathbf{r}) + \Phi(\mathbf{r}). \tag{A15}$$

The second variational derivative of LDA functional is:

$$\frac{\delta^2 E_{LDA}[\rho]}{\delta \rho(\mathbf{r})\delta \rho(\mathbf{r}')} = \frac{\delta}{\delta \rho(\mathbf{r}')}(-V_S[\rho](\mathbf{r}) + V_{LDA}(\mathbf{r})) = \frac{\delta V_{LDA}(\mathbf{r})}{\delta \rho(\mathbf{r}')} - \frac{\delta V_S[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}')} . \tag{A16}$$

The variational derivative of LDA potential [Eq. (A7)] is obtained in a straightforward way:

$$\frac{\delta V_{LDA}(\mathbf{r})}{\delta \rho(\mathbf{r}')} = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \delta(\mathbf{r} - \mathbf{r}') \frac{\delta V_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}')} . \tag{A17}$$
The second term in Eq. (A16), \( \delta V_S[\rho](r)/\delta \rho(r') \) is more complicated. Let us first solve an inverse problem – to calculate response function:

\[
\chi(r, r') \equiv \frac{\delta \rho(r)}{\delta V_S(r')}. \tag{A18}
\]

First-order perturbation theory for eigenfunctions and eigenvalues of Kohn-Sham equations (A3) gives:

\[
\frac{\delta \psi_i(r)}{\delta V_S(r')} = \sum_{j \neq i} \psi_j(r) \frac{\psi_j^*(r') \psi_i(r')}{\epsilon_i - \epsilon_j}, \tag{A19}
\]

\[
\frac{\delta \epsilon_i}{\delta V_S(r')} = \psi_i^*(r') \psi_i(r'). \tag{A20}
\]

Then response function in Eq. (A18) is:

\[
\chi(r, r') \equiv \frac{\delta \rho(r)}{\delta V_S(r')} = \sum_i n_i \sum_{j \neq i} \psi_j(r) \frac{\psi_j^*(r) \psi_j^*(r') \psi_i(r')}{\epsilon_i - \epsilon_j} + c.c. \tag{A21}
\]

The second term in Eq. (A16) is defined by the inverse response function:

\[
\frac{\delta V_S(r)}{\delta \rho(r')} = \chi^{-1}(r, r'). \tag{A22}
\]

This inverse response function can be obtained solving integral equation:

\[
\int dr'' \chi(r, r'')\chi^{-1}(r'', r') = \delta(r - r'). \tag{A23}
\]

Then the second variational derivative of LDA functional is:

\[
\frac{\delta^2 E_{LDA}}{\delta \rho(r) \delta \rho(r')} = \frac{1}{|r - r'|} + \delta(r - r') \frac{\delta V_{xc}(r)}{\delta \rho(r')} - \chi^{-1}(r, r') \equiv W(r, r'), \tag{A24}
\]

\( W(r, r') \) can be interpreted as an effective interaction strength between density fluctuations \( \delta \rho(r), \delta \rho(r') \) in LDA functional. The first variational derivative of the LDA functional can be obtained from Eq. (A14):

\[
\frac{\delta E_{LDA}}{\delta \rho(r)} = -\Phi[\rho](r), \tag{A25}
\]

where \( \Phi[\rho](r) \) is constrain potential needed to obtain electron density \( \rho(r) \) in self-consistent solution of Kohn-Sham equations [Eqs. (A3) and (A15)].

Let us consider variation of the LDA functional Eq. (A2) in respect to the occupancies \( n_i \) and orbitals \( \psi_i(r) \) defining electron density \( \rho(r) \) in Eq. (A1):

\[
\delta E_{LDA} = \sum_i \left( \delta n_i \frac{\delta E_{LDA}}{\delta n_i} + \int dr \delta \psi_i(r) \frac{\delta E_{LDA}}{\delta \psi_i(r)} \right), \tag{A26}
\]
\[
\frac{\delta E_{\text{LDA}}}{\delta n_i} = \frac{\delta T}{\delta n_i} + \int d\mathbf{r} \frac{\delta (E_{\text{LDA}} - T)}{\delta \rho(\mathbf{r})} \frac{\delta \rho(\mathbf{r})}{\delta n_i}
\]
\[
= \int d\mathbf{r} \psi_i^*(\mathbf{r})(-\nabla^2)\psi_i(\mathbf{r}) + \int d\mathbf{r} \psi_i^*(\mathbf{r})V_{\text{LDA}}(\mathbf{r})\psi_i(\mathbf{r})
\]
\[
= \int d\mathbf{r} \psi_i^*(\mathbf{r})(-\nabla^2 + V_{\text{LDA}}(\mathbf{r}))\psi_i(\mathbf{r}) = \epsilon_i.
\]

\[
\frac{\delta E_{\text{LDA}}}{\delta \psi_i(\mathbf{r})} = n_i(-\nabla^2)\psi_i^*(\mathbf{r}) + n_i V_{\text{LDA}}(\mathbf{r})\psi_i^*(\mathbf{r})
\]
\[
= n_i(-\nabla^2 + V_{\text{LDA}}(\mathbf{r}))\psi_i^*(\mathbf{r}) = n_i \epsilon_i \psi_i^*(\mathbf{r}),
\]

\[
\delta E_{\text{LDA}} = \sum_i \left( \delta n_i \epsilon_i + n_i \epsilon_i \int d\mathbf{r} \delta \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}) \right).
\]

As orbitals are normalized:

\[
\int d\mathbf{r} \delta \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}) = \delta \left( \int d\mathbf{r} \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}) - 1 \right) = 0
\]
and from Eq. (A29) it follows that:

\[
\frac{\delta E_{\text{LDA}}}{\delta \psi_i} = \epsilon_i.
\]

All this was proven to be valid for the LDA eigenfunctions \( \psi_i(\mathbf{r}) \) which are solutions of Kohn-Sham equations [Eq. (A3)]. Let us prove that the derivative of LDA functional over the Wannier function occupancy \( Q_n \) [Eq. (61)] is equal to the energy \( E_n \) [Eq. (60)] of this WF.

The charge density expressed via Wannier functions \( W_n(\mathbf{r}) \) [Eq. (57)] and its occupancies \( Q_n \) is:

\[
\rho(\mathbf{r}) = \sum_T \sum_n Q_n W_n(\mathbf{r} - \mathbf{T})^2.
\]

Then derivative over Wannier function occupancy \( Q_n \) (with fixed functions \( W_n(\mathbf{r}) \)) can be calculated using Eq. (A27):

\[
\frac{\delta E_{\text{LDA}}}{\delta Q_n} = \int d\mathbf{r} W_n^*(\mathbf{r})(-\nabla^2 + V(\mathbf{r}))W_n(\mathbf{r}) = \int d\mathbf{r} W_n^*(\mathbf{r})\hat{H}_{\text{LDA}}W_n(\mathbf{r}) = E_n.
\]
APPENDIX B: PROJECTION OPERATOR IN ODF FUNCTIONAL

In ODF functional Eq. (44) Wannier functions occupancies $Q_n$ [Eq. (61)] can be expressed via projection operator $\hat{Q}_n$:

$$Q_n = \sum_i \langle \psi_i | \hat{Q}_n | \psi_i \rangle,$$  \hspace{1cm} (B1)

$$\hat{Q}_n = |W_n^T \rangle \langle W_n^T|$$

(summation $\sum_i$ is over occupied states only in all equations below). The variational derivative of occupancy $Q_n$ with respect to the one-electron wave function $\delta \psi_i (r)$ is:

$$\frac{\delta Q_n}{\delta \psi_i (r)} = \hat{Q}_n \psi_i^* (r).$$  \hspace{1cm} (B2)

Then variation of the correction term in ODF functional Eq. (44) will give the following correction to the corresponding expression for LDA functional [see Eq. (A28)]:

$$\frac{\delta E_{ODF}}{\delta \psi_i (r)} = \frac{\delta E_{LDA}}{\delta \psi_i (r)} - \sum_n \frac{\partial E_n}{\partial Q_n} (Q_n - \frac{1}{2}) \frac{\delta Q_n}{\delta \psi_i (r)}$$

$$= (-\nabla^2 + V_{LDA} (r)) \psi_i^* (r) + \sum_n \frac{\partial E_n}{\partial Q_n} (\frac{1}{2} - Q_n) \hat{Q}_n \psi_i^* (r)$$

$$= (-\nabla^2 + V_{LDA} (r) + \sum_n \delta V_n \hat{Q}_n) \psi_i^* (r).$$

This proves Eqs. (45) and (46) for ODF correction to LDA Hamiltonian.

APPENDIX C: TOTAL ENERGY IN LDA AND ODF FUNCTIONALS

Kinetic energy term in Eq. (A2) can be calculated using Eq. (A3):

$$(-\nabla^2) \psi_i (r) = (\epsilon_i - V_{LDA} (r)) \psi_i (r).$$  \hspace{1cm} (C1)

Multiplying Eq. (C1) by $\psi_i^* (r)$, integrating over $r$ and summing over occupied states $i$ one can obtain:

$$\sum_i \int d\mathbf{r} \psi_i^* (\mathbf{r}) (-\nabla^2) \psi_i (\mathbf{r}) = \sum_i \epsilon_i - \int d\mathbf{r} V_{LDA} (\mathbf{r}) \rho (\mathbf{r}).$$  \hspace{1cm} (C2)

Then total energy in Eq. (A2) is equal to:

$$E_{LDA} = \sum_i \epsilon_i - \int d\mathbf{r} V_{LDA} (\mathbf{r}) \rho (\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho (\mathbf{r}) \rho (\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$+ \int d\mathbf{r} V_Z (\mathbf{r}) \rho (\mathbf{r}) + \int d\mathbf{r} \varepsilon_{xc} (\rho (\mathbf{r})) \rho (\mathbf{r}).$$  \hspace{1cm} (C3)
Using Eq. (A7) for LDA potential $V(r)$ the final expression for total energy is:

$$E_{LDA} = \sum_i \epsilon_i - \frac{1}{2} \int dr \int dr' \frac{\rho(r)\rho(r')}{|r-r'|} + \int dr (\varepsilon_{xc}(\rho(r)) - V_{xc}(\rho(r)))\rho(r). \quad (C4)$$

In the case of ODF functional [Eq. (44)] there will be an additional term in expression for kinetic energy [Eq. (C2)] due to the ODF potential correction [Eq. (B3)]:

$$-\sum_i \int dr \psi_i^*(r)(\sum_n \delta V_n Q_n)\psi_i(r) = -\sum_n \delta V_n Q_n. \quad (C5)$$

The additional terms to total energy expression Eq. (C4) are

$$E_{ODF} = \tilde{E}_{LDA} - \sum_n \delta V_n Q_n - \frac{1}{2} \sum_n \frac{\partial E_n}{\partial Q_n} Q_n(Q_n - 1) \quad (C6)$$

$$\quad \quad = \tilde{E}_{LDA} + \frac{1}{2} \sum_n \frac{\partial E_n}{\partial Q_n} (Q_n)^2.$$  

Here $\tilde{E}_{LDA}$ is defined as right part of Eq. (C4). $\tilde{E}_{LDA}$ differs from $E_{LDA}$ because it is taken for $\rho(r)$ which does not minimize $E_{LDA}$.

1. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
2. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
3. F. Gygi and G. Galli, Mater. Today 8, 26 (2005).
4. R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989).
5. W. E. Pickett, Rev. Mod. Phys. 61, 433 (1989).
6. L. Hedin, Phys. Rev. 139, A796 (1965).
7. J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
8. V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991).
9. V. I. Anisimov, F. Aryasetiawan, and A. Lichtenstein, J. Phys.: Condens. Matter 9, 767 (1997).
10. A. D. Becke, Phys. Rev. A 38, 3098 (1988); J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13 244 (1992); J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
11. J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. 49, 1691 (1982).
12. D. Vollhardt, in Correlated Electron Systems, edited by V. J. Emery (World Scientific, Singapore, 1993), p. 57.
13. Th. Pruschke, M. Jarrell, and J. K. Freericks, Adv. in Phys. 44, 187 (1995).
A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).

N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997); N. Marzari, I. Souza, and D. Vanderbilt, Psi-k Newsletter 57, 112 (2003) [psi-k.dl.ac.uk/newsletters/News_57/Highlight_57.pdf].

V. I. Anisimov and A. V. Kozhevnikov, Phys. Rev. B 72, 071525 (2005).

J. C. Slater, Quantum Theory of Molecules and Solids (McGraw-Hill, New York, 1974), Vol. IV.

K. Held, I. A. Nekrasov, N. Blümer, V. I. Anisimov, and D. Vollhardt, Int. J. Mod. Phys. B 15, 2611 (2001); K. Held, I. A. Nekrasov, G. Keller, V. Eyert, N. Blümer, A. K. McMan- 

h, R. T. Scalettar, T. Pruschke, V. I. Anisimov, and D. Vollhardt, in Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms, edited by J. Grotendorst, D. Marks, and A. Muramatsu, NIC Series No. 10 (NIC Directors, Forschunszentrum Jülich, 2002), pp. 175-209; K. Held, I. A. Nekrasov, G. Keller, V. Eyert, N. Blümer, A. K. McMa-

han, R. T. Scalettar, Th. Pruschke, V. I. Anisimov, and D. Vollhardt, Psi-k Newsletter 56, 65 (2003) [psi-k.dl.ac.uk/newsletters/News_56/Highlight_56.pdf]; A. I. Lichtenstein, M. I. Katsnelson, and G. Kotliar, in Electron Correlations and Materials Properties, 2nd ed., edited by A. Gonis, N. Kiovoss, and M. Ciftan (Kluwer Academic/Plenum, New York, 2002), p. 428.

V. I. Anisimov, D. E. Kondakov, A. V. Kozhevnikov, I. A. Nekrasov, Z. V. Pchelkina, 

J. W. Allen, S.-K. Mo, H.-D. Kim, P. Metcalf, S. Suga, A. Sekiyama, G. Keller, I. Leonov, 

X. Ren, and D. Vollhardt, Phys. Rev. B 71, 125119 (2005).

G. H. Wannier, Phys. Rev. 52, 191 (1937).

Wei Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, Phys. Rev. Lett. 89, 167204 (2002).

O. K. Andersen, Phys. Rev. B 12, 3060 (1975); O. Gunnarsson, O. Jepsen, and O. K. Andersen, 

ibid. 27, 7144 (1983).

H. L. Skriver, The LMTO Method, Springer Series on Solid State Science, No. 41 (Springer, 

New York, 1984).

J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, 

and N. J. Koeman, Nature (London) 380, 231 (1996).

J. P. Dekker, J. van Ek, A. Lodder, and J. N. Huiberts, J. Phys.: Condens. Matter 5, 4805 (1993); Y. Wang and M. Y. Chou, Phys. Rev. Lett. 71, 1226 (1993); M. Gupta and J. P. Burger, 

Phys. Rev. B 22, 6074 (1980).

J. A. Alford, M. Y. Chou, E. K. Chang, and S. G. Louie, Phys. Rev. B 67, 125110 (2003); 

E. K. Chang, X. Blase, and S. G. Louie, ibid. 64, 155108 (2003).
27 Zhigang Wu, R. E. Cohen, D. J. Singh, R. Gupta, and M. Gupta, Phys. Rev. B 69, 085104 (2004).

28 K. K. Ng, F. C. Zhang, V. I. Anisimov, and T. M. Rice, Phys. Rev. Lett. 78, 1311 (1997); Phys. Rev. B 59, 5398 (1997).

29 J. Shinar, B. Dehner, R. G. Barnes, and B. J. Beaudry, Phys. Rev. Lett. 64, 563 (1990); J. Peterman, J. H. Weaver, and D. T. Peterson, Phys. Rev. B 23, 3903 (1981).

30 A. T. M. van Gogh, D. G. Nagengast, E. S. Kooij, N. J. Koeman, J. H. Rector, R. Griessen, C. F. J. Flipse, and R. J. J. G. A. M. Smeets, Phys. Rev. B 63, 195105 (2001).

31 T. Grabo, T. Kreibich, S. Kurth, and E. K. U. Gross, in Strong Coulomb Correlations in Electronic Structure Calculations, edited by V. I. Anisimov (Gordon and Breach Science Publishers, Amsterdam, 2000), pp. 203-305.

32 A. Görling and M. Levy, Phys. Rev. A 50, 196 (1994).
FIG. 1: LaH$_3$ band structure and density of states calculated in standard LDA.

FIG. 2: LaH$_3$ band structure and density of states calculated in orbital densities functional (ODF) theory [Eq. (44)]. Zero of energy is at the Fermi energy.
FIG. 3: LaH$_{2.75}$ density of states calculated (a) in standard LDA and (b) in orbital densities functional (ODF) theory [Eq. (44)].

FIG. 4: LaH$_{2.5}$ density of states calculated (a) in standard LDA and (b) in orbital densities functional (ODF) theory [Eq. (44)].
FIG. 5: (a) LaH$_{2.5}$ and (b) LaH$_{2.75}$ densities of states calculated with ODF fluctuation Hamiltonian [Eq. (47)] in DMFT-QMC.