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Self-interaction correction to the local-density approximation in the calculation of the energy band gaps of semiconductors based on the full-potential linearized augmented-plane-wave method

N. Hamada and S. Ohnishi
Fundamental Research Laboratories, NEC Corporation, 4-1-1 Miyazaki,
Miyamae-ku, Kawasaki, Kanagawa 213, Japan

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We present a new procedure for the self-interaction correction, taking into account the contribution from atomic regions. It much improves the calculated energy band gaps of diamond, Si, AlAs, and GaAs and superlattices of $(\mathrm{AlAs})_1(\mathrm{GaAs})_1$ and $(\mathrm{AlAs})_2(\mathrm{GaAs})_2$ compared with the local-density approximation.

It is now of great importance to find an efficient way of calculating the energy band gaps of semiconductors and insulators by applying the Hohenberg-Kohn-Sham density-functional theory.[1] Since the local-density approximation (LDA) to the exchange-correlation potential has been recognized as not being an adequate approximation for the direct calculation of the single-particle excitation energy despite its success in describing ground-state properties,[2] considerable efforts using various approaches have been made to improve the method for solving the energy-band-gap problem. Perdew and Levy[3] and Sham and Schluter[4] pointed out the central problem in the energy-band-gap calculation based on the density-functional scheme: The energy gap given by the difference of one-electron orbital energies of the valence and conduction bands based on the LDA needs the correction term Δ related to the electron self-energy operator, which originates from the discontinuity in the derivative of the exchange-correlation energy with respect to the occupation number. There has been intensive discussion concerning the effects of the electron self-energy on the energy gap with direct application of the energy-dependent nonlocal-density-functional scheme[5,6] and the self-interaction correction (SIC) scheme.[7] In both approaches, the energy gaps are very much improved by taking into account the self-energy potential which requires elaborate calculations. The SIC scheme is found to be very efficient for localized electron systems like free atoms[8,9] and ionic and rare-gas crystals,[7,9] which, in fact, implies the importance of SIC for the valence electrons in semiconductors, because a considerable amount of charge is localized around the atomic region even in covalent bonding. However, the same procedure using Wannier functions as in the work by Heaton and co-workers[7] for LiCl is not applicable to semiconductors with smaller energy gaps. Thus we attempt to introduce a new procedure for applying SIC to energy band calculations. In this paper, we focus on the "atomic" contributions of SIC to the energy gap.

Our scheme for the energy band calculation is based on the all-electron, full-potential, linearized, augmented-plane-wave (FLAPW) method[10] with energy parameters and corresponding radial wave functions for the basis functions in the muffin-tin sphere.[11] The eigenfunction with the wave number $\mathbf{k}$ and band index n is given by

$$\Psi^{n\mathbf{k}}(\mathbf{r})=\begin{cases}\sum\limits_{\mathbf{G}} C_{\mathbf{G}}^{n\mathbf{k}} \exp[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}] & \text{in the interstitial region,}\\ \sum\limits_{i,l,m} B_{ilm}^{n\mathbf{k}}\phi_{il}(r)Y_{lm}(\hat{\mathbf{r}}) & \text{in the muffin-tin sphere,}\end{cases}$$

where, in accordance with the augmentation of plane waves, $B_{ilm}^{n\mathbf{k}}$ is a linear function of the expansion coefficient $C_{\mathbf{G}}^{n\mathbf{k}}$, and ϕ_{il} is the basis function in the muffin-tin sphere associated with the ith energy parameter for each angular momentum l. Eigenstates are determined by the variation with respect to $C_{\mathbf{G}}^{n\mathbf{k}}$ of the Hamiltonian, $H=H_{\mathrm{LDA}}+\Delta V^{\mathrm{SIC}}$, with the self-interaction correction potential ΔV^{SIC}. We investigate SIC effects on the energy band structure by taking into account the atomic SIC in an approximate way as

$$\Delta V^{\mathrm{SIC}}=\begin{cases}0 & \text{in the interstitial region,}\\ \sum\limits_{i,l} |il\rangle v_{il}^{\mathrm{SIC}}(r)\langle il| & \text{in the muffin-tin sphere,}\end{cases}$$

where $v_{il}^{\mathrm{SIC}}(r)$ represents the atomic self-interaction corrected potential. Inside the muffin-tin sphere, we can calculate SIC in the same way as in the free atom case[8] except that we allow a noninteger occupation number at each quantum state. In this treatment, we consider two states, $i=c,v$, corresponding to the conduction and valence bands, respectively. According to Takeda and Kübler,[11] two radial wave functions, $\phi_{il}(r)$, are prepared for each angular momentum l. They are solutions of the Schrödinger equation corresponding to two energy parameters E_{il} with the spherical part of the potential given by the LDA $v(r)$ and its SIC $v_{il}^{\mathrm{SIC}}(r)$ in the muffin-tin sphere for each spin (spin index is omitted for brevity):

$$\left[-\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{l(l+1)}{2r^2}+v(r)+v_{il}^{\mathrm{SIC}}(r)\right]\phi_{il}(r)=E_{il}\phi_{il}(r)\ .$$

The SIC potential[8] is defined by assigning an effective occupation number f_{il} for each state to the atomic SIC potential as

$$v_{il}^{\mathrm{SIC}}(r) = -f_{il}\left[v_{\mathrm{xc}}(\rho_{il},0) + \int d^3r' \frac{\rho_{il}(r')}{|\mathbf{r}-\mathbf{r}'|} \right] ,$$

where v_{xc} is the exchange-correlation potential functional[12] and $\rho_{il}(r) = |\phi_{il}(r)|^2/4\pi$. f_{vl} for the valence band is given by the partial density of states $D_l(E)$ with angular momentum l,

$$f_{vl} = \int_{-\infty}^{E_F} D_l(E)dE ,$$

$$D_l(E) = [1/(2l+1)] \sum_{n,\mathbf{k}} \sum_{i,l,m} \delta(E - \varepsilon_{n\mathbf{k}}) B_{ilm}^{n\mathbf{k}*} O_{ijl} B_{jlm}^{n\mathbf{k}} ,$$

where $O_{ijl} = \int r^2 dr\, \phi_{il}(r)\phi_{jl}(r)$. This fractional occupation number gives the effective weight of the SIC potential for each electron of the quantum state l in the atomic region.[13] The energy parameter E_{vl} for the valence band is set as the center of gravity of the partial density of states for the valence band

$$E_{vl} = (1/f_{vl}) \int_{-\infty}^{E_F} E D_l(E)dE .$$

As for the conduction band, f_{cl} and E_{cl} are set so as not to change the LDA results $f_{cl} = 0$ and E_{cl}, the energy of the lowest unoccupied level, because the self-interaction energy of the extended electron is considered to be negligible. This procedure is incorporated in the whole self-consistent scheme of the LDA calculation. E_{il} and f_{il} are determined self-consistently.

Figure 1 shows the energy band structures of Si as a typical case. We have found that the effect of the SIC on the valence energy levels is to pull down the energy levels globally. The large shift of the valence band is due to the direct effect of the SIC potential. The small shift of the conduction band is caused by a change in the charge distribution due to the SIC, because the SIC potential does not affect the conduction band under the condition of $f_{cl} = 0$. As a result, the energy gap becomes larger in the SIC-LDA than in the LDA. Table I shows the fundamental energy gaps for several semiconductors. The energy gaps in our new SIC scheme, SIC-LDA, are from 57% to 95% of experimental values, while those in the LDA are only 22% to 75%.[14]

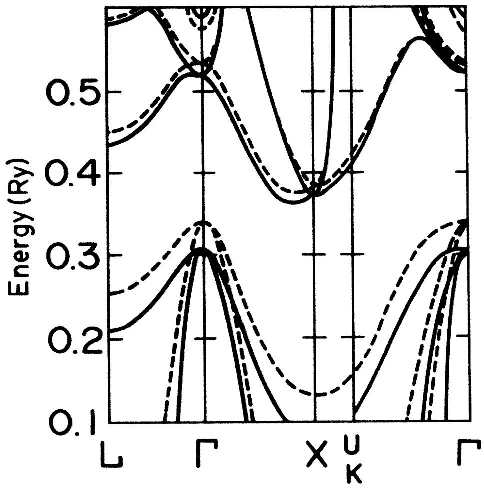

FIG. 1. Energy band structures of Si along high symmetry lines. Solid curves represent the SIC-LDA calculation, and dashed curves the LDA. Fundamental energy band gap is given by the difference between the conduction band minimum near X point and the valence band top at Γ point. Note that the energy gap in SIC-LDA is about two times of that in LDA.

TABLE I. Fundamental energy band gaps of semiconductors by the FLAPW method with self-interaction correction (in eV).

	Theory			
	LDA	SIC-LDA	LDA+$\|\Delta E_{v1}\|$	Experiment[a]
Diamond	4.07	5.17	5.98	5.48
Si	0.46	0.73	1.26	1.17
AlAs	1.32	2.08	2.27	2.23
GaAs	0.29	0.83	1.30	1.52
$(\mathrm{AlAs})_1(\mathrm{GaAs})_1$	0.84	1.56	1.92	2.05[b]
$(\mathrm{AlAs})_2(\mathrm{GaAs})_2$	0.93	1.61	1.95	2.02[b]

[a] Reference 15. [b] Reference 16.

The fractional occupation numbers f_{vl} listed in Table II indicate how many valence electrons are localized inside the muffin-tin sphere, for example, 0.9 s electrons and 1.3 p electrons in Si, and 1.5 sp electrons in the Ga site and 3.0 in the As site in GaAs. More than one-half of the valence electrons are localized in the muffin-tin region, and they contribute to the SIC. The remaining effects of the SIC in the interstitial region, which will be taken into account by establishing additional atomic regions for the bond charges with the atomic number $= 0$, will be not so big but will improve the results.

Shifts from the LDA values of the energy parameters E_{vl} due to the SIC are also listed in Table II. Among them, the energy-parameter shift for $l = 1$, ΔE_{v1}, is the most important parameter for the band-gap problem because the state at the top of the valence band is comprised almost entirely of the p state of the C, Si, and As atoms in GaAs, AlAs, and their superlattices, which means that the top of the valence band is very sensitive to the SIC of the p

TABLE II. Effective occupation f_{vl} and shifts of energy parameters E_{il} due to self-interaction correction in the muffin-tin sphere.

		l	f_{vl}	ΔE_{vl}
Diamond	C	0	0.37	−2.22
		1	0.27	−1.91
Si	Si	0	0.46	−1.67
		1	0.21	−0.80
AlAs	Al	0	0.32	−1.27
		1	0.12	−0.99
	As	0	0.64	−2.61
		1	0.30	−0.95
GaAs	Ga	0	0.40	−1.55
		1	0.13	−1.02
	As	0	0.64	−2.71
		1	0.28	−1.01

state in the atomic region. The energy gap is corrected by this energy parameter shift ΔE_{v1}, which gives the rigid-band-shift model. As shown in Table I, LDA+$|\Delta E_{v1}|$-corrected energy band gaps show remarkable agreement with experimental results. Energy gaps at high-symmetry points also agree very well with the experiments:[15] 2.19 eV (2.1 eV in experiment) at the L point in Si, 2.27 (2.23) at X in AlAs, and 1.86 (1.82) at L in GaAs. This good agreement implies that the dominant contribution of the SIC to the energy-band-gap problem comes from the "atomic" part. It should be noted that the values of ΔE_{v1} in GaAs and AlAs at each atomic site are almost the same, -1 eV, which is related to the homogeneity of the SIC potential.[9]

The calculated energy band gaps of the superlattices consisting of AlAs and GaAs agree quite well with the experimental results[16] at the Γ point. The averaged As ΔE_{v1} is used for the correction. In both cases, averaged lattice constants of GaAs and AlAs are used. In the two-by-two-layer superlattice, the energy gap at the L point is 2.29 eV by the LDA+$|\Delta E_{v1}|$ method, which clearly indicates a direct gap. In the one-by-one-layer case, the energy gaps are 1.92 and 1.94 eV at the Γ and L points, respectively. The difference between them is very small.

We can conclude from our analysis of the energy band gaps of semiconductors that the inclusion of the atomic SIC to the energy band calculation improves the energy gaps considerably. The effect of SIC on the energy gap strongly depends on the bonding nature and charge density at the state of the valence band top. Different from other treatments of the direct nonlocal potential and the SIC with the Wannier function, the present approach essentially does not change the calculational effort and is flexible enough to make it generally applicable and accurate.

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