PHYSICAL REVIEW B VOLUME 59, NUMBER 8 15 FEBRUARY 1999-II

Band-structure calculations for semiconductors within generalized-density-functional theory

I. N. Remediakis and Efthimios Kaxiras*
Physics Department, University of Crete, 71110 Heraclion, Greece
(Received 20 August 1998)

We present band-structure calculations of several semiconductors and insulators within the framework of density-functional theory in the local-density approximation (DFT/LDA), employing the correction for excited states proposed by Fritsche and co-workers. We applied the method to examine typical elemental (C,Si,Ge), compound group-IV (SiC, SiGe, GeC) and compound III-IV semiconductors (AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InP, InAs, InSb), and examined in detail the approximations involved in the conduction-band energy correction. This quite simple method (referred to as generalized density-functional theory), while not a substitute for more rigorous theoretical approaches such as the *GW* method, gives results in reasonable agreement with experiment. Thus, it makes possible the calculation of semiconductor band gaps with the computational effort of a DFT/LDA calculation, at least for systems where more elaborate methods are not readily applicable. [S0163-1829(99)02208-0]

I. INTRODUCTION

In the past two decades, remarkable progress has been made toward accurate calculations of the total energy, using density-functional theory in the local-density approximation (DFT/LDA) (Refs. 1 and 2) and more recently in the generalized gradient approximation.[3] In contrast, the problem of accurate band-gap calculations for semiconductors and insulators remains an important theoretical challenge. The quasiparticle spectrum and the electronic excitation properties are much more difficult to compute accurately than the total energy, and DFT/LDA gives unacceptable results for these quantities (often more than 50% off from experimental values). The electronic excitation problem has been addressed by Hedin's *GW* approximation.[4] Applications of this theory, beginning with the work of Hybertsen and Louie,[5] Godby, Schlüter, and Sham,[6] and other workers[7,8] have proven very successful: this scheme works essentially perfectly for a wide range of materials, including perfect crystals, surfaces, point defects, etc. However, the *GW* method requires significant additional computational effort over DFT/LDA because it involves the computation of the dielectric function and the Green's function, and relies on the solution of the Dyson equation, which is more demanding than the single-particle Kohn-Sham equations due to the energy dependence of the self-energy operator.

From a practical point of view, it would be very desirable to have a simple, efficient, and reasonably accurate scheme for the calculation of band gaps without extensive computational effort beyond that required for a DFT/LDA calculation. For example, a fast but reasonably reliable method for calculating electronic excitations would be very useful as a guide for the design of new materials which have not yet been produced in the laboratory, for optical and electronic device applications.

Several attempts have been made towards such a simplified scheme. Interesting examples are the theory of Sham and Schlütter,[9] which is based on the discontinuity of the exchange and correlation potential, and the work of Gygi and Baldereschi,[7] which gives a correction to the LDA band structure based on *GW* theory. A correction of the band structure, using the framework of the so-called generalized density-functional theory (GDFT), was also proposed by Fritsche and co-workers.[10] Fritsche's approach has the added advantage of relying entirely on quantities obtained in a DFT/LDA calculation, so that it is both inherently consistent and computationally efficient. In the present paper we examine the ability of this approach to give reasonably accurate results for the minimum band gap of semiconductors. The paper is organized as follows: In Sec. II we review the basic ideas of GDFT, including the correction to the DFT/LDA eigenvalues, and give a detailed discussion of the approximations which lead to it. In Sec. III we present an application of the method to elemental and compound semiconductors and discuss the results we obtained. We conclude in Sec. IV with some remarks on the usefulness of this theory.

II. REVIEW OF GDFT

The main idea of both the GDFT and the DFT approach is to map the real system of interacting electrons to one of fictitious, noninteracting particles. A theory of this kind should prove that such a mapping is not only possible but unique, and additionally, it should give a recipe for calculating the properties of the real system from those of the fictitious one. The theorem of Hohenberg and Kohn[1] states that all ground-state properties can be expressed uniquely using functionals of the density; this implies that if the ground-state density of the fictitious system equals that of the real one, then, at least for the ground state, all properties of the two systems are identical.

The GDFT approach is based on the observation that knowledge of the pair density $\rho_2(\mathbf{r},\mathbf{r}')$ allows the determination of the exchange and correlation effects, whether the state under consideration is the ground state or an excited one. There exists a relationship between the infinitesimal change of the density $\delta\rho$ and the corresponding change $\delta\rho_2$, which gives again a central role to the density. Based on this theoretical framework, Fritsche derived a simple formula for correcting the excitation energies of the single-particle

 ©1999 The American Physical Society

spectrum, which, as is well known, are incorrect within DFT. The question of whether or not GDFT can describe in a practical way all excited states is still open, but the method seems to work reasonably well when applied to the first few conduction bands of semiconductors, as the results presented below indicate.

In the following we give a brief description of GDFT and the correction to the eigenvalues of excited states for two reasons: first so that we provide the reader with a complete description of the calculations presented, and second, and more importantly, so that we can identify in detail all the approximations involved, which has not been done explicitly elsewhere. We only include here the steps that are absolutely necessary to make the approximations evident, and refer the reader to the original work for more detailed derivations. For simplicity, in the present work we will omit spin indices and deal with an unpolarized electron gas. The extension to spin-polarized formulas is straightforward.

A. The GDFT concept

The basic statement of GDFT is that any eigenstate Ψ_n of the real-system Hamiltonian (in atomic units),

$$H=\sum_{j=1}^{N}\left[-\frac{\nabla_j^2}{2}+V_{\rm ext}(\mathbf{r}_j)\right]+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}, \tag{1}$$

can be uniquely mapped to a single Slater determinant Φ_n, built from N orbitals which satisfy the Kohn-Sham equations:[2]

$$\left[-\frac{\nabla^2}{2}+V_{\rm ext}(\mathbf{r})+V_H^{(n)}(\mathbf{r})+V_{\rm xc}^{(n)}(\mathbf{r})\right]\psi_j^{(n)}(\mathbf{r})=\varepsilon_j^{(n)}\psi_j^{(n)}(\mathbf{r}), \tag{2}$$

where $V_H^{(n)}(\mathbf{r})$ is the Hartree potential and $V_{\rm xc}^{(n)}(\mathbf{r})$ is the function that connects the infinitesimal change of the density with the corresponding change in the exchange and correlation energy:

$$\delta E_{\rm xc}^{(n)}=\int V_{\rm xc}^{(n)}(\mathbf{r})\,\delta\rho_n(\mathbf{r})d^3r+\int W_{\rm xc}^{(n)}(\mathbf{r})\,\delta\sigma_n(\mathbf{r})d^3r. \tag{3}$$

For details about the meaning of σ and W, see the original work of Fritsche;[10] here we note only that for the ground state $\sigma_0(\mathbf{r})=0$. $E_{\rm xc}^{(n)}$ is defined by

$$\langle V_{e\text{-}e}\rangle^{(n)}\equiv\frac{1}{2}\int\frac{\rho_n(\mathbf{r})\rho_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r'+E_{\rm xc}^{(n)}, \tag{4}$$

where $\langle V_{e\text{-}e}\rangle^{(n)}$ denotes the total electron-electron interaction energy in the eigenstate Ψ_n. If one defines the exchange and correlation energy per particle $\varepsilon_{\rm xc}^{(n)}$ by

$$E_{\rm xc}^{(n)}\equiv\int\varepsilon_{\rm xc}^{(n)}(\mathbf{r})\rho_n(\mathbf{r})d^3r, \tag{5}$$

it is easy to find that

$$\varepsilon_{\rm xc}^{(n)}(\mathbf{r})=-\frac{1}{2}\int\frac{\rho_n(\mathbf{r}')f^{(n)}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r', \tag{6}$$

where $f^{(n)}(\mathbf{r},\mathbf{r}')$ is the correlation factor. The $E_{\rm xc}^{(n)}$ defined here is clearly different from the DFT one as already pointed out by Biagini,[11] but $E_{\rm xc}^{\rm DFT}$ and $E_{\rm xc}^{(0)}$ change in the same way when the density changes, that is, $V_{\rm xc}^{(0)}(\mathbf{r})=V_{\rm xc}^{\rm DFT}(\mathbf{r})$ as argued by Fritsche.[12] Thus, GDFT coincides with DFT when the ground state is considered.

The N orbitals which are contained in Φ_n have to be selected so that the density equals that derived directly from Ψ_n, and therefore the following relation holds:

$$\begin{aligned}\rho_n(\mathbf{r})&\equiv N\int|\Psi_n(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)|^2d^3r_2\cdots d^3r_N\\&=\int|\Phi_n(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)|^2d^3r_2\cdots d^3r_N\\&=\sum_j|\psi_j^{(n)}(\mathbf{r})|^2.\end{aligned} \tag{7}$$

The energy $E_n=\langle\Psi_n|H|\Psi_n\rangle$ can be calculated in terms of the ψ_j's and ε_j's.[10] The result is

$$\begin{aligned}E_n=&\sum_j\varepsilon_j^{(n)}-\frac{1}{2}\int\frac{\rho_n(\mathbf{r})\rho_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r'\\&+\int[\bar{\varepsilon}_{\rm xc}^{(n)}(\mathbf{r})-V_{\rm xc}^{(n)}(\mathbf{r})]\rho_n(\mathbf{r})d^3r,\end{aligned} \tag{8}$$

with

$$\bar{\varepsilon}_{\rm xc}^{(n)}(\mathbf{r})=\int_0^1\varepsilon_{\rm xc}^{(n)}(\mathbf{r},\lambda)d\lambda, \tag{9}$$

where $\varepsilon_{\rm xc}^{(n)}(\mathbf{r},\lambda)$ is the exchange and correlation energy per particle in a system of electrons whose interaction is $V_{e\text{-}e}(\mathbf{r},\mathbf{r}')=\lambda/|\mathbf{r}-\mathbf{r}'|$. By analogy, all quantities denoted by a symbol with a bar imply a similar integral over λ as in Eq. (9).

B. Elementary excitations

The preceding discussion would be useful if one could find Ψ_n and construct from it the density ρ_n and the potentials, which in general is not feasible. However, when considering the ground state, the situation is much better because the energy has to have a minimum: this leads to the choice of the N lowest-energy orbitals ψ_j for the sum in Eq. (7). This is a physically clear choice, although there is no rigorous proof of its validity. The next step is to find an approximation for $V_{\rm xc}$ and solve Eq. (2) self-consistently.

An elementary excitation of the system, Ψ_1, can be approximately mapped to a determinant Φ_1 similar to Φ_0 except that it has an orbital ψ_f where Φ_0 has ψ_i. The other orbitals in Φ_1 will be slightly different from the initial ones due to the change of the density and the corresponding change of the potential. The correct excitation energy is

$$\Delta E=E_1-E_0=\varepsilon_f-\varepsilon_i+\Delta_{fi}. \tag{10}$$

The above equation can be interpreted as meaning that the eigenvalues of the Kohn-Sham Hamiltonian (2) for the unoccupied states (denoted by the subscript f), which are not

included in forming the Slater determinant from the N-lowest ones (denoted by the subscript i), have to be corrected and the correction is

$$\varepsilon_f^{\rm corr}=\varepsilon_f+\Delta_{fi}\,. \tag{11}$$

Using Eqs. (10) and (8) we have

$$\Delta_{fi}=\sum_{j\neq i}\Delta\varepsilon_j-\Delta E_H+\Delta\bar{E}_{\rm xc}-\Delta E'_{\rm xc}, \tag{12}$$

with the definitions

$$E_H=\frac{1}{2}\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r d^3r', \tag{13}$$

$$\bar{E}_{\rm xc}=\int\bar{\varepsilon}_{\rm xc}(\mathbf{r})\rho(\mathbf{r})d^3r, \tag{14}$$

$$E'_{\rm xc}=\int V_{\rm xc}(\mathbf{r})\rho(\mathbf{r})d^3r. \tag{15}$$

The change of the density can be divided into two parts:

$$\Delta\rho=\Delta\rho_0+\Delta\rho_R, \tag{16}$$

where

$$\Delta\rho_0=|\psi_f(\mathbf{r})|^2-|\psi_i(\mathbf{r})|^2, \tag{17}$$

and $\Delta\rho_R$ is the response (hence the subscript R) in the density due to the slight change of the orbitals not involved in the transition.

We can treat the difference between the Kohn-Sham potential for the excited state and that for the ground state as a perturbation to the latter, and obtain for the eigenvalue difference

$$\Delta\varepsilon_j=\int|\psi_j(\mathbf{r})|^2[\Delta V_H(\mathbf{r})+\Delta V_{\rm xc}(\mathbf{r})]d^3r, \tag{18}$$

so that

$$\sum_{j\neq i}\Delta\varepsilon_j=\int\rho_0(\mathbf{r})\Delta V_H(\mathbf{r})d^3r+\int\rho_0(\mathbf{r})\Delta V_{\rm xc}(\mathbf{r})d^3r-\int|\psi_i(\mathbf{r})|^2[\Delta V_H(\mathbf{r})+\Delta V_{\rm xc}(\mathbf{r})]d^3r. \tag{19}$$

The last term of the above expression is expected to be small.

The terms involving the Hartree potential can be written in the form

$$\Delta E_H=\int\rho_0(\mathbf{r})\Delta V_H(\mathbf{r})d^3r+\frac{1}{2}\int\Delta\rho(\mathbf{r})\Delta V_H(\mathbf{r})d^3r. \tag{20}$$

The last term is quadratic in the density change and thus it can be omitted. As for the term in Eq. (15), we have

$$\Delta E'_{\rm xc}=\int\rho_0(\mathbf{r})\Delta V_{\rm xc}(\mathbf{r})d^3r+\int\Delta\rho_0(\mathbf{r})V_{\rm xc}^{(0)}(\mathbf{r})d^3r+\int\Delta\rho_R(\mathbf{r})V_{\rm xc}^{(0)}(\mathbf{r})d^3r+\int\Delta\rho(\mathbf{r})\Delta V_{\rm xc}(\mathbf{r})d^3r. \tag{21}$$

The last term is almost zero, as we will show below.

To calculate $\Delta\bar{E}_{\rm xc}$ we use the definition (5) and Eq. (6), omitting terms which are higher order than linear in changes of the density.

We can divide the change of the correlation factor into two parts, Δf_0 and Δf_R. These two terms do not have an obvious definition, but they do have a clear physical meaning by analogy to the partition of $\Delta\rho$ into $\Delta\rho_0$ and $\Delta\rho_R$. These quantities can be calculated in the case where Φ_n is the true wave function of the system:

$$f^{(n)}(\mathbf{r},\mathbf{r}')=-\frac{\left|\sum_j\psi_j^{(n)*}(\mathbf{r}')\psi_j^{(n)}(\mathbf{r})\right|^2}{\rho_n(\mathbf{r})\rho_n(\mathbf{r}')}. \tag{22}$$

Using the above division for Δf, keeping terms only linear in changes of the density, and using the symmetry $f(\mathbf{r},\mathbf{r}')=f(\mathbf{r}',\mathbf{r})$, we have

$$\Delta\bar{E}_{\rm xc}=\int 2\bar{\varepsilon}_{\rm xc}^{(0)}(\mathbf{r})\Delta\rho_0(\mathbf{r})d^3r+\Delta\bar{E}_{\rm xc_0}+\Delta\bar{E}_{\rm xc}^R, \tag{23}$$

$$\Delta\bar{E}_{\rm xc_0}=-\frac{1}{2}\int\frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')\Delta\bar{f}_0(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r d^3r'. \tag{24}$$

For the response term $\Delta\bar{E}_{\rm xc}^R$ we can make use of Eq. (3), since $\Delta\rho_R\ll\Delta\rho$ and for the ground state $\sigma_0=0$:

$$\Delta\bar{E}_{\rm xc}^R=\int\Delta\rho_R(\mathbf{r})V_{\rm xc}^{(0)}(\mathbf{r})d^3r. \tag{25}$$

Using Eqs. (12), (17), (19), (20), (21), (23), (25), and omitting the small terms, we obtain the desired result,

$$\Delta_{fi}=\int[2\bar{\varepsilon}_{\rm xc}^{(0)}(\mathbf{r})-V_{\rm xc}^{(0)}(\mathbf{r})][|\psi_f(\mathbf{r})|^2-|\psi_i(\mathbf{r})|^2]d^3r, \tag{26}$$

which is the formula that Fritsche[10] gives.

Fritsche and Gu[10] noted that this expression is similar to the correction of the DFT quasiparticle spectrum obtained by Godby *et al.*,[6] although a rigorous identification of the terms in the two expressions is lacking.

C. The approximations

The previous derivation is exact, as we will show below, in the case of a transition where the energy difference between the final and the initial state is small compared with the Fermi energy. This condition is satisfied in the cases we study, that is, the lowest conduction bands of semiconductors.

In perturbation theory the change of an eigenvalue depends linearly on the mean of the perturbation. This can be

viewed from the opposite side: the difference between the effective potentials, $\tilde{V}^{(1)}-\tilde{V}^{(0)}$, is indeed small, as it was assumed in Eq. (18), if $\varepsilon_f-\varepsilon_i$ is small compared with ε_f or alternatively with the Fermi energy. Thus, the perturbative approach is correct for the lowest conduction bands of the semiconductors we study, since in these materials the energy gap is about one-tenth of the Fermi energy. This small change of the potential shows that the density should also not change much, since in principle the potential depends solely on it. This is the reason why the terms quadratic in $\Delta\rho$ can be neglected.

Under the same conditions one expects that the response of the states not involved in the transition should be of less importance. The excitation energy is very small compared with the ground-state energy and it is not expected to induce large rearrangements to the low-energy occupied states; thus, the change in the density due to the transition is dominated by the portion $\Delta\rho_0$ when such an elementary excitation is considered.

Similar arguments justify the neglect of the last term of Eq. (19). Having in mind the Hartree-Fock equations, where each particle moves in the potential created by the others, the change of the eigenvalue due to a perturbational change of the remaining states (the portion $\Delta\rho_R$) should be infinitesimal.

Sham and Schlütter[9] proved that for a semiconducting system, where the one-particle energies form almost continuous bands with a gap between ε_N and ε_{N+1}, the exchange and correlation potential has a discontinuity when the number of particles changes from $N-1$ to $N+1$, or equivalently when the number of quasiparticles changes from -1 to $+1$ (hole or particle excitation). This discontinuity, which they write as $V_{\mathrm{xc}}^{(+)}-V_{\mathrm{xc}}^{(-)}$, is independent of $\mathbf{r}$. They use the approximation $V_{\mathrm{xc}}^{(-)}=V_{\mathrm{xc}}^{(0)}$, which is reasonable because ε_{N-1} is very close to ε_N. $V_{\mathrm{xc}}^{(+)}$ and $V_{\mathrm{xc}}^{(-)}$ have the physical meaning of the effective potentials which govern the motion of a particle or hole excitation, respectively. Thus $V_{\mathrm{xc}}^{(+)}$ can be identified with our $V_{\mathrm{xc}}^{(1)}$; then the difference $V_{\mathrm{xc}}^{(1)}-V_{\mathrm{xc}}^{(0)}$ must be a constant, so the last term in Eq. (21) is proportional to the integral of $\Delta\rho$ which is zero, since both ρ_0 and ρ_1 integrate to the total number of electrons, N.

Since there is a linear relation between $\delta\rho_2$ and $\delta\rho$ [it is this relation that leads to Eq. (3)] there is also a similar relation between δf and $\delta\rho$. It is then a reasonable approximation to omit the terms which are higher order than linear in changes of the density in Eq. (23).

A less clear approximation is that the second term on the right side of Eq. (23) is small. The idea is that the change of the density is more important than the change of the correlation factor, that is,

$$\int \frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')\Delta\bar{f}_0(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r d^3r' \ll \int \frac{\Delta\rho_0(\mathbf{r})\rho_0(\mathbf{r}')\bar{f}^{(0)}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r d^3r'. \quad (27)$$

$\Delta\bar{f}_0$ is the change in $\bar{f}$ when the states other than f and i are taken to be ''frozen.'' Fritsche[10] argues by analogy to the

TABLE I. Minimum band gaps as obtained from the present GDFT/LDA calculations, compared to experiment and GW theory. For each material we give in the first row the gap at the experimental lattice constant and in the second row the gap at the theoretical lattice constant (determined by minimizing the total energy). Experimental and GW values are taken from Ref. 13 and Ref. 8, respectively, except where other references are given.

Material	Lattice	Gap (eV)		
	const. (Å)	GDFT/LDA	Expt.	(GW)
Si	5.43	1.223	1.17	1.21 [a]
	5.38	1.168		
C	3.57	4.718	5.48	5.43 [a]
	3.55	4.748		
Ge	5.66	0.000	0.74	0.75 [a]
	5.57	0.494		
SiC	4.36	2.646	2.39	2.34 [b]
	4.32	2.624		
SiGe	5.50	1.239		
	5.46	1.203		
GeC	4.45	2.808		
	4.50	2.818		
AlP	5.45	2.801	2.50	2.59
	5.39	2.685		
AlAs	5.62	2.573	2.32	2.18 [c]
	5.59	2.543		
GaP	5.44	2.484	2.39	2.80 [d]
	5.30	2.468		
GaAs	5.65	1.062	1.52	1.58 [c]
	5.51	1.717		
AlN	4.37	6.010		
	4.31	6.077		
GaN	4.52	3.910	3.52 [e]	
	4.37	4.621		
AlSb	6.13	1.956	1.68	1.64
	6.06	2.009		
GaSb	6.12	0.259	0.80	0.62
	5.95	0.925		
InP	5.87	1.804	1.42	1.44
	5.66	2.550		
InAs	6.04	0.259	0.41	0.31
	5.85	1.396		
InSb	6.48	0.000	0.23	0.08
	6.28	0.996		

[a]Reference 5.
[b]Reference 14.
[c]Reference 6.
[d]Reference 7.
[e]Reference 15.

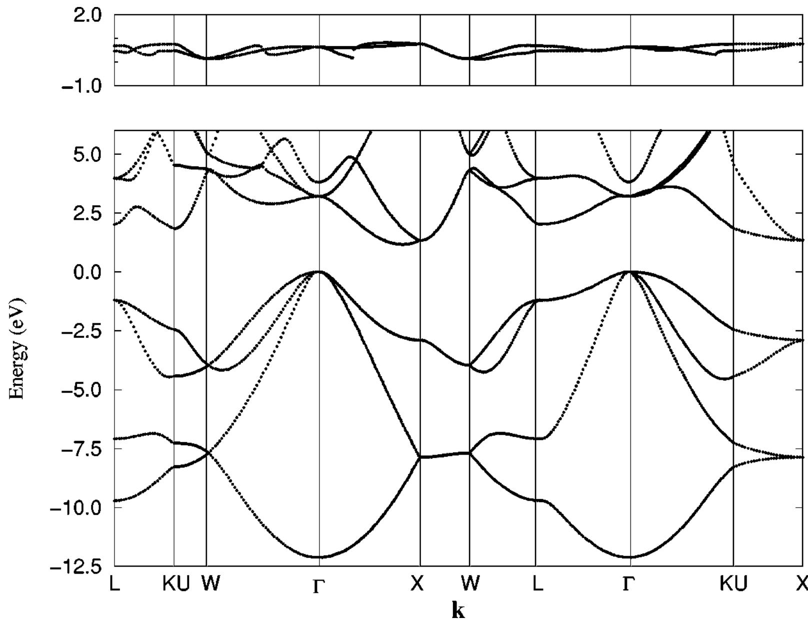

FIG. 1. Band structure of Si (lower panel) and Δ_{fi} correction for the two lowest conduction levels (upper panel). The apparent cusps in Δ_{fi} correspond to band crossings.

exchange-only case that this term is indeed small, but a more thorough justification for omitting this term is lacking.

III. IMPLEMENTATION AND RESULTS

We used the familiar LDA expression for the exchange-correlation energy:

$$\bar{\varepsilon}_{\mathrm{xc}}^{(n)}(\mathbf{r})\approx\varepsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r})=\varepsilon_{\mathrm{xc}}^{\mathrm{hom}}(\rho_n(\mathbf{r})), \tag{28}$$

where $\varepsilon_{\mathrm{xc}}^{\mathrm{hom}}(\rho)$ is the exchange-correlation energy per particle of a homogeneous electron gas of density ρ. For the latter we use the results of Ceperley and Alder as they have been parametrized by Perdew and Zunger.[16] The interaction between valence electrons and ionic cores is described by the nonlocal norm-conserving pseudopotentials of Bachelet *et al.*[17] The conduction-band structure was corrected using Eq. (11) while Eq. (26) was used with $\bar{\varepsilon}_{\mathrm{xc}}^{(0)}(\mathbf{r})=\varepsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r})$ and $V_{\mathrm{xc}}^{(0)}(\mathbf{r})=V_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r})$. The highest valence band played the role of the initial state ψ_i at each k point in the Brillouin zone.

In Table I we present band gaps at both the experimental lattice constant and that derived from total energy minimization (we refer to this as the theoretical lattice constant). We use the latter lattice constant in the figures displaying the band structures. For GeC and SiGe, which do not occur in the zinc-blende structure, the lattice constant labeled ''experimental'' is the average of the experimental lattice constants of the elemental crystals. We used a plane-wave basis with a cutoff of 24 Ry, except for C, SiC, and GeC (60 Ry) and AlN and GaN (70 Ry). A grid of $8\times8\times8\mathbf{k}$ points was used in the full Brillouin zone, reduced to a smaller set according to the symmetry of the crystal.

We calculated the band structure of seventeen semiconductors and insulators in the zinc-blende or diamond lattice structure which we discuss in groups below.

Elemental group-IV semiconductors. The theory works essentially perfectly for Si, where the gap is the same with

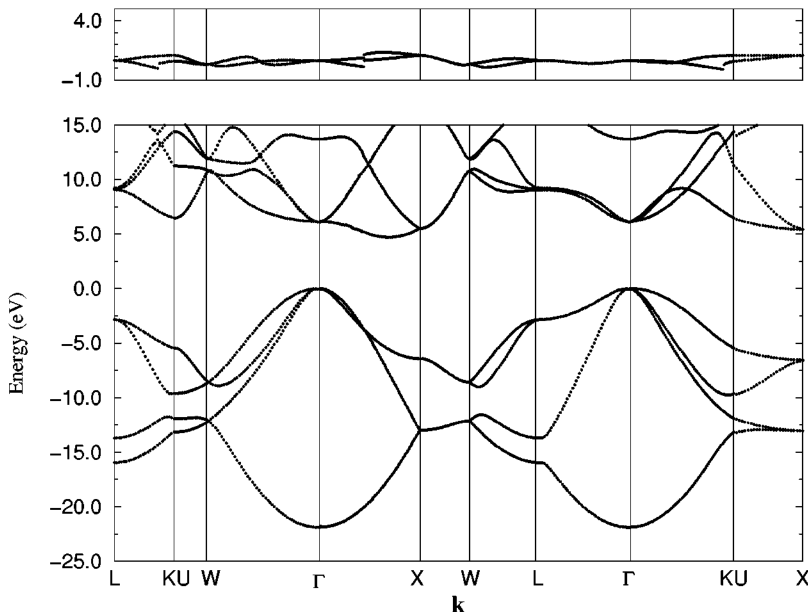

FIG. 2. Same as Fig. 1 for C.

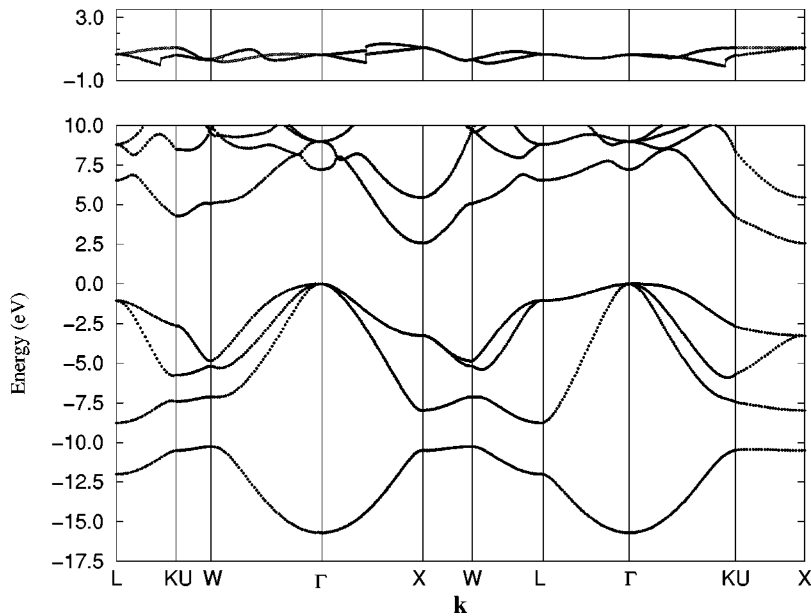

FIG. 3. Same as Fig. 1 for SiC.

the experimental value for the theoretical lattice constant and is off by 4.5% at the experimental lattice constant. For diamond the gap is off by 15%. For germanium, at the experimental lattice constant the method gives a zero gap, but the situation is better at the theoretical lattice constant, where the gap is off by 32%. We give the explicit band structures of Si and C in Figs. 1 and 2 as examples.

For both Si and C the band gap is indirect, occurring between Γ [the valence-band maximum (VBM) as in all the semiconductors we considered] and a point along the ΓX line [the conduction-band minimum (CBM)]. For Ge the gap is direct.

Comparing these results with those from the work of Fritsche and Gu,[10] which use a model correlation factor for ε_{xc} rather than a local approximation, we see that these authors achieved a better result for the band gap of C; we believe this difference is due to the small size of the core in C which results in larger density gradients, making the local approximation employed here less accurate.

Compound group-IV semiconductors. Results in good agreement with experiment are also obtained for SiC, where the gap is off by 9%. It is interesting that the error in SiC is close to the average of the percentage errors for Si and C. This leads us to believe that the gap values for the other two mixed group-IV materials (SiGe and GeC), if they could be synthesized in the zinc-blende structure, would be correct to about 20%. We give the explicit band structure of SiC in Fig. 3 as an example.

The minimum gap is indirect for SiC, SiGe, and GeC with the CBM occurring at X for SiC and GeC, and along ΓX for SiGe.

Common polar III-V semiconductors. We performed calculations for almost all polar III-V semiconductors which are shown in Table I in the order they have in the Periodic Table. For Al compounds and GaAs we obtained good results within about 10% of experiment. For GaP the error is only 3%. We give the explicit band structure of GaAs in Fig. 4 as an example.

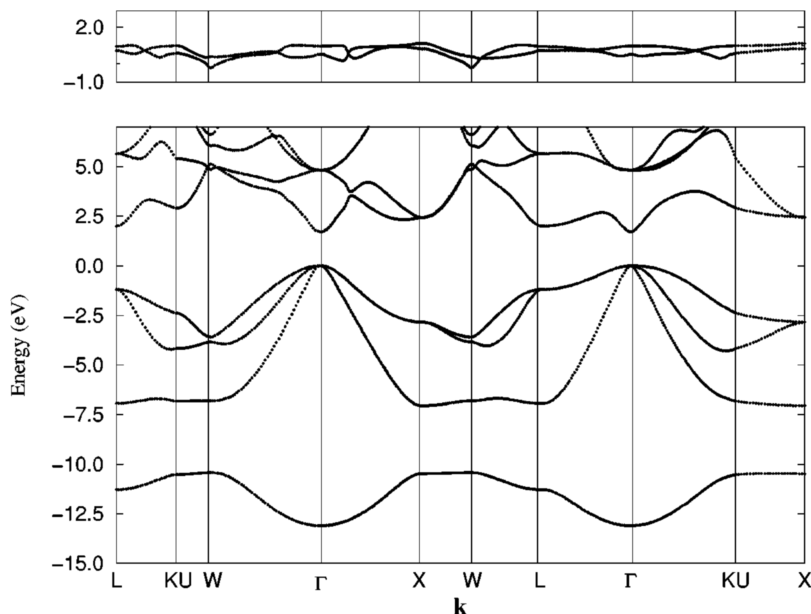

FIG. 4. Same as Fig. 1 for GaAs.

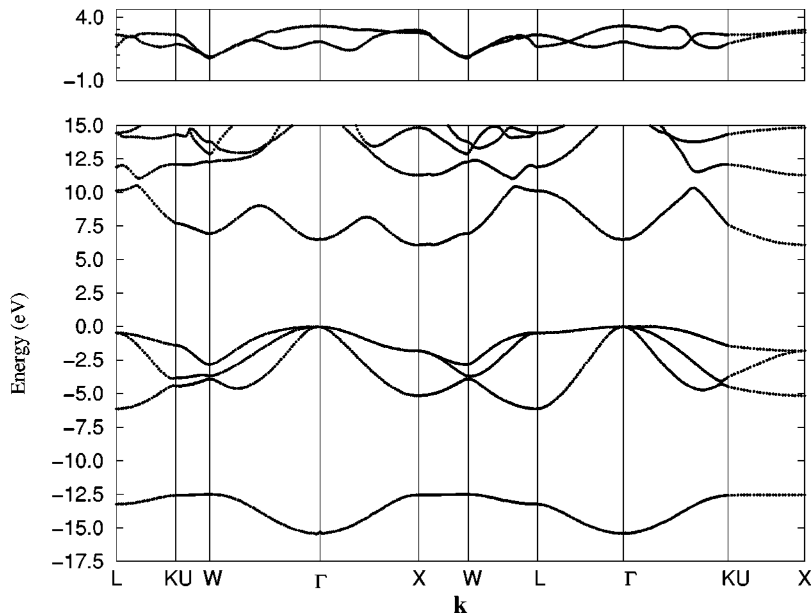

FIG. 5. Same as Fig. 1 for AlN.

For AlP and AlAs the gap is indirect with the CBM at X. GaAs has a direct gap. For GaP we found an indirect gap with CBM along ΓX at the theoretical lattice constant, while the same material at the experimental lattice constant has a direct gap.

Group-III nitride wide gap semiconductors. Recently much attention has been focused on III-V materials with N as the group-V element, which are wide gap semiconductors with possible applications in optoelectronics. These materials appear both in the wurtzite and the zinc-blende (metastable) structures. In Figs. 5 and 6 we give the band structures for AlN and GaN as obtained from the present calculations for the zinc-blende structure. For AlN, where we were not able to find experimental data for the zinc-blende structure, we estimate the band gap we calculated should deviate from the experimental value by about 10%.

GaN was found to have a direct gap at the theoretical lattice constant and an indirect gap at the experimental lattice constant with the CBM occurring along ΓX but very close to Γ. AlN has an indirect minimum gap with the CBM at X.

Compound III-V semiconductors with fifth-row elements. The gap values we obtained for III-V semiconductors involving the fifth-row elements In and Sb are not as satisfactory. We believe the neglect of spin-orbit effects is partially responsible for these poor results. Apparently, relativistic effects are important when studying the electronic behavior of heavier elements like In and Sb. The results are better for III-Sb's because due to the polar bond, the Sb core is screened; for the same reason, results are particularly poor for compounds containing In.

All these materials were found to have a direct minimum gap, except AlSb, where the CBM occurs along the ΓX line.

Statistical data. For the six materials for which we give the band structures (Figs. 1–6), the correction shows similar

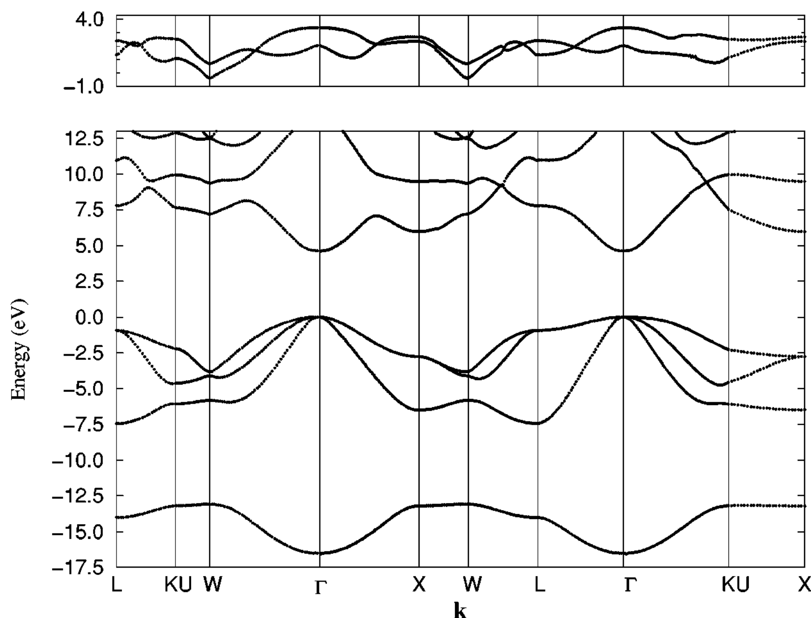

FIG. 6. Same as Fig. 1 for GaN.

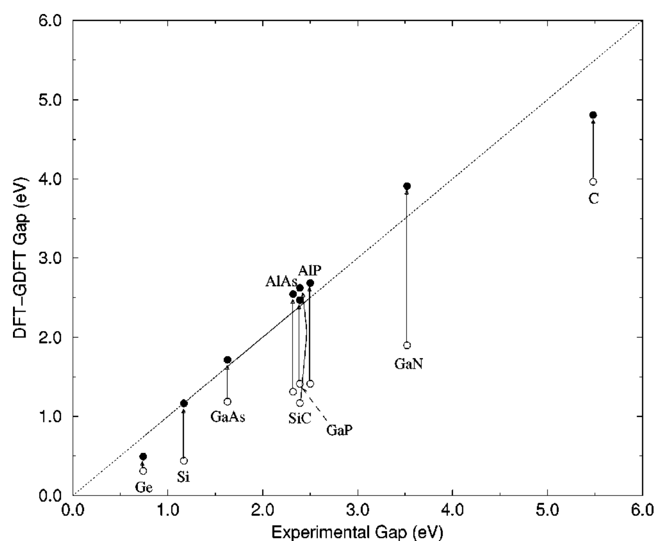

FIG. 7. DFT (open circles) and GDFT (filled circles) band gap vs the experimental value for several semiconductors in the zinc-blende structure.

behavior: The mean value $\langle \Delta_{fi} \rangle$ is about 36% of the energy gap and has a fluctuation of about 33% around its mean value.

Δ_{fi} is positive for the first conduction band, except in some cases (C,GaN) around the point W. In particular, Δ_{fi} is positive for all materials in the region Γ to X, which determines the minimum band gap. Accordingly, the minimum DFT/LDA band gap is increased in all cases, by about 40% on average. This correction cannot be treated as a constant, since it has large fluctuations (see Figs. 1–6), especially for the two nitrides (see Figs. 5 and 6).

IV. SUMMARY AND CONCLUSIONS

In summary, GDFT/LDA/pseudopotential calculations can be used to derive reasonable band structures for elements in intermediate rows of the Periodic Table like Si, AlP, AlAs, GaAs, etc. The success of the method is obvious from Fig. 7 where theoretical band gaps are plotted versus the experimental values. The arrows show the correction to the DFT values and clearly most points move close to the ''exact theory'' line when the GDFT correction is applied. We excluded from this figure the case of compound III-V semiconductors which involve fifth-row elements (In and Sb), since the neglect of spin-orbit coupling in the present work gives considerably poorer results for those materials. In the same figure the experimental lattice constant is used for GaN since the theoretical one is off by more than 3.5%, which is significantly worse than the rest.

We suggest that the simplicity of the method, which is based on the well-known DFT/LDA scheme, its physical clarity, and the relatively small computational effort it requires render it a useful tool for reasonably reliable band-structure calculations. We believe this work demonstrates that the well studied DFT/LDA/pseudopotential scheme can give results comparable to more rigorous methods, at least for materials containing third- and fourth-row elements. For other cases, qualitative results can be obtained. Since the correction to the band structure is not constant as a function of **k**, as the upper panels in Figs. 1–6 demonstrate, this theory appears to be more realistic than a ''scissor operator'' which is often used as an *ad hoc* fix of DFT/LDA band-structure calculations. Nevertheless, the method does involve several approximations as discussed in Sec. II C, some of which cannot be rigorously justified. As such it cannot be considered a substitute for more rigorous exact treatments, like GW theory.

ACKNOWLEDGMENT

The calculations were performed at the Computational Center of the University of Crete.

*On leave from the Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[3] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16 533 (1996).
[4] L. Hedin, Phys. Rev. **139**, A796 (1965).
[5] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); Phys. Rev. B **34**, 5390 (1986).
[6] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986); Phys. Rev. B **37**, 10 159 (1988).
[7] F. Gygi and A. Baldereschi, Phys. Rev. Lett. **62**, 2160 (1989).
[8] X. Zhu and S. G. Louie, Phys. Rev. B **43**, 14 142 (1991).
[9] L. J. Sham and M. Schlüttter, Phys. Rev. B **32**, 3883 (1985).
[10] L. Fritsche, Phys. Rev. B **33**, 3976 (1986); Physica B **172**, 7 (1991); J. Cordes and L. Fritsche, Z. Phys. D **13**, 345 (1989); L. Fritsche and Y. M. Gu, Phys. Rev. B **48**, 4250 (1993); L. Fritsche, *Excited States and Electron-atom Scattering*, in *Density Functional Theory*, edited by E. K. U. Gross and R. M. Dreizler (Plenum Press, New York, 1995).
[11] M. Biagini, J. Phys.: Condens. Matter **8**, 2233 (1996).
[12] L. Fritsche, J. Phys.: Condens. Matter **8**, 2237 (1996).
[13] *Physics of Group IV Elements and III-V Compounds*, of *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, Group III, Vol. 17a,* edited by O. Madelung, M. Schultz, and H. Weiss (Springer, New York, 1982).
[14] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. B **48**, 17 791 (1993).
[15] S. Strite, J. Ruan, Z. Li, A. Salvador, H. Chen, D. J. Smith, W. J. Choyke, and H. Morkos, J. Vac. Sci. Technol. B **9**, 1924 (1991).
[16] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[17] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).