Transition state method and Wannier functions

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We propose a computational scheme for materials where standard Local Density Approximation (LDA) fails to produce a satisfactory description of excitation energies. The method uses Slater's "transition state" approximation and Wannier functions basis set. We define a correction to LDA functional in such a way that its variation produces one-electron energies for Wannier functions equal to the energies obtained in "transition state" constrained LDA calculations. In the result eigenvalues of the proposed functional could be interpreted as excitation energies of the system under consideration. The method was applied to MgO, Si, NiO and BaBiO$_3$ and gave an improved agreement with experimental data of energy gap values comparing with LDA.

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I. INTRODUCTION

The one-electron eigenvalues in LDA calculations are Kohn-Sham energies that were defined as auxiliary Lagrange multipliers in the problem of Density Functional minimization. As such they formally cannot be used to calculate spectral properties of the system because they do not directly correspond to excitation energies. However for the cases where electron states are itinerant, for example wide band metals, excitation spectra calculated with LDA eigenvalues were found to be in good agreement with experimental photoemission and optical spectra. The agreement is much worse for band insulators and semiconductors where LDA gives systematically underestimated values of the energy gap. For Mott insulators, for example transition-metal oxides, LDA calculated spectra could be qualitatively wrong, giving metallic state while experimentally those systems are wide gap insulators.

There were many attempts to cure this deficiency of LDA. Among the most widely used methods one can mention GW, SIC and LDA+U. 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 of better methods continues in scientific community.

The basic problem of a Density Functional Theory (DFT) (and consequently of the LDA as one of its approximations) is that DFT was designed to reproduce a ground state properties of a system. In order to obtain excitation energy in the spirit of DFT one must calculate total energy of the system in the excited state. Then its difference from the ground state total energy corresponds to excitation energy. The excited state can be calculated minimizing LDA functional with the constraining condition that occupancy of specific one-electron state differs from its occupancy in the ground state. Such "constrained LDA" calculations indeed could give good results for excitation energies.

Slater had shown that a good approximation for excitation energy can be one-electron energy for the specific one-electron state calculated in a so called "transition state", where its occupancy is equal 0.5 being half way between the values for the final and initial state of the excitation process. Transition state calculations indeed gave excitation energies for free atoms and ions in a good agreement with experimental data.

However this approach can not be directly applied to extended systems such as solids with translation symmetry where one-electron states are Bloch functions extended over infinite crystals. The change of their occupancies produces infinitesimal change of electron density and so constrained LDA calculations for "transition state" give exactly the same one-electron energy values as in a ground state.

A full set of Bloch functions can be replaced by the equivalent set of Wannier functions produced by some unitary transformation (see Eqs. (1) and (2)). In contrast to Bloch states Wannier functions are localized in a specific space area. If one choose Wannier functions as one-electron states in "transition state" constrained LDA calculations then there will be a significant change in the charge density comparing with a ground state and hence a corresponding correction to the excitation energy.

The idea of our "generalized transition state method" developed in the present work is to use "transition state" approximation to define a modified functional in such a way that Wannier functions one-electron energies calculated with this functional would have a meaning of excitation energies for electrons on the corresponding Wannier function states. This is achieved by adding to LDA functional a correction changing Wannier functions energies from LDA values to those obtained in the "transition state" calculations.

The main effect of "transition state" calculations comparing with standard LDA is lower one-electron energy values for the occupied states and higher values for the unoccupied states due to the decreased occupancy of the former and increased one for the latter. Then application of the correction should enhance energy separation between occupied...
and empty bands and hence give an increased value for the energy gap thus improving agreement with the experimental data.

To test our method we chose a band insulator MgO, semiconductor Si, Mott insulator NiO and Peierls insulator BaBiO₃. In all those systems LDA gave strongly underestimated energy gap values. Calculations by “generalized transition state method” resulted in band structure for all those materials being in a good agreement with experimental spectroscopy data.

The paper is structured as follows. In Sec. III we give the details of our calculation scheme. In Sec. IV the results for the electronic structure of MgO, Si, NiO and BaBiO₃ obtained by the method developed in this work are presented and compared with the standard LDA calculations and experimental data. Finally in Sec. V we close this work with a conclusion.

II. METHOD

The orbital projection calculation scheme for Wannier functions (WF’s) used in the present work was described in details in the earlier paper where the LDA+DMFT (DMFT - Dynamical Mean-Field Theory) method in Wannier function basis set was proposed. Below we present the main formulas of this scheme.

A. Definition and construction of Wannier functions

The concept of WF’s has a very important place in the electron theory in solids since its first introduction in 1937 by Wannier. WF’s are the Fourier transformation of Bloch states $|\psi_{i\mathbf{k}}\rangle$

$$|W_i^T\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{kT}}|\psi_{i\mathbf{k}}\rangle,$$

where $N$ is the number of discrete $\mathbf{k}$ points in the first Brillouin zone (or, the number of cells in the crystal) and $\mathbf{T}$ 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 $|\psi_{i\mathbf{k}}\rangle$ can be used in Eq. (1). In general it means that the freedom of choice of Wannier functions corresponds to freedom of choice of a unitary transformation matrix $U_{ji}^{(k)}$ for Bloch functions $|\psi_{i\mathbf{k}}\rangle$.

$$|\tilde{\psi}_{i\mathbf{k}}\rangle = \sum_j U_{ji}^{(k)}|\psi_{j\mathbf{k}}\rangle.$$

There is no rigorous way to define $U_{ji}^{(k)}$. This calls for an additional restriction on the properties of WF’s. Among others Marzari and Vanderbilt used the condition of maximum localization for WF’s, resulting in a variational procedure to calculate $U_{ji}^{(k)}$. To get a good initial guess the authors proposed choosing a set of localized trial orbitals $|\phi_n\rangle$ and projecting them onto the Bloch functions $|\psi_{i\mathbf{k}}\rangle$. It was found that this starting guess is usually quite good. This fact later led to the simplified calculating scheme 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 and will be discussed later.

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. Non-orthogonalized WF’s in reciprocal space $|\tilde{\psi}_{i\mathbf{k}}\rangle$ are then projection of the set of site-centered atomiclike trial orbitals $|\phi_n\rangle$ on Bloch functions $|\psi_{i\mathbf{k}}\rangle$ of the chosen bands defined by band indices ($N_1$ to $N_2$) or by energy interval ($E_1, E_2$):

$$|\tilde{W}_{n\mathbf{k}}\rangle \equiv \sum_{i=N_1}^{N_2} |\psi_{i\mathbf{k}}\rangle \langle \psi_{i\mathbf{k}} | \phi_n\rangle = \sum_{(E_1 \leq \epsilon_i(k) \leq E_2)} |\psi_{i\mathbf{k}}\rangle \langle \psi_{i\mathbf{k}} | \phi_n\rangle.$$

In the present work we have used LMTO method to solve a band structure problem and the trial orbitals $|\phi_n\rangle$ were LMTO’s. Note that in the multi-band case a WF in reciprocal space $|\tilde{W}_{n\mathbf{k}}\rangle$ does not coincide with the eigenfunction $|\psi_{i\mathbf{k}}\rangle$ due to the summation over band index $i$ in Eq. (3). One can consider them as Bloch sums of WF’s analogous to
the basis function Bloch sums $\phi_{\mu}^{k}(r)$ (Eq. 5). The coefficients $\langle \psi_{ik}|\phi_{n}\rangle$ in Eq. 3 define (after orthonormalization) the unitary transformation matrix $U_{ij}^{(k)}$ in Eq. 2.

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

$$|\psi_{ik}\rangle = \sum_{\mu} c_{\mu i}^{k} |\phi_{\mu}^{k}\rangle.$$ (4)

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

$$\phi_{\mu}^{k}(r) = \frac{1}{\sqrt{N}} \sum_{T} e^{i k T} \phi_{\mu}(r - R_{q} - T),$$ (5)

where $\mu$ is the combined index representing $qlm$ ($q$ is the atomic number 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

$$\tilde{W}_{nk} = \sum_{i=N_{1}}^{N_{2}} |\psi_{ik}\rangle c_{ni}^{k*} = \sum_{i=N_{1}}^{N_{2}} \sum_{\mu} c_{\mu i n}^{k} c_{ni}^{k*} = \sum_{\mu} \tilde{b}_{\mu n}^{k} |\phi_{\mu}^{k}\rangle,$$ (6)

with

$$\tilde{b}_{\mu n}^{k} \equiv \sum_{i=N_{1}}^{N_{2}} c_{\mu i n} c_{ni}^{k*}.$$ (7)

For a nonorthogonal basis set orthogonalization of the Hamiltonian must be done before using Eq. 4.

In order to orthonormalize the WF’s Eq. 3 one needs to calculate the overlap matrix $O_{nn'}(k)$

$$O_{nn'}(k) \equiv \langle \tilde{W}_{nk}|\tilde{W}_{n'k}\rangle = \sum_{i=N_{1}}^{N_{2}} \tilde{c}_{ni}^{k} \tilde{c}_{n'i}^{k*},$$ (8)

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

$$S_{nn'}(k) \equiv O_{nn'}^{-1/2}(k).$$ (9)

In the derivation of Eq. 8 the orthogonality of Bloch states $\langle \psi_{nk}|\psi_{n'k}\rangle = \delta_{nn'}$ was used.

From Eqs. 4 and 9 the orthonormalized WF’s in $k$ space $|W_{nk}\rangle$ can be obtained as

$$|W_{nk}\rangle = \sum_{n'} S_{nn'}(k) |\tilde{W}_{n'k}\rangle = \sum_{i=N_{1}}^{N_{2}} |\psi_{ik}\rangle \tilde{c}_{ni}^{k*} = \sum_{\mu} \tilde{b}_{\mu n}^{k} |\phi_{\mu}^{k}\rangle,$$ (10)

with

$$\tilde{c}_{ni}^{k*} \equiv \langle \psi_{ik}|W_{nk}\rangle = \sum_{n'} S_{nn'}(k) \tilde{c}_{n'i}^{k*},$$ (11)

$$\tilde{b}_{\mu n}^{k} \equiv \langle \phi_{\mu}^{k}|W_{nk}\rangle = \sum_{i=N_{1}}^{N_{2}} \tilde{c}_{\mu i n}^{k} \tilde{c}_{ni}^{k*}.$$ (12)

The real space site-centered WF’s at the origin $|W_{n}^{0}\rangle$ are given by the Fourier transform of $|W_{nk}\rangle$ (Eq. 11) with $T = 0$. From Eqs. 11 and 12 one finds

$$W_{n}(r) = \frac{1}{\sqrt{N}} \sum_{k} \langle r|W_{nk}\rangle = \sum_{T,\mu} \left( \frac{1}{N} \sum_{k} e^{i k T_{j} k} \tilde{b}_{\mu n}^{k} \right) \phi_{\mu}(r - T)$$

$$= \sum_{T,\mu} w'(n, \mu, T) \phi_{\mu}(r - T)$$

$$= \sum_{s} w(n, s) \phi_{\alpha(s)}(r - T_{s}),$$ (13)
where \( w' \) and \( w \) are the expansion coefficients of WF in terms of the corresponding LMTO orbitals, in particular,

\[
w(n, s) = \frac{1}{N} \sum_k e^{i k T_s b_k^{\alpha(s)n}}.
\]

Here \( s \) is an index counting the orbitals of the neighboring cluster for the atom where orbital \( n \) is centered (\( T_s \) is the corresponding translation vector, \( \alpha(s) \) is a combined qlm index). The explicit form of the real space WF Eq. (13) can be used to produce, e.g., shapes of chemical bonds. For other applications only the matrix elements of the various operators in the basis of WF Eq. (10) are needed.

Using Eqs. (10), (11), and (12) one can find energies of WF’s:

\[
E_{n}^{WF} = \langle W_n^T | \left( \sum_{i,k} |\psi_{ik}\rangle \epsilon_i(k) \langle \psi_{ik}| \right) W_n^T \rangle
\]

\[
= \frac{1}{N} \sum_k N_2 \sum_{i=N_1}^{N_2} c_{ni}^k c_{n'i}^k \epsilon_i(k)
\]

and their occupancies:

\[
Q_{n}^{WF} = \langle W_n^T | \left( \sum_{i,k} |\psi_{ik}\rangle \theta(E_f - \epsilon_i(k)) \langle \psi_{ik}| \right) W_n^T \rangle
\]

\[
= \frac{1}{N} \sum_k N_2 \sum_{i=N_1}^{N_2} c_{ni}^k c_{n'i}^k \epsilon_i(k)
\]

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 WF basis set is defined by the explicit form of WF’s Eqs. (10), (12), and by the expressions for matrix elements of the Hamiltonian and density matrix operators in WF basis (Eqs. (15) and (16)). The transformation from WF to LMTO basis can also be defined using Eq. (10). Such transformation is needed in calculations using correction potential in the form of Eq. (25) and for constrained LDA calculations determining "transition state" energies of WF’s. For example if constrain potential is diagonal in WF basis \( (H_{nn'} = \Lambda_n \delta_{nn'}) \), then in LMTO basis its matrix elements can be calculated via:

\[
\hat{H}_{constr} = \sum_{n,T} |W_n^T \rangle \Lambda_n \langle W_n^T |
\]

\[
|W_n^T \rangle = \sum_{j,k} e^{-i k T_j b_k^{j}} |\phi_j^k\rangle
\]

\[
H_{\mu\nu}(k) = \langle \phi_\mu^k | \hat{H}_{constr} | \phi_\nu^k \rangle
\]

B. “Generalized transition state” method

Transition state calculation scheme proposed by Slater allows to calculate excitation energy for the process of adding (removing) an electron to (from) the system from (to) the infinity where potential is supposed to be equal zero. For that one should calculate LDA eigenvalue (Kohn-Sham equations eigenvalue) of the corresponding one-electron state with its occupancy equal 0.5. In other words for the occupied states the occupancy is reduced by one half and for the empty ones it is increased by one half.

This scheme can be derived in the following way. The total energy difference between final and initial states for the process of electron addition to the one-electron state \( j \) can be calculated as an integral of total energy derivative
over occupancy \( q_j \) (this derivative is\(^2\) the corresponding LDA eigenvalue \( \epsilon_j = \frac{\partial E}{\partial q_j} \)):

\[
E(q_j = 1) - E(q_j = 0) = \int_0^1 dq_j \left( \frac{\partial E}{\partial q_j} \right) = \int_0^1 dq_j \epsilon_j(q_j) \approx \epsilon_j(0.5)
\]

It means that the one-electron energy (LDA functional eigenvalue) calculated with its occupancy value half way between final and initial states is a good approximation for the total energy difference (excitation energy). This equation becomes exact if LDA eigenvalue \( \epsilon_j(q_j) \) is a linear function of occupancy \( q_j \) \((\frac{\partial \epsilon_j(q_j)}{\partial q_j} = \text{const})\), which is usually with a good accuracy true. In this case for empty state \( (q_j = 0) \):

\[
\epsilon_j(0.5) = \epsilon_j(0) + \frac{1}{2} \frac{\partial \epsilon_j(q_j)}{\partial q_j}
\]

For occupied states \( (q_j = 1) \) a sign plus in Eq. (21) will be replaced by minus. The general formula will be:

\[
\epsilon_j(0.5) = \epsilon_j(q_j) + \frac{1}{2} (1 - q_j) \frac{\partial \epsilon_j(q_j)}{\partial q_j}
\]

So effect of ”transition state” correction to LDA values is to increase energy for empty states (addition energy) and to decrease it for the occupied states (removal energy). That will also results in a larger value of energy for the excitation from occupied to empty states of the system.

Transition state method can be reformulated in a functional formalism. For that equation \((22)\) should be obtained via variation of an auxiliary functional. This ”transition state” functional \( E_{TS} \) is defined by adding to LDA functional \( E_{LDA}[\rho] \) the correction term depending on the occupancies \( q_j \):

\[
E_{TS} = E_{LDA}[\rho] - \frac{1}{2} \sum_j \frac{\partial \epsilon_j(q_j)}{\partial q_j} (q_j - \frac{1}{2})^2
\]

All eigenvalues obtained from this functional will automatically have a correction \((\frac{1}{2} - q_j) \frac{\partial \epsilon_j(q_j)}{\partial q_j}\) to LDA eigenvalues like in the right part of Eq. \((22)\). Then one calculation for the ground state of the functional \( E_{TS} \) gives result equivalent to a set of ”transition state” calculations for every one-electron state. However one still needs to run a set of constrained LDA calculations in order to determine derivatives \( \frac{\partial \epsilon_j(q_j)}{\partial q_j} \).

The ”transition state” method to calculate excitation energies has proved to be sufficiently successful for small size systems like atoms and ions\(^8\) but it can not be directly applied to solids. Bloch functions are extended over the crystal and a change of their occupancy will have a negligible effect on the charge density. In this case ”transition state” calculations will give the same one-electron energies as the ground state results.

For a case of fully occupied bands transformation from a set of Bloch states to Wannier functions does not change charge density distribution. It is more than that, many-electron functions defined as a Slater determinant constructed from one-electron Bloch functions is identical to the Slater determinant made out of Wannier functions. (The determinant value is not changed in the result of adding to one of its rows a linear combination of other rows and Wannier functions are by definition linear combinations of Bloch functions (see Eqs. \((11)\) and \((22)\)). Then ground state properties are invariant to such transformation.

However for excited states there is an important difference between Bloch and WF representations. As WF is localized, a change of its occupancy will result in a finite charge density modification in the area of its localization and hence ”transition state” calculations will result in a significant correction for the WF one-electron energy. While in standard LDA one-electron energies are Kohn-Sham energies that were defined as auxiliary Lagrange multipliers and hence ”transition state” calculations will result in a significant correction for the WF one-electron energy. While in standard LDA one-electron energies are Kohn-Sham energies that were defined as auxiliary Lagrange multipliers in the problem of minimizing Density Functional\(^3\). WF energies obtained in ”transition state” calculations have a meaning of excitation energies for an electron on the corresponding WF states.

The idea of our ”generalized transition state” method (GTS) is to replace in the original formulation of ”transition state” method (Eqs. \((20),(22)\)) a set of one-electron states in a form of Bloch functions for an infinite crystal by an equivalent set of Wannier functions. The corresponding functional will be analogous to Eq. \((22)\) but with occupancies \( Q_n^{WF} \) (Eq. \((10)\)) and energies \( E_n^{WF} \) (Eq. \((16)\)) corresponding to Wannier functions:

\[
E_{GTS} = E_{LDA} - \frac{1}{2} \sum_n \frac{\partial E_n^{WF}}{\partial Q_n^{WF}} (Q_n^{WF} - \frac{1}{2})^2
\]
The variation of the correction term in \((24)\) will produce a correction Hamiltonian \(\hat{H}_{\text{corr}}\) in the form of projection operator:

\[
\hat{H}_{\text{corr}} = \sum_{nT} |W_{nT}^T\rangle \delta V_{nT} \langle W_{nT}^T|.
\]

Then Hamiltonian operator for "generalized transition state" method is given by:

\[
\hat{H}_{\text{GTS}} = \hat{H}_{\text{LDA}} + \hat{H}_{\text{corr}}.
\]

\(|W_{nT}^T\rangle\) in Eq. \((25)\) are Wannier functions (Eq. \((18)\)) and \(\delta V_{nT}\) are defined as a difference between Wannier functions one-electron energies calculated in "transition state" and ground state (see Eq. \((22)\)):

\[
\delta V_{nT} = \frac{\partial E_{nW}^W}{\partial Q_{nW}} \left( \frac{1}{2} - Q_{nW} \right)
\]

The values of derivatives \(\frac{\partial E_{nW}^W}{\partial Q_{nW}}\) (or equivalently \(\delta V_{nT}\) themselves) should be determined in constrained LDA calculations.

The calculation scheme is the following (see Fig. 1). To define correction operator (Eq. \((25)\)) one needs to know a set of "transition state" corrections to WF’s energy values \(\delta V_{nT}\) (Eq. \((27)\)) and explicit form of WF’s determined by expansion coefficients in the basis orbitals (LMTO) \(b_k^{n}\) (Eq. \((12)\)). Both \(\delta V_{nT}\) and \(b_k^{n}\) should be calculated self-consistently. On every self-consistency loop Bloch functions \(|\psi_{nk}\rangle\) calculated with "generalized transition state" method Hamiltonian \(\hat{H}_{\text{GTS}}\) (Eq. \((26)\)) are used to define new Wannier functions \(|W_{nk}^n\rangle\) via Eq. \((3)\) to get a new set of coefficients \(b_k^{n}\). Then a series of constrained LDA calculations (using constrain potential in the form of Eq. \((17)\)) for every type of WF \(|W_{nk}^n\rangle\) (Eq. \((13)\)) is performed where the occupancy (Eq. \((16)\)) of this particular WF is kept to be 0.5. The energy of this WF’s is then calculated using Eq. \((15)\). The new \(\delta V_{nT}\) is defined as a difference between this "transition state" value and the corresponding value from calculation where the WF occupancy is the same as in ground state.

The important question is what set of bands and trial orbitals should be used in projection procedure (Eq. \((3)\)) to calculate WF’s. In band insulators and semiconductors valence band corresponds to bonding states and conduction band to antibonding ones. So if one will calculate WF’s via projection procedure separately for valence and conduction bands (summation over band indices in Eq. \((3)\) is running over occupied bands only for valence WF’s and over empty bands for conduction states WF’s) then the results will be bonding and antibonding functions extending over neighboring atoms. But if WF’s will be obtained using a full set of valence and conduction bands (summation over band indices in Eq. \((3)\) is running over combined set of occupied and empty bands both for valence and conduction states WF’s), then the opposite sign contributions on neighboring atoms from bonding and antibonding functions cancel each other and the resulting WF resembles an original atomic orbital.

For spectral properties where excitation occurs from (to) valence (conduction) states WF should represent the corresponding bonding (antibonding) functions. Then the most natural choice would be to use in projection procedure (Eq. \((3)\)) two separate sets of occupied and empty bands and two sets of atomic-like orbitals that give a strongest contribution to the corresponding bands. For example in MgO case the orbitals for occupied bands would be oxygen 2p and for empty bands Mg 3s and 3p orbitals. The application of the correction operator (Eq. \((25)\)) will shift relative energies of the bands but will not change significantly wave functions themselves. They will remain the same as were obtained in LDA calculations. Then charge and spin electron density will be not modified by GTS correction.

This approximation could be satisfactory for semiconductors and band insulators where the only problem of LDA is underestimation of excitation energies. However for Mott insulators LDA calculations could give even ground state properties qualitatively wrong. For example for parent high-Tc compound La2CuO4 LDA gives nonmagnetic metallic solution while experimentally it is an antiferromagnetic insulator. For NiO LDA gave strongly underestimated value of magnetic moment on Ni ion (1.0 \(\mu_B\) versus experimental value \(\approx 1.8-1.9 \mu_B\)). The problem with these systems could be traced to underestimation in LDA of the energy of virtual excitations from occupied oxygen 2p to empty transition-metal 3d orbitals. This leads to overestimation of hybridization between those orbitals and hence decreases a tendency to magnetic moment formation.

In order to correct the LDA underestimation of virtual excitations energies one must use in "transition state" calculations WF’s resembling pure atomic orbitals such as oxygen 2p and transition-metal 3d orbitals and not their bonding (antibonding) combinations which are valence (conduction state) WF’s. As it was explained above for that one should choose in projection procedure (Eq. \((3)\)) the combined single set of valence and conduction bands instead of the two separate sets of occupied and empty bands. The "transition state" calculations for these Wannier functions...
will give the result which have a meaning of energies for virtual excitations between atomic orbital states and not real excitations which happen in spectroscopy experiments from (to) valence (conduction) band states. The corresponding correction in the form of Eq. (25) will increase the energy of virtual excitations from occupied oxygen 2p to empty transition-metal 3d orbitals and hence decrease hybridization between those orbitals that should enhance a tendency to magnetic moment formation.

That means that a different definition of WF's is needed in calculations for ground state properties (atomic orbital WF's obtained by projection on the combined single set of valence and conduction bands) and in calculations for spectral properties (valence (conduction state) WF's projected by using separately valence bands for occupied states and conduction bands for unoccupied ones).

In the present work we performed two steps of calculation for every system (see Fig.1). In the first one (part of the Fig.1 scheme bounded in a bold line rectangle) we chose a single combined set of bands to define WF's resembling pure atomic orbitals. Calculations are repeated till achieving full self-consistency in charge and spin densities \( \rho(\vec{r}) \) (defining one-electron LDA potential and hence parameters of LDA Hamiltonian \( H_{LDA} \), set of "transition state" corrections...
TABLE I: Comparison of calculated and experimental energy gap values (eV)

|         | LDA   | GTS   | Expt. |
|---------|-------|-------|-------|
| MgO     | 5.04  | 7.73  | 7.83\textsuperscript{a} |
| Si      | 0.44  | 1.04  | 1.17\textsuperscript{b} |
| NiO     | 0.11  | 3.76  | 4.0-4.3\textsuperscript{c} |
| BaBiO\textsubscript{3} | 0.15  | 0.51  | 0.48\textsuperscript{d} |

\textsuperscript{a}Ref. 16  
\textsuperscript{b}Ref. 17  
\textsuperscript{c}Ref. 18-19  
\textsuperscript{d}Ref. 20

In order to test the proposed "generalized transition state" (GTS) method, we have performed calculations for four systems representing various types of electronic structure: simple metal oxide band insulator MgO, covalent bond semiconductor Si, transition metal oxide Mott insulator NiO, and Peierls insulator BaBiO\textsubscript{3}. In all those cases we have obtained significant change of electronic structure leading to good agreement of calculated and experimental energy gap values (see Table I).

A. MgO

Simple metal oxide MgO is a good example of a band insulator. It has a cubic NaCl crystal structure with lattice parameter equal to 4.21 Å. Experimental value of energy gap (7.83 eV\textsuperscript{19}) is nearly 3 eV larger than LDA calculated value (5.04 eV in our calculations in good agreement with other works\textsuperscript{21}). The choice of energy bands and orbitals needed for calculation of Wannier functions via Eq. (3) is straightforward in this case: oxygen 2p orbitals for three occupied valence bands and magnesium 3s and 3p orbitals for unoccupied conduction bands. Constrained LDA calculations for transition state gave the following corrections to the energies of Wannier functions: \(\delta V_{Mg3s} = 1.44\) eV, \(\delta V_{Mg3p} = 1.81\) eV, \(\delta V_{O2p} = -2.41\) eV. Stronger effect of GTS correction for O2p states comparing with Mg3s, 3p WF’s could be understood taking into account more extended nature of magnesium orbitals comparing with oxygen ones. On Fig. 2 band structure calculated by GTS method is presented together with the results of standard LDA calculations. According to the \(\delta V\) correction values valence bands formed by O2p states are pushed down and conduction Mg3s, 3p bands are pushed up increasing the energy gap value to good agreement with experimental data (see Table I). Please note that GTS correction potential (Eq. (25)) is not a rigid shift of bands and so the difference between LDA and GTS gap values is not simply given by the corresponding difference of \(\delta V\) correction values.

B. Si

While MgO is an ionic compound, silicon represents a simplest case of a covalent bond semiconductor. Si has diamond crystal structure with lattice parameter equal to 5.43 Å. For this system we used four types of Wannier
functions: Si\(_3s_1\) and Si\(_3p_1\) calculated for the valence bands and Si\(_3s_2\) and Si\(_3p_2\) for conduction bands. The corresponding values of GTS potential (Eq. 25) corrections obtained in constrained LDA transition state calculations are: \(\delta V_{\text{Si}3s_1} = -0.82\) eV, \(\delta V_{\text{Si}3p_1} = -0.44\) eV, \(\delta V_{\text{Si}3s_2} = 0.28\) eV, \(\delta V_{\text{Si}3p_2} = 0.71\) eV. The resulting band structure is shown on Fig. 3. Negative potential correction for valence bands and a positive one for conduction bands produce a sizable increasing (0.60 eV) of the energy gap value resulting in a good agreement with experimental data (see Table I).

C. NiO

In contrast to energy gap values the ground state properties for MgO and Si are satisfactory reproduced by LDA and the first step of GTS calculations with atomic-orbital-like WF’s (see Sec. II B and Fig. 1) did not lead to significant changes comparing with pure LDA. However for transition metal oxides even the type of the ground state can be given wrong by LDA, like for cuprates. For nickel oxide NiO (cubic NaCl crystal structure with lattice parameter equal to 4.17 Å) the LDA error is not so severe: the LDA solution is an antiferromagnetic insulator in agreement with experiment. However LDA magnetic moment value for Ni ion is strongly underestimated: 1.0 \(\mu_B\) versus experimental value \(\approx 1.8-1.9\) \(\mu_B\). In this case the first step of GTS calculations responsible for the "transition state" correction to energy parameters of virtual excitations was essential: calculated magnetic moment value was increased in the results of GTS correction from 1.0 \(\mu_B\) to 1.8 \(\mu_B\) in good agreement with experimental data. There were five different types of Wannier functions in calculations for NiO: Ni3d-\(t_{2g}\) \(\uparrow\), Ni3d-\(e_g\) \(\uparrow\), Ni3d-\(t_{2g}\) \(\downarrow\), Ni3d-\(e_g\) \(\downarrow\) (the only unoccupied states for NiO) and O2p (by symmetry O2p states are not spin-polarized). Constrained LDA calculations for transition state gave the following corrections to the energies of Wannier functions: \(\delta V_{\text{Ni}3d-\text{t}_{2g}\uparrow} = -1.97\) eV, \(\delta V_{\text{Ni}3d-\text{e}_g\uparrow} = -1.97\) eV, \(\delta V_{\text{Ni}3d-\text{t}_{2g}\downarrow} = -2.39\) eV, \(\delta V_{\text{Ni}3d-\text{e}_g\downarrow} = 2.11\) eV and \(\delta V_{\text{O}2p} = -1.14\) eV.

The energy band dispersions obtained in GTS calculations together with LDA bands are shown on Fig. 4. The energy gap value was increased dramatically: from tiny 0.11 eV to a 3.76 eV value in good agreement with experimental data (see Table I). Not only the energies of unoccupied \(\text{Ni}3d-\text{e}_g\downarrow\) states were pushed up and those for occupied bands pushed down as it was the case for MgO and Si. The different values of \(\delta V\) correction for occupied Ni3d and O2p states result in a smaller energy separation between the corresponding bands in the occupied part of the calculated DOS (see Fig. 4). Note also decreased strength of admixture of \(\text{Ni}3d - \text{e}_g\downarrow\) states to the oxygen band energy area

FIG. 2: MgO band structure. Dashed lines shows LDA results and solid lines correspond to GTS calculations
resulting in a more ionic nature of GTS solution comparing with pure LDA and hence magnetic moment value 1.8 \( \mu_B \) closer to pure ionic value 2.0 \( \mu_B \)

D. BaBiO\(_3\)

BaBiO\(_3\) is an interesting example of the Peierls insulator or "negative U" system\(^{22}\). Formal valency of bismuth is +4 and this corresponds to the half-filled Bi6s shell. Stable valent states for Bi are +3 and +5 and those chemical arguments are often used to explain the experimental distorted cubic perovskite crystal structure of BaBiO\(_3\).\(^{23}\) In addition to the tilting of BiO\(_6\) octahedra there is also so called "breathing" distortion producing inequivalent Bi1 and Bi2 crystallographic positions with expanded and contracted Bi-O bond lengths. Bi1 can be associated with Bi\(^{+3}\) and Bi2 with Bi\(^{+5}\). This distortion leads to opening an energy gap so BaBiO\(_3\) can be seen as a three-dimensional Peierls insulator. The Fermi level in LDA calculations for ideal cubic perovskite crystal structure crosses half-filled band of Bi6s symmetry which can be described by an effective half-filled Hubbard model. An experimentally observed instability toward formation sites with empty (Bi\(^{+5}\)) and completely filled (Bi\(^{+3}\)) Bi6s shell can be interpreted as a negative value for a Coulomb interaction parameter \( U \).

LDA calculations for BaBiO\(_3\) gave a negative or very small positive values for energy gap\(^{24,25}\) while spectroscopy measurements demonstrate a sizable value of \( \approx 0.5 \) eV\(^{20}\). For our GTS calculations we have chosen a minimal set of two Wannier functions calculated using orbitals of Bi1-6s and Bi2-6s symmetry and bands located in the energy window of \( \pm 5 \) eV around Fermi energy. Constrained LDA calculations for transition state gave the following corrections to the energies of Wannier functions: \( \delta V_{Bi1-6s} = -0.19 \) eV \( \delta V_{Bi2-6s} = 0.43 \) eV. The energy band dispersions obtained in GTS calculations together with LDA bands are shown on Fig.\( ^{\text{III}} \). Only two bands close to Fermi energy were effected by GTS correction and energy gap value has increased from 0.15 eV to a 0.48 eV value in good agreement with experimental data (see Table\( ^{\text{I}} \)).
IV. CONCLUSION

We developed a calculation scheme based on "transition state" idea of Slater and Wannier functions set of one-electron states. This method was applied to the four materials representing ionic compounds (MgO), covalent bond semiconductors (Si), transition metal oxide Mott insulators (NiO) and Peierls insulator BaBiO$_3$. The results have shown a systematic improvement of energy gap values. Not only excitation energies but also ground state properties such as magnetic moment value for NiO can be significantly improved comparing with LDA results. Encouraged by the promising results reported in the present paper we plan to apply this method to other materials where standard LDA approach fails. Such calculations are in progress.

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FIG. 5: Total and partial densities of states for NiO obtained in LDA (left panel) and GTS (right panel) calculations.

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FIG. 6: BaBiO$_3$ band structure. Dashed lines shows LDA results and solid lines correspond to GTS calculations

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