A local-density approximation for the exchange energy functional for excited states: The band-gap problem

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ABSTRACT

We present excited-state density functional theory (DFT) to calculate band gap for semiconductors and insulators. For the excited-state exchange-correlation functional, we use a simple local-density approximation (LDA) like functional and it gives the result which is very close to experimental results. The linear muffin-tin potential is used to solve the self-consistent Kohn–Sham equation.

1. Introduction

First-principle calculations based on the density functional theory (DFT) have been eminently successful for the study of ground-state properties of electrons in a solid [1]. However, it has always been understood that the spectrum and wavefunctions of the associated one-electron like Kohn–Sham equation have no specific significance beyond the fact that they are used to obtain the ground-state density [2]. Thus the unoccupied part of the Kohn–Sham spectrum cannot be expected to describe correctly the excitations of a many-electron system. On the other hand, the energy eigenvalue of the highest occupied (HO) orbital, i.e. the orbital energy corresponding to the top of the valence band, is the exact ionization potential of the system [3]. This is known as the ionization potential theorem. Since adding an extra electron at the bottom of the conduction band would hardly change the density of a bulk system, the ionization potential theorem leads one to expect that the difference in the Kohn–Sham orbital energies corresponding to the bottom of the conduction band and the top of the valence band should give the correct band gap of semiconductors and insulators. However, it is well known that such an interpretation leads to gross underestimation of the band gaps of semiconductors in comparison to experiments. This is true even in solids like Ge, Si and the III–V semiconductors which are not "strongly correlated". This underestimation of the band gap has been explained in terms of the derivative discontinuity [4,5] of the exchange-correlation energy functional. To circumvent this difficulty, we propose to look at the calculation of the band gap as an excited-state problem. As such, the question we ask is: could we set up a DFT for excited states, calculate the total energy for appropriate excited state and obtain the excitation energy as its difference from the ground-state total energy. We may then go on to interpret the band gap in a semiconductor as the difference of the energies between the ground state and an excited state where an electron in the HO state of the ground state is removed from it and excited to the lowest unoccupied (LU) state.

The mathematical basis of a DFT for total energies in excited states had been set up by Görling [6] and Levy and Nagy [7], based on the constrained-search approach [8]. The theory has been put on a strong footing by Samal and Harbola [9]. The energy of the excited state of electrons in a solid may be expressed as a bi-functional of both the excited state density and the

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ground-state density.

$$E[\rho_{\text{ex}}, \rho_{\text{gr}}] = F[\rho_{\text{ex}}, \rho_{\text{gr}}] + \int \mathrm{d}^3\mathbf{r} V(\mathbf{r})\rho_{\text{ex}}(\mathbf{r}) \tag{1}$$

where $V(\mathbf{r})$ is the ion–electron potential. $F[\rho_{\text{ex}}, \rho_{\text{gr}}]$ is a bi-functional of the excited-state density $\rho_{\text{ex}}(\mathbf{r})$ and the ground-state density $\rho_{\text{gr}}(\mathbf{r})$. It is defined [7] from the constrained-search formulation:

$$F[\rho_{\text{ex}}, \rho_{\text{gr}}] = \min_{\Phi \to \rho_{\text{ex}}} \langle \Phi | (\hat{T} + \hat{V}_{ee}) | \Phi \rangle \tag{2}$$

where the constrained search is carried out with the wavefunctions giving the excited-state density, $\hat{T}$ and $\hat{V}_{ee}$ are the kinetic energy and electron–electron interaction potential operators, respectively, and the wavefunctions Φ are orthogonal to all the lower states determined by ρ_{gr}. For example, in defining $F[\rho_{\text{ex}}, \rho_{\text{gr}}]$ for the first excited state, the Φ's chosen would be such that they are orthogonal to the ground-state wavefunction obtained from ρ_{gr}. The exchange-correlation energy functional is then

$$E_{\text{xc}}[\rho_{\text{ex}}, \rho_{\text{gr}}] = F[\rho_{\text{ex}}, \rho_{\text{gr}}] - T_0[\rho_{\text{ex}}] - V_{\text{H}}[\rho_{\text{ex}}] \tag{3}$$

Here T_0 represents the kinetic energy of a non-interacting system of electrons, suitably chosen so that its charge density is the same as that of the interacting system. The effective potential seen by the system of non-interacting electrons is variationally obtained and the single-particle wavefunctions of the non-interacting system satisfies the Kohn–Sham equation:

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \mathrm{d}^3\mathbf{r}'\frac{\rho_{\text{ex}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}^{\text{ex}}(\mathbf{r}) \right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}) \tag{4}$$

where $V(\mathbf{r}) = \sum_n v(\mathbf{r} - \mathbf{R}_n)$ and $\mathbf{R}_n$ are the positions of the ion-core labeled by n. The excited-state density is obtained from $\rho(\mathbf{r}) = \sum_i f_i|\phi_i(\mathbf{r})|^2$ where the occupation number f_i is 0 or 1 depending on whether the state labeled by i is occupied or not.

As in the ground-state theory, the exchange-correlation energy functional in excited-state theory too has to be approximated. The problem of finding an excited-state exchange-correlation energy functional is a challenging one and is further compounded by the fact that the functional is expected to be state dependent. Thus different functionals may have to be constructed for different classes of the excited states. Recently, Samal and Harbola [10] have proposed a local-density approximation (LDA) for the exchange energy functional for a theory of excited states with one gap. The functional has been applied to a large number of atomic excited states to obtain very accurate excitation energies for single and double-electron excitations. The functional has precisely the form required to calculate band gaps of semiconductors using excited-state DFT. The purpose of the present work is then to employ this excited-state DFT to obtain the band gaps of a number of semiconducting and insulating materials. In the following we give a brief description of the methodology employed by us and then present our results.

As we discussed earlier, the band gap in a semiconductor or an insulator can be thought of as the lowest energy required to excite one electron out of a many-electron ground state to one of the excited states of the system. Thus, in terms of the transition energy,

$$\Delta E = E_{\text{ex}}[\rho_{\text{ex}}, \rho_{\text{gr}}] - E_{\text{gr}}[\rho_{\text{gr}}] \tag{5}$$

where $E_{\text{ex}}[\rho_{\text{ex}}, \rho_{\text{gr}}]$ is the total excited-state energy functional of Eq. (1) minimized by varying ρ_{ex} and $E_{\text{gr}}[\rho_{\text{gr}}]$ is the ground-state energy corresponding to the configurations mentioned above.

To obtain the total energies we turn to the solution of the variationally obtained Kohn–Sham equation (4) [2]. The charge

density is given by

$$\rho(\mathbf{r}) = \sum_{i=1}^{\infty} f_i|\varphi_i(\mathbf{r})|^2 \quad \text{with} \sum_{i=1}^{\infty} f_i = N_e$$

Here ρ is either the ground state or the excited-state densities depending upon the occupation numbers f_i. The total energy functional is

$$E[\rho] = \sum_{i=1}^{\infty} f_i\varepsilon_i - \frac{1}{2}\int\int \mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int \mathrm{d}^3\mathbf{r}\frac{\delta\widetilde{E}_{\text{xc}}}{\delta\rho(\mathbf{r})}\rho(\mathbf{r}) + \widetilde{E}_{\text{xc}}$$

$$= E_{\text{KS}} - E_{\text{H}}[\rho] + \widehat{E}_{\text{xc}} \tag{6}$$

Here ρ is either ρ_{gr} or ρ_{ex} depending on whether we are talking about the ground or the excited state, $\widetilde{E}_{\text{xc}}$ is the "modified exchange" energy functional which includes the difference between the interacting and non-interacting kinetic energies as well. This is of the form $\widetilde{E}_{\text{xc}}[\rho_{\text{gr}}]$ or $\widetilde{E}_{\text{xc}}[\rho_{\text{ex}}, \rho_{\text{gr}}]$, again depending upon whether we are talking about the ground or the excited state. E_{H} is the Hartree energy and $\widehat{E}_{\text{xc}}$ is the contribution from the modified exchange-correlation energy functional given by the last two terms in the Eq. (6). Note that for the sake of notational clarity the bi-functional notation for the excited-state functionals in the above equation has been dropped.

2. The excited-state exchange-correlation functional

There have been many attempts at obtaining accurate but approximate forms for the exchange-correlation functional for the ground state. The simplest of them, the LDA, follows the Dirac [11] approach and proposes the functional on the basis of exchange energy for the homogeneous electron gas (HEG). As mentioned above, adopting the same approach, Samal and Harbola [10] proposed an excited-state functional for the exchange energy and applied it to atoms to obtain accurate excited-state energies. In the following we discuss the construction of such a functional for semiconductors and insulators and employ it to get the band gap of these materials as defined by Eq. (5) above. The accuracy or otherwise of our proposition will be evident from the applications to several semiconductors and insulators.

The standard procedure for setting up of the exchange-correlation functional is to start from the equivalent expression for the HEG. This is shown in Fig. 1. In the semiconductor or insulator in its ground state, the electrons are filled up to the Fermi level, that is, in reciprocal space electrons occupy states labeled by wave vectors from $k = 0$ to k_F. The same picture is true
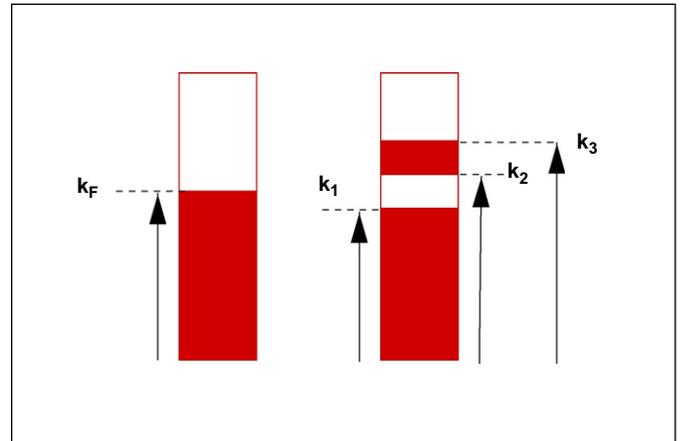

Fig. 1. The pictures of the ground-state configuration of an HEG (left) and an excited state (right).

for the HEG, but in addition we have

$$k_F^3 = 3\pi^2 \rho_{gr}(\mathbf{r}) \tag{7}$$

where $\rho_{gr}(\mathbf{r})$ is the almost uniform electron density in the ground state.

On the other hand, for the lowest excited state in the semiconductor or insulator, the electron in the HO state in the ground-state configuration is removed from that state and now occupies the LU state. For the HEG this excited-state configuration corresponds to the following: first, we shall call all states which were occupied in the ground state as well as in the excited state: *core states*. If $\rho_{core}(\mathbf{r})$ is the electron density due to the electrons occupying the core states, then all states from $k = 0$ to k_1 are occupied, where

$$k_1^3 = 3\pi^2 \rho_{core}(\mathbf{r}) \tag{8}$$

Next, if $\rho_{rem}(\mathbf{r})$ is the electron density due to the electron in the HO state of ground-state configuration which has been removed in the excited-state configuration, then

$$k_2^3 - k_1^3 = 3\pi^2 \rho_{rem}(\mathbf{r}) \tag{9}$$

Finally, if ρ_{add} is the electron density due to the electron in the lowest excited state of the ground-state configuration, which has been added in the excited-state configuration, then

$$k_3^3 - k_2^3 = 3\pi^2 \rho_{add}(\mathbf{r}) \tag{10}$$

All states between the labels k_1 and k_2 which were occupied in the ground state become unoccupied in the excited state. Whereas all states between the labels k_2 and k_3 which were unoccupied in the ground state become occupied in the excited state.

The ground-state density is $\rho_{gr}(\mathbf{r}) = \rho_{core}(\mathbf{r}) + \rho_{rem}(\mathbf{r})$ and the excited-state density is $\rho_{ex}(\mathbf{r}) = \rho_{core}(\mathbf{r}) + \rho_{add}(\mathbf{r}) = \rho_{gr}(\mathbf{r}) - \rho_{rem}(\mathbf{r}) + \rho_{add}(\mathbf{r})$. Note that in an excited state of the system the electrons will occupy the k-space differently from the ground state.

As stated before, the standard starting point for building up the ground-state exchange-correlation functional, whose exact form is in general unknown, is the exact expression for the HEG. We shall use the same idea for the excited state. This new functional will be the basis for our LDA generalized for excited states (MLDA).

The exchange energy in the MLDA can be obtained by integration over the reciprocal space equi-energetic spherical shell surfaces. In a recent paper Samal and Harbola [10] have explicitly obtained the expression for the exchange energy functional for the excited state, as described above. We shall quote their results here and refer the interested reader to the above mentioned reference for the mathematical details.

$$E_x^{MLDA} = E_x^{core} + E_x^{add} + E_x^{add-core}$$

where

$$E_x^{core} = -\frac{1}{4\pi^3} \int d^3\mathbf{r}\, k_1^4$$

$$E_x^{add} = -\frac{1}{8\pi^3} \int d^3\mathbf{r} \left[2(k_3^3 - k_2^3)(k_3 - k_2) \right.$$
$$\left. + (k_3^2 - k_2^2)^2 \ln\left(\frac{k_3 + k_2}{k_3 - k_1}\right) \right]$$

$$E_x^{add-core} = -\frac{1}{8\pi^3} \int d^3\mathbf{r} \left[2(k_3 - k_2)k_1^3 + 2(k_1^3 - k_2^3)k_1 \right.$$
$$\left. + \cdots + (k_2^2 - k_1^2)^2 \ln\left(\frac{k_2 + k_1}{k_2 - k_1}\right) - (k_3^2 - k_1^2)^2 \ln\left(\frac{k_3 + k_1}{k_3 - k_1}\right) \right] \tag{11}$$

It is easy to check from above that when $k_1 = k_2 = k_2 = k_F$, Eq. (11) reduces to the ground-state exchange functional.

Eqs. (8)–(11) will then provide the basis for the calculation of the total energies. If we now go back to Eq. (6), we note that the expressions for the ground state and excited state total energies are

$$E_{gr} = E_{gr}^{KS} - E_H[\rho_{gr}] + \widehat{E}_x^{LDA}[\rho_{gr}]$$

$$E_{ex} = E_{ex}^{KS} - E_H[\rho_{ex}] + \widehat{E}_x^{MLDA}[\rho_{ex}, \rho_{gr}]$$

Here E^{KS} refers to $\sum_i f_i \varepsilon_i$ where f_i are the occupation numbers already defined and ε_i are the Kohn–Sham energies. Assuming no change in the orbital eigenvalues corresponding to the ground- and excited-state configurations, which is a good assumption for bulk systems, the band gap will be given by the minimum value for different excitations of

$$\Delta E = \Delta E^{KS} - \Delta E_H + \{\widehat{E}_x^{MLDA}[\rho_{ex}; \rho_{gr}] - \widehat{E}_x^{LDA}[\rho_{gr}]\} \tag{12}$$

where ΔE^{KS} is the conventional Kohn–Sham gap, ΔE_H is the difference in the Hartree energy corresponding to the excited-state and the ground-state densities, where both ρ_{ex} and ρ_{gr} are calculated from the orbitals obtained from a single ground-state calculation. If the sum of the last two terms is small, we may expect the Kohn–Sham gap to be the band gap. However, we expect the major correction to the conventional Kohn–Sham gap to come from these terms. What these terms accomplish is to replace the LDA exchange energy corresponding to the excited-state density ρ_{ex} by the MLDA exchange energy. The latter is tailor-made—and therefore more appropriate—for getting exchange energy for an excited state of the kind considered for the band-gap calculation. We note that the functional proposed by Samal and Harbola also has self-interaction correction (SIC) terms in it. For extended systems we expect these terms to be negligible and shall justify our assumption by application to a few of the systems studied by us.

3. Application to solids

We shall base our calculations in solids on the tight-binding linear muffin-tin orbitals method within the atomic-sphere approximation (TB-LMTO-ASA) [12–15]. In this method the muffin-tin spheres are inflated to the Wigner–Seitz cell (WSC) volume and the interstitial contribution is neglected. The wavefunction is expanded in a basis of linearized muffin-tin orbitals:

$$\psi_\sigma(\mathbf{r}, E_{\mathbf{k}n\sigma}) = \sum_{RL} u_{RL\sigma}(E_{\mathbf{k}n\sigma}) \chi_{L\sigma}^R(r, E_{\mathbf{k}n\sigma}) Y_L(\hat{r}) \xi_\sigma$$

$$\chi_{L\sigma}^R(r, E_{\mathbf{k}n\sigma}) = [\varphi_{R\ell\sigma}(r) + (E_{\mathbf{k}n\sigma} - E_{\nu R\ell})\dot{\varphi}_{R\ell\sigma}(r)]$$

Here, $Y_L(\hat{r})$ are the spherical harmonics and ξ_σ are the spinor wavefunctions. The muffin-tin orbitals $\chi_{L\sigma}^R(r, E_{\mathbf{k}n\sigma})$ belong to an atom of type R, the angular momentum $L = (\ell, m)$, $\varphi_{R\ell\sigma}(r)$ are the partial wave solutions in the muffin-tin spheres, $\dot{\varphi}_{R\ell\sigma}$ are the energy derivatives of the partial waves, both evaluated at the expansion energies $E_{\nu R\ell\sigma}$ used for linearization. Tail cancellation ensures that the muffin-tin orbitals labeled by R vanish outside the atomic spheres centered at R. The quantum states of the electrons in the solid are labeled by the quantum numbers $\mathbf{K} = (\mathbf{k}n\sigma)$.

From the Kohn–Sham band-structure we can identify the HO and LU states in reciprocal space. Using these values of $\mathbf{K}$ we construct the removed and added electron densities. The core electron density is obtained from the atomic-like the core states. These expressions are then used in Eqs. (8)–(12) to obtain the band gap. We again point out that both the ground- and the excited-state densities are constructed from a single ground-state

calculation. This is justified since one does not expect LU state to change much even if an excited-state KS calculation is performed. An advantage of this is that the computational demand of our calculations is pretty much at the same level as the ground-state calculations.

Application of our methodology to molecules and clusters have already been carried out without any difficulty earlier [9,10]. However, in its application to solids there have been two points of confusion. This is related to the fact that in a bulk solid the extended Bloch-like electronic wavefunctions for a given quantum state are infinitely thinly spread over the whole solid. The charge densities corresponding to a single quantum state are also $O(1)$ while the charge density of the valence cloud is $O(N)$ (N is the number of atoms).[1]

There are two questions we must answer: First, are we really exciting a *single* electron out of a sea of N ($N \rightarrow \infty$) electrons, from the HO to the LU state? Second, can we use this infinitely small ($O(1)$ as compared to $O(N)$) change to produce the finite energy differences which we define to be the band gap in Eq. (12)?

In this section we shall argue that the way we obtain the energy differences within the LMTO technique by normalizing the solution within a WSC and considering only energies per cell addresses this problem successfully. We should also note that the arguments given is not confined to the LMTO, but holds good for any electronic structure method that are based on "cellular" techniques, e.g. KKR, APW or LAPW.

As we have seen earlier, quantum states of electrons in a solid are labeled by $\mathbf{K}$. If there are N ($N \rightarrow \infty$) atoms constituting the solid each contributing m electrons to the valence electron cloud, then the total number mN of available states are occupied, each state by one electron. If $\rho(\mathbf{r})$ is the total charge density of occupied electron states, then

$$\int_{\Omega} \mathrm{d}^3\mathbf{r}\rho(\mathbf{r}) = mN \quad \text{integrated over the whole volume}$$

In all electronic structure techniques which divide the solid into identical WSC centered at the sites R such that

$$\Omega = \bigcup_{R=1}^{N} \Omega_R \quad \text{where } \Omega_R \bigcap \Omega_{R'} = \emptyset \quad \forall R' \neq R$$

where Ω is the volume of the solid and Ω_R that of a WSC centered at R, the basis of representation are WSC centered functions of the form

$$\chi_{L\sigma}^R(\mathbf{r}) = \begin{cases} \chi_{L\sigma}^R(r)Y_L(\hat{r})\xi_\sigma & \text{for } \mathbf{r} \in \text{WSC centered at } R \\ 0 & \text{otherwise} \end{cases} \quad (13)$$

L is a composite index, which for the KKR or the APW and their linearized versions, LMTO and LAPW, denote the angular momenta indices ($\ell m \sigma$). These basis functions are centered at WSCs and do not overlap. The charge density also may be broken up as

$$\rho(\mathbf{r}) = \sum_{R=1}^{N} \sum_{\mathbf{K}} f_{\mathbf{K}} \rho_{\mathbf{K}}^R(\mathbf{r}) = \sum_{R=1}^{N} \rho^R(\mathbf{r}) \quad (14)$$

where

$$\rho^R(\mathbf{r}) = \begin{cases} \rho^R(\mathbf{r}) & \text{for } \mathbf{r} \in \text{WSC centered at } R \\ 0 & \text{otherwise} \end{cases}$$

Note that each quantum state labeled by $\mathbf{K}$ can be occupied by a single electron. Here $f_{\mathbf{K}}$ is the occupation number of the quantum state labeled by $\mathbf{K}$. For example, in the ground state mN of the

[1] A quantity is called $O(N^\alpha)$ if it scales as N^α with the number N of atomic-spheres in the system. For example, total energy is $O(N)$ while the energy per atom is $O(1)$.

lowest energy states are occupied, so mN of the $f_{\mathbf{K}}$ are 1 the rest are 0. In a crystalline solid, the densities within each WSC labeled by R are identical. However, since these partial charge densities have the same structure as Eq. (13), and are 0 outside the WSC labeled by R, we shall retain this label to indicate this. From the above it is clear that since $\rho(\mathbf{r})$ integrates to mN over N WSC:

$$\int_{\Omega_R} \mathrm{d}^3\mathbf{r}\,\rho^R(\mathbf{r}) = m \quad \text{and} \quad \int_{\Omega_R} \mathrm{d}^3\mathbf{r}\,\rho_{\mathbf{K}}^R(\mathbf{r}) = 1/N \quad (15)$$

In the output of the cellular methods (including the KKR, APW, LMTO, LAPW), the charge densities per WSC are scaled such that they are normalized to 1 within a cell.

$$\int_{\Omega_R} \mathrm{d}^3\mathbf{r}\,\widetilde{\rho}_{\mathbf{K}}^R(\mathbf{r}) = 1$$

So that the *scaled* charge densities per $\mathbf{K}$ labeled state which we get as output from the cellular methods are related to the true charge densities per state as

$$\rho_{\mathbf{K}}^R(\mathbf{r}) = (1/N)\widetilde{\rho}_{\mathbf{K}}^R(\mathbf{r}) \quad (16)$$

If we now remove or add a scaled charge density $\widetilde{\rho}_{\mathbf{K}}^R(\mathbf{r})$ integrating to 1 in a WSC, then that is equivalent to removing or adding a true charge density integrating to $1/N$ in that cell. The total charge density added or removed in the whole solid then integrates over the whole volume to 1. In other words, we *are* exciting 1 electron from the valence cloud in the solid from the HO to LU state.

The total energy expressions of Eq. (6) can also be broken up as

$$E[\rho] = \sum_{R=1}^{N} E_R[\rho^R(\mathbf{r})]$$

We now go back to the way we construct the charge density of the excited state: We divide the total charge density of the ground state into a density of the "core" which does not change on excitation $\rho_{\mathrm{core}}(\mathbf{r})$ and that due to the HO state $\rho_{\mathrm{rem}}(\mathbf{r})$. We then remove $\rho_{\mathrm{rem}}(\mathbf{r})$ and replace it by the density due to the LU $\rho_{\mathrm{add}}(\mathbf{r})$.

$$\rho_{\mathrm{ex}}(\mathbf{r}) = \rho_{\mathrm{core}}(\mathbf{r}) + \rho_{\mathrm{add}}(\mathbf{r}) = \rho_{\mathrm{core}}(\mathbf{r}) + \rho_{\mathrm{rem}}(\mathbf{r}) + (\rho_{\mathrm{add}}(\mathbf{r}) - \rho_{\mathrm{rem}}(\mathbf{r}))$$
$$= \rho_{\mathrm{gr}}(\mathbf{r}) + \delta\rho(\mathbf{r})$$

We also note from Eq. (11) that when $\delta\rho \rightarrow 0$ $E^{MLDA}[\rho_{\mathrm{gr}}] = E^{LDA}[\rho_{\mathrm{gr}}]$. Combining these two, we get

$$\Delta E[\rho] = E^{MLDA}[\rho_{\mathrm{ex}}(\mathbf{r})] - E^{LDA}[\rho_{\mathrm{gr}}(\mathbf{r})]$$
$$= E^{MLDA}[\rho_{\mathrm{gr}}(\mathbf{r}) + \delta\rho(\mathbf{r})] - E^{LDA}[\rho_{\mathrm{gr}}(\mathbf{r})]$$
$$= \sum_{R=1}^{N} \{E_R^{MLDA}[\rho_{\mathrm{gr}}^R(\mathbf{r}) + \delta\rho^R(\mathbf{r})] - E_R^{LDA}[\rho_{\mathrm{gr}}^R(\mathbf{r})]\}$$
$$= \sum_{R=1}^{N} \left\{ \int_{\Omega_R} \mathrm{d}^3\mathbf{r}\,\delta\rho^R(\mathbf{r}) \frac{\delta E_R[\rho^R(\mathbf{r})]}{\delta\rho^R(\mathbf{r})}\bigg|_{\rho^R=\rho_{\mathrm{gr}}^R} + \cdots \right.$$
$$\left. + \frac{1}{2!} \int_{\Omega_R} \int_{\Omega_R} \mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{r}'\,\delta\rho^R(\mathbf{r})\delta\rho^R(\mathbf{r}') \frac{\delta^2 E_R[\rho(\mathbf{r})]}{\delta\rho^R(\mathbf{r})\delta\rho^R(\mathbf{r}')}\bigg|_{\rho^R=\rho_{\mathrm{gr}}^R} + \cdots \right\}$$
$$= \sum_{R=1}^{N} \left\{ \int_{\Omega_R} \mathrm{d}^3\mathbf{r}\,\delta\rho^R(\mathbf{r})A[\rho_{\mathrm{gr}}^R(\mathbf{r})] + o(\{\delta\rho^R(\mathbf{r})\}^2) \right\}$$
$$= N \left\{ \int_{\Omega_R} \mathrm{d}^3\mathbf{r}\,\delta\rho^R(\mathbf{r})A[\rho_{\mathrm{gr}}^R(\mathbf{r})] + o(\{\delta\rho^R(\mathbf{r})\}^2) \right\}$$
$$= \int_{\Omega_R} \mathrm{d}^3\mathbf{r}\,\delta\widetilde{\rho}^R(\mathbf{r})A[\rho_{\mathrm{gr}}^R(\mathbf{r})] + No(\{\delta\rho^R(\mathbf{r})\}^2) \quad (17)$$

Here $o(x^n)$ stands for terms which scale as $x^m, m \geqslant n$. Note that $\delta\rho^R(\mathbf{r}) \sim 1/N$ so that all terms $N\,o(\{\delta\rho^R(\mathbf{r})\}^2)$ become negligible as $N \rightarrow \infty$. In this limit we may forget these latter terms.

The last but one step follows from the fact that all WSCs are identical in a crystalline solid. We note from Eq. (15) that although
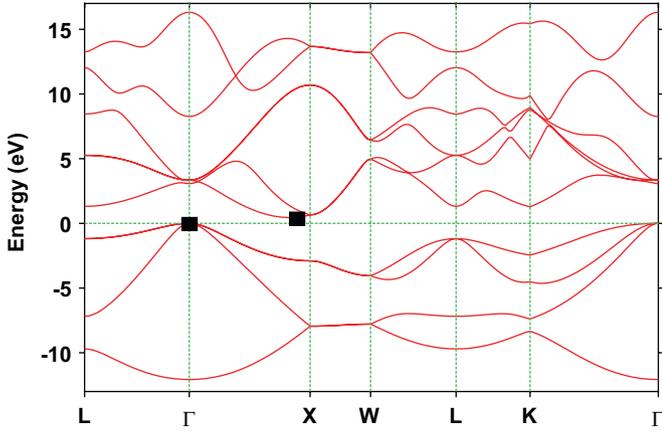
Fig. 2. The Kohn–Sham band structure of Si showing the HO and LU states used in our calculations.

Table 1
Comparison of the calculated band gap (ΔE) by the present work (LMTO-MLDA) with the TB-LMTO Kohn–Sham gap, the LMTO based Hartree-Fock (LMTO-HF) gap, the LMTO based exact exchange gap (LMTO-EXX) and the experimental (Exp) gap for diamond lattice Si and Ge, zinc-blende III–V semiconductors and wurzite oxides of Zn, Ca and Mg.

System	a (Å)	LMTO (LDA) (eV)	LMTO (MLDA) (eV)	LMTO (HF) (eV)	LMTO (EXX) (eV)	Exp (eV)
Si	5.43 [23]	0.49	1.01	5.6 [18]	1.25 [24]	1.17 [20]
Ge	5.55	0.08	0.53	4.2 [18]	1.57 [16]	0.74 [27]
GaP	5.45 [27]	1.62	2.30	–	–	2.32 [27]
GaAs	5.65 [23]	0.37	1.59	–	–	1.52 [27]
GaSb	6.00 [23]	0.07	0.94	–	–	0.81 [27]
InP	5.87 [23]	0.71	1.65	–	–	1.42 [27]
InAs	6.04 [23]	0.03	0.61	–	–	0.43 [27]
InSb	6.48 [23]	0.01	0.59	–	–	0.23 [27]
MgO	4.21 [26]	4.49	7.64	25.30 [19]	7.77 [21]	7.83 [22]
CaO	4.80 [26]	3.35	6.85	15.80[19]	7.72 [21]	7.09 [22]
ZnO	3.25,5.21 [25]	0.87	3.35	–	–	3.44 [27]

the total energies on the right-hand side of the above equation are individually $O(N)$, the difference ΔE should be $\sim O(1)$. Since $\delta\rho(\mathbf{r})$ scales like $1/N$ and the summation of R provides a factor of N, the functional $A[\rho_{gr}^R(\mathbf{r})] \sim O(1)$.

The energies calculated in the TB-LMTO are energies *per unit cell*. The energy difference calculated within the TB-LMTO is

$$\Delta E[\tilde{\rho}^R] = \int_{\Omega_R} \delta\tilde{\rho}^R(\mathbf{r}) A[\tilde{\rho}_{gr}^R(\mathbf{r})] \qquad (18)$$

The only way in which both $\Delta E[\rho]$ and $\Delta E[\tilde{\rho}^R]$ can be $O(1)$ is if the functional $A[\rho]$ has a specific scaling behavior with ρ. Let $A[\tilde{\rho}] = A[N\rho] = N^{\alpha} A[\rho]$, then $\alpha = 0$ for the above to hold. In that case, it now follows that

$$\Delta E[\tilde{\rho}^R] = \Delta E[\rho] = E_g$$

The calculation in the solid is thus reduced to the calculation within a single WSC using the scaled charge density $\tilde{\rho}(\mathbf{r})$ and the differences in energies per unit cell. We are exciting one electron from the entire valence cloud of the solid from the HO to LU state and the total energy difference is $E_g = O(1)$.

4. Results and discussion

We shall first illustrate our calculations with a specific example, i.e. that of Si. Fig. 2 shows the Kohn–Sham band structure of Si and the HO and LU states as obtained from the regular Kohn–Sham LDA calculation. In addition to these states, the calculations also give the Kohn–Sham gap ΔE^{KS}. These states are then used to construct the removed and added electron densities for the excited state. When employed in Eq. (12), these densities yield the band gap of silicon. The numerical results are shown in Table 1 while a comparison is shown in Fig. 3.

As is clear from Table 1 and Fig. 3, our method improves the Kohn–Sham band gap substantially, bringing it very close to the exact exchange [16] and experimental [20] band gaps. Interestingly the correction to the Kohn–Sham band gap is 0.52 eV and arises essentially from the exchange-energy difference between the ground and the excited state. This difference is very close to
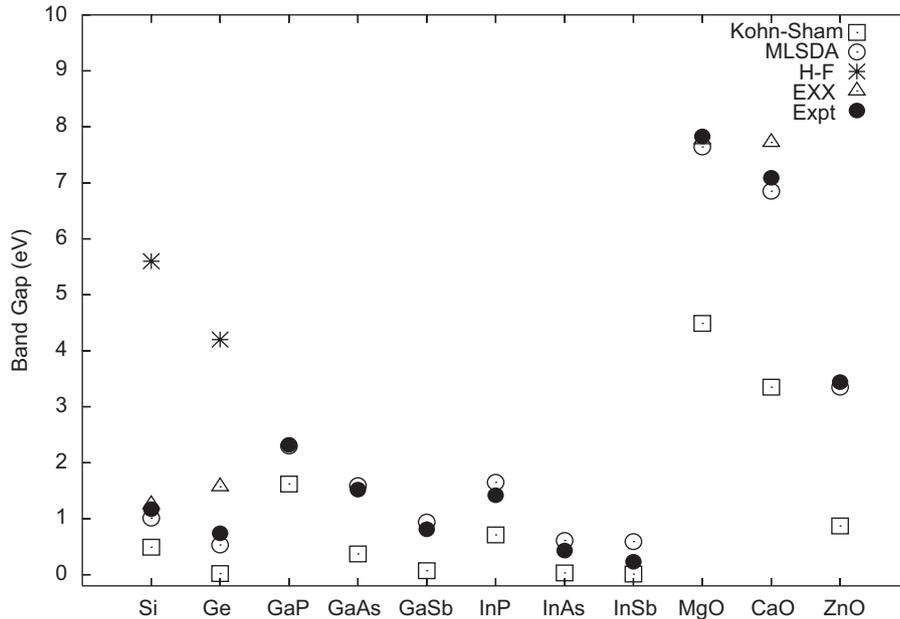

Fig. 3. Band gaps calculated by different methods compared with the experimental band gaps of a series of semiconductors and insulators.

the derivative discontinuity of 0.58 eV in the exchange-correlation potential for Si obtained [17] from a GW calculation.

Having obtained accurate results for Si, we have performed similar calculations for Ge, the III–V zinc-blende semiconductors GaP, GaAs, GaSb, InP, InAs and InSb, two zinc-blende oxides MgO and CaO, and one Wurzite structure oxide ZnO. The results are displayed in Table 1 and Fig. 3. It is evident from the results that our procedure yields uniformly accurate results for the band gaps of narrow band gap to large band-gap materials. However, for semiconductors like InAs and InSb which actually turn out to be metals with zero Kohn–Sham gaps, our procedure is problematic. Therefore we did the initial calculation with a lattice constant slightly smaller than the equilibrium one, so that a very small Kohn–Sham gap appears and then redid our calculations. The estimated band gaps in the MLSDA are slight over-estimations.

As mentioned before, since the band gap is calculated as an energy difference, we expect the difference in self-energy correction (SIC) between the added and the removed states to be small. We have carried out SIC corrections, as proposed by Samal and Harbola [9,10], for Si, GaSb and ZnO. For Si the gap changes from 1.01 to 1.02 eV; for GaSb from 0.94 to 1.06 eV and for ZnO from 3.35 to 3.37 eV. In all cases the correction is $\sim$ 1% confirming our assumption.

Our correction is to the exchange energy functional alone. Corrections to the correlation part is being implemented in a subsequent communication. However, even with the pure exchange correction major part of the correction to the Kohn–Sham gap is achieved. We are now applying this technique to a series of semiconducting and insulating systems.

Acknowledgments

References

[1] R.M. Martin, Electronic Structure: Basic Theory and Practical Calculations, Cambridge University Press, Cambridge, 2004.
[2] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133.
[3] J.P. Perdew, R.G. Parr, M. Levy, J.L. Balduz Jr., Phys. Rev. Lett. 49 (1982) 1691.
[4] J.P. Perdew, M. Levy, Phys. Rev. Lett. 51 (1983) 1884.
[5] L.J. Sham, M. Schluter, Phys. Rev. Lett. 51 (1983) 1888.
[6] A. Görling, Phys. Rev. A 59 (1999) 3359.
[7] M. Levy, Á. Nagy, Phys. Rev. Lett. 83 (1999) 4361;
Á. Nagy, M. Levy, Phys. Rev. A 63 (2001) 052502.
[8] M. Levy, Proc. Nat. Acad. Sci. U.S.A. 76 (1979) 6062;
E.H. Lieb, Internat. J. Quant. Chem. 23 (1983) 243.
[9] P. Samal, M.K. Harbola, J. Phys. B 39 (2006) 4065.
[10] P. Samal, M.K. Harbola, J. Phys. B 38 (2005) 3765.
[11] P.A.M. Dirac, Proc. Cambridge Philos. Soc. 26 (1930) 376.
[12] O.K. Andersen, R.V. Kasowski, Phys. Rev. B 4 (1971) 1064.
[13] R.V. Kasowski, O.K. Andersen, Solid State Comm. 11 (1972) 1064.
[14] O.K. Andersen, R.G. Woolley, Molecular Phys. 28 (1973) 905.
[15] O.K. Andersen, Phys. Rev. B 12 (1975) 3060.
[16] T. Kotani, Phys. Rev. Lett. 74 (1995) 2989.
[17] R.W. Godby, M. Schluter, L.J. Sham, Phys. Rev. Lett. 56 (1986) 2415.
[18] A. Svane, Phys. Rev. B 35 (1987) 496.
[19] R.P. Pandey, J.E. Jaffe, A.B. Kunz, Phys. Rev. B 43 (1991) 9228.
[20] M.S. Hybertsen, S.G. Louie, Phys. Rev. B 34 (1986) 5390.
[21] T. Kotani, Phys. Rev. B 50 (1994) 14816.
[22] R.C. Whited, C.J. Flaten, W.C. Walker, Solid State Comm. 13 (1973) 1903.
[23] I.N. Remediakis, E. Kaxiras, Phys. Rev. B 59 (1999) 5536.
[24] T. Kotani, H. Akai, Phys. Rev. B 52 (1995) 17153.
[25] S.C. Abrahams, Acta Cryst. B 24 (1982) 1968.
[26] K.H. Hellwege, A.M. Hellwege (Eds.), Landolt-Börnstein Tables, Group III, vol. 7b, Springer, Berlin, 1975.
[27] C. Kittel, Introduction to Solid State Physics, sixth ed., Wiley, New York, 1986, p. 185.