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Implementation of an approximate self-energy correction scheme in the orthogonalized linear combination of atomic orbitals method of band-structure calculations

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Based on the Sterne-Inkson model for the self-energy correction to the single-particle energy in the local-density approximation (LDA), we have implemented an approximate energy-dependent and **k**-dependent *GW* correction scheme to the orthogonalized linear combination of atomic orbital-based local-density calculation for insulators. In contrast to the approach of Jenkins, Srivastava, and Inkson, we evaluate the on-site exchange integrals using the LDA Bloch functions throughout the Brillouin zone. By using a **k**-weighted band gap E_g and a plasmon frequency ω_p determined by valence-electron density for the estimation of the dielectric constant, our approach retains the first-principles nature for the single-particle energy correction. Test calculations on semiconductors such as diamond, Si, Ge, GaAs, GaP, and ZnSe show good results with the *GW*-corrected gap values generally within 10% of the experimental values. It is shown that an accurate and well-converged LDA result is very important for the correct self-energy correction, and its convergence with respect to the number of **k** points needed in the computation is much slower than that in the LDA calculation.

I. INTRODUCTION

In recent years, the density-functional theory [DFT] (Refs. 1 and 2) has been recognized as a very successful and practical theory for the study of solids and molecules. It provides a formal theoretical justification in solving a many-particle system by using an effective potential for single-particle calculation. DFT and the related local-density approximation (LDA) has been very successful in calculating the ground-state properties. However, in case of semiconductors and insulators, the band gap predicted by the DFT in the LDA is always smaller than that observed experimentally. This posted an enormous difficulty to the physics of the materials that involves unoccupied states such as in the optical absorptions or in inverse photoemission. This apparent shortcoming in the DFT-LDA theory and its appropriate remedy has attracted the attention of many theorists in condensed-matter physics.

Generally speaking, there are two approaches in addressing the problem of gap underestimation by the DFT-LDA theory. Since the gap can be interpreted as the difference in the LDA total energies of the N and the $N-1$ particle systems,[3] some researchers suspect that the major culprit is with the LDA approximation for the exchange-correlation potential, which is obtained from that of a uniform electron gas. Perhaps the LDA excitation energies, and hence the gap value, can be improved by going beyond the local approximation. To this end, many different strategies have been tried. For example, gradient correction to the density expansion[4,5] has been applied to account for the nonhomogeneity of the electron density in atoms, molecules and solids.[6–12] The need for a self-interaction correction (SIC) (Ref. 13) has been recognized. In the LDA, the Hartree term and the exchange term no longer cancel exactly, resulting in some degree of unphysical self-interaction. Band calculations with a SIC have been attempted by several groups.[14–16] Carlsson introduced an extra electrostatic energy term to account for the fact that the exchange-correlation hole is not totally screened under the LDA.[17] All these and similar efforts have led to a certain degree of improvement of the calculated gap values in insulators, but there is no conclusive evidence for unambiguous success in any of these strategies.

The other approach is to go beyond the DFT framework, and use a Green's-function formalism to study the self-energy term of quasiparticles in the many-particle system. This approach of using Green's function for quasiparticle excitation was pioneered by Hedin and Lundquist more than 20 years ago.[18,19] Due to the rapid advance of computing technology in recent years, and a steady progress in the techniques of computational physics, an accurate first-principles calculation of quasiparticles becomes possible.[20] From the work of Sham and Schlüter[21] and also Perdew and Levy,[22] it was shown that in semiconductors and insulators, the real single-particle excitation gap E_g differs from that of the Kohn-Sham gap ε_g by a finite amount Δ such that $E_g=\varepsilon_g+\Delta$. This difference originates from the discontinuity of the exchange-correlation potential across the energy gap. Later investigations[23] indicate that this discontinuity in the exchange-correlation potential is the dominating factor and can account for about 80% of the total error in the band gap. Hence much of the recent research concentrates on this second front.[23–28]

The elementary excitation of a many-particle system is based on the concept of the quasiparticle. The energy of a quasiparticle is manifested as the peak position in the spectral function, while the width of the peak is related to its lifetime. For a nonuniform electron system, the quasiparticle energy and wave function are determined from the Dyson equation:[19]

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$$(T+V_{\rm ext}+V_H)\Psi_{nk}(\mathbf{r})+\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}',E_{nk})\Psi_{nk}(\mathbf{r}')=E_{nk}\Psi_{nk}(\mathbf{r}) . \quad (1)$$

In Eq. (1), T stands for the kinetic energy, $V_{\rm ext}$ and V_H are the external and Hartree-Coulomb potentials, respectively. Σ is the self-energy operator which includes all the exchange interactions among the electrons. Σ is nonlocal, non-Hermitian, and energy dependent. According to Hedin's theory,[18] the self-energy operator is determined by a set of self-consistent equations involving the Green's function G. After repeated iterations, the self-energy operator can be expressed as the lowest order in the perturbation series expansion of the screened Coulomb potential W, resulting in the so-called GW approximation:

$$\Sigma(\mathbf{r},\mathbf{r}',E)=\frac{i}{2\pi}\int dE'G(\mathbf{r},\mathbf{r}',E-E')W(\mathbf{r},\mathbf{r}',E')e^{i\delta E'} , \quad (2)$$

where $G(\mathbf{r},\mathbf{r}',E-E')$ is the single-particle Green's function, and δ is an infinitesimally small quantity. The screened Coulomb potential $W(\mathbf{r},\mathbf{r}',E')$ can be expressed as

$$W(\mathbf{r},\mathbf{r}',E)=\int \epsilon^{-1}(\mathbf{r},\mathbf{r}'',E)V(\mathbf{r}'',\mathbf{r}')d\mathbf{r}'' , \quad (3)$$

where ϵ^{-1} is the inverse dielectric matrix, and V is the bare Coulomb interaction. In general, the generalized Levine-Louie model[29] is used to obtain the matrix elements of ϵ^{-1}, using the exact sum rule to extend to finite frequency ranges.

From the work of Hybertsen and Louie (HL),[20] it is generally accepted that satisfactory results can be obtained by the GW approximation for the self-energy correction. It is also shown that the correction can be obtained from the first one or two iterations in Hedin's equation. Further iteration is unnecessary. This is because the self-energy operator Σ is expanded as a series in the screened Coulomb interaction W which has a faster convergence, not the bare Coulomb interaction V. For this reasons, most recent quasiparticle calculations were based on the GW approximation. However, because of the nonlocal nature of the self-energy operator and its energy dependence, a first-principles calculation for the self-energy correction in the GW approximation is extremely complicated and time consuming. This has greatly limited the scope of its application. Most of such calculations have been limited to bulk single crystals,[20,30–34] or surfaces, interfaces, and short-period semiconductor superlattices.[35] Only very recently, the method has also been applied to more complex systems such as C_{60} crystals.[36] Nevertheless, there remains a strong interest in finding a simpler way to calculate the GW-based self-energy correction that is computationally less intensive. Hanke and Sham (HS),[37] and also Stern and Inkson (SI),[38] presented rather similar models along this line. They used a two-band tight-binding model and an approximate expression for the plasmon pole in the screened Coulomb potential to derive an analytic formula for the self-energy operator. Very recently, Jenkins, Srivastava, and Inkson (JSI) (Ref. 39) used an extended version of the SI model to estimate the self-energy corrections for five semiconductor crystals, which corrected an error in the earlier paper and included a more complete discussion of the on-site exchange term. With the exception of ZnSe, the corrected band gaps are in good agreement with the experimental data and also with other more rigorous theoretical calculations. Bechstedt and Del Sole[40] made static approximation to the Coulomb hole-screened exchange (COHSEX) (to be explained below) in the self-energy calculation, while ignoring the effect of the local field and dynamically screened interaction. They used a model dielectric function and tight-binding wave function to derive an expression for the self-energy correction. Very recently, they introduced two parameters to account for the contributions for the local field and dynamic screening to the self-energy.[41] Gygi and Baldereschi[42] separated the self-energy corrections into short- and long-range parts. The short-range part is replaced by the LDA-exchange-correlation potential, and the long-range part is obtained by making the static COHSEX approximation. They have obtained quite satisfactory results based on this model.

In Sec. II, we present the Sterne-Inkson model and its analytic formula for the gap correction. In Sec. III, we outline the method of applying this model to the first-principles orthogonalized linear combinations of atomic orbitals (OLCAO) method of band-structure calculation. In Sec. IV, we present and discuss the results of applying this method of self-energy correction to six semiconductor crystals: diamond, Si, Ge, GaP, GaAs, and ZnSe. Section V gives a brief conclusion for the work completed.

II. STERNE-INKSON MODEL OF SIMPLIFIED SELF-ENERGY CORRECTION

Under the GW approximation, the self-energy operator Σ is determined from the Green's function G and the screened Coulomb potential according to Eq. (3). Because the self-consistent Kohn-Sham equation under the LDA is reasonably accurate in describing the ground-state properties of a solid, the self-energy calculation for quasiparticles, in the first-order approximation, entails the construction of the Green's function from the LDA eigenenergies ε_{nk} and wave functions $\Psi_{nk}(\mathbf{r})$:

$$G(\mathbf{r},\mathbf{r}',E)=\sum_{n,k}\frac{\Psi_{nk}(\mathbf{r})\Psi^*_{nk}(\mathbf{r}')}{E-\varepsilon_{nk}-i\delta_{nk}} , \quad (4)$$

where $\delta_{nk}=0^+$ (0^-) when ε_{nk} is less (greater) than the chemical potential μ. Thus, from Eqs. (2) and (3), it is obvious that the key to the accurate evaluation of quasiparticle self-energy is the calculation of a full inverse dielectric matrix $\epsilon^{-1}(\mathbf{r},\mathbf{r}',E)$ which accounts for the dynamic screening (energy dependence E) and the local-field effect (nondiagonal matrix in $\mathbf{r}$ and $\mathbf{r}'$).

If the quasiparticle energies in semiconductors or insulators are well defined, we can ignore the contribution from the imaginary part of Σ to the quasiparticle energy spectrum, and consider only the real part. The real part of Σ consists of two terms. The first is from the imaginary part of G and the real part of W. This is the dynamically screened exchange interaction originated from the pole of the Green's function, and is denoted by Σ_{SX}. The second part is from the real part of G and the imaginary part of W, which reflects the contribution from the screened Coulomb interaction of the hole, and is denoted by Σ_{CH}. These two terms constitute the so-called COHSEX approximation:[20]

$$\Sigma(\mathbf{r},\mathbf{r}',E)=\Sigma_{SX}(\mathbf{r},\mathbf{r}',E)+\Sigma_{CH}(\mathbf{r},\mathbf{r}',E)\ . \tag{5}$$

Sterne and Inkson,[38] using a two-band tight-binding model with a band gap E_g and in the random-phase approximation (RPA), obtained an approximate dielectric function:

$$\epsilon(\mathbf{r},\mathbf{r}',E)=\delta(\mathbf{r}-\mathbf{r}')-N_0(E)\sum_{R,\nu}\int d\mathbf{r}''V(\mathbf{r}-\mathbf{r}'')A_\nu(\mathbf{r}''-R)A_\nu^*(\mathbf{r}'-R)\ , \tag{6}$$

where $N_0(E)=-4E_g/(E_g^2-E^2)$, and $A_\nu(\mathbf{r}-\mathbf{R})=\phi_\nu^{c\,*}(\mathbf{r}-R)\phi_\nu^v(\mathbf{r}-\mathbf{R})$. ϕ_ν^c and ϕ_ν^v are the Wannier functions for the conduction band (CB) and the valence band (VB) respectively. ν denotes the bond index, R the lattice vector, and V is the bare Coulomb potential. Ordinarily, the transformation from ϵ to ϵ^{-1} is a rather complicated process. However, under the tight-binding approximation, it can be shown[43,44] that

$$\epsilon^{-1}(\mathbf{r},\mathbf{r}',E)=\delta(\mathbf{r}-\mathbf{r}')-\frac{4E_g}{E_g^2+(\hbar\omega_p)^2-E^2}\sum_{R,\nu}\int d\mathbf{r}''V(\mathbf{r}-\mathbf{r}'')A_\nu(\mathbf{r}''-R)A_\nu^*(\mathbf{r}'-R)\ . \tag{7}$$

where the plasmon energy $\hbar\omega_p$ is given by

$$(\hbar\omega_p)^2=(4\pi\hbar n e^2)/(m\Omega_0)\ , \tag{8}$$

Ω_0 is the cell volume, and n is the valence electron density.

By substituting (7) into (3), the screened Coulomb interaction can be expressed as

$$W(\mathbf{r},\mathbf{r}',E)=V(\mathbf{r}-\mathbf{r}')-\frac{4E_g}{E_g^2+(\hbar\omega_g)^2-E^2}\times\sum_{\mathbf{R},\nu}D_\nu(\mathbf{r}-\mathbf{R})D_\nu^*(\mathbf{r}'-\mathbf{R})\ , \tag{9}$$

$$D(\mathbf{r}-\mathbf{R})=\int d\mathbf{r}'v(\mathbf{r}-\mathbf{r}')A_\nu(\mathbf{r}'-R)\ . \tag{10}$$

$D(\mathbf{r}-\mathbf{R})$ represents the dipole moment at $\mathbf{r}$ due to the bond ν in cell $\mathbf{R}$.

The major simplification of the SI model is the replacement of the nonlocal self-energy in Eq. (1) with a local but energy-dependent exchange-correlation potential $V_{XC}^n(\mathbf{r})$ such that

$$\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}',E_{nk})\Psi_{nk}(\mathbf{r}')=V_{XC}^n(\mathbf{r})\Psi_{nk}(\mathbf{r})\ . \tag{11}$$

Using two-band bond orbitals ϕ_ν to construct the Green's function in Eq. (4) and the screen Coulomb potential (9), they have obtained an analytical expression for V_{XC}^n in the local field:

$$\begin{aligned}V_{XC}^v(\mathbf{r})&=V_X^{\text{LDA}}(\mathbf{r})(1+\varepsilon_0^{-1})\\&\quad-\mathbb{C}/2[(\varepsilon_0-1)/(\varepsilon_0+\sqrt{\varepsilon_0})]\ .\\V_{XC}^c(\mathbf{r})&=V_X^{\text{LDA}}(\mathbf{r})(1-\varepsilon_0^{-1})\\&\quad-\mathbb{C}/2[(\varepsilon_0-1)/(\varepsilon_0-\sqrt{\varepsilon_0})]\ ,\end{aligned} \tag{12}$$

where the subscripts v and c replace band index n to represent the VB and CB, respectively, and $\mathbb{C}$ is an on-site exchange integral given by

$$\mathbb{C}=\int d\mathbf{r}\,d\mathbf{r}'\phi_\nu^c(\mathbf{r}-\mathbf{R})\phi_\nu^{v\,*}(\mathbf{r}-\mathbf{R})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\times\phi_\nu^{c\,*}(\mathbf{r}'-R)\phi_\nu^v(\mathbf{r}'-R)\ , \tag{13}$$

and the dielectric constant can be estimated from

$$\varepsilon_0=[E_g^2+(\hbar\omega_p)^2]/E_g^2\ . \tag{14}$$

$V_X^{\text{LDA}}(\mathbf{r})$ is the usual LDA exchange potential given by

$$V_X^{\text{LDA}}(\mathbf{r})=-e^2[3/\pi]^{1/3}\rho^{1/3}(\mathbf{r})\ . \tag{15}$$

Since the quasiparticle overlaps the LDA wave function by about 99.9%, as demonstrated by the calculation of HL,[20] we may use the LDA wave function to estimate the self-energy correction to the LDA energy eigenvalue for the VB and CB:

$$\begin{aligned}\Delta E_k^v&=\langle\Psi_k^v|V_{\text{xc}}^v-V_{\text{xc}}^{\text{LDA}}|\Psi_k^v\rangle\\&\cong\langle\Psi_k^v|V_X^{\text{LDA}}|\Psi_k^v\rangle\varepsilon_0^{-1}-\mathbb{C}/2[(\varepsilon_0-1)/(\varepsilon_0+\sqrt{\varepsilon_0})]\ ,\\\Delta E_k^c&=\langle\Psi_k^c|V_{\text{xc}}^c-V_{\text{xc}}^{\text{LDA}}|\Psi_k^c\rangle\\&\cong-\langle\Psi_k^c|V_X^{\text{LDA}}|\Psi_k^c\rangle\varepsilon_0^{-1}-\mathbb{C}/2[(\varepsilon_0-1)/(\varepsilon_0-\sqrt{\varepsilon_0})]\ .\end{aligned} \tag{16}$$

In arriving at the right side of (16), one may replace the LDA exchange-correlation potential V_{XC}^{LDA} with the LDA exchange potential V_X^{LDA} since the self-energy correction involves only the matrix of V_X^{LDA}, thus greatly reducing the computational complexity. Our test calculation shows the error introduced by this substitution is small and can be neglected. Thus, in the SI model, the self-energy correction to the LDA energy band reduces to the proper evaluation of the on-site exchange integral $\mathbb{C}$ and the matrix elements of V_X^{LDA} for the VB and CB, separately.

III. IMPLEMENTATION OF THE STERNE-INKSON MODEL TO THE OLCAO METHOD

The first-principles OLCAO is one of the versatile modern band-structure methods.[45] Recently, this method has been applied to calculate the linear and nonlinear optical properties of 18 cubic semiconductors[46,47] and ten wurtzite crystals.[48] The method is based on the LDA of the DFT. The exchange-correlation potential used is of the Wigner interpolation formula type, but other forms are equally effective. The crystal wave function is in the form of the linear combinations of Bloch sums $b_1(\mathbf{k},\mathbf{r})$ which are constructed from the atomic or atomiclike orbitals $\varphi_i(\mathbf{r}-\mathbf{R}_\mu)$ centered at each lattice site $\mathbf{R}_\mu$:

$$\begin{aligned}\Psi_{nk}(\mathbf{r}) &= \sum_i C^i_{nk} b_i(\mathbf{k},\mathbf{r}) \\ &= \sum_i C^i_{nk} N^{-1/2} \sum_\mu \exp(i\mathbf{k}\cdot\mathbf{R}_\mu)\varphi_i(\mathbf{r}-\mathbf{R}_\mu) \\ &= N^{-1/2} \sum_\mu \exp(i\mathbf{k}\cdot\mathbf{R}_\mu) \sum_i C^i_{nk}\varphi_i(\mathbf{r}-\mathbf{R}_\mu)\ . \end{aligned} \tag{17}$$

In the above expression, we assume only one atom per unit cell. Generalization to multiatom per unit cell is straightforward. The atomic orbitals are labeled by i (principal and orbital quantum numbers, and also the spin quantum number in the spin-polarized calculation). A minimal basis consists of the atomic orbitals of the entire shell of the highest occupied atomic states, while for the extended basis set an additional shell of excited empty states are added to the basis set. As will be discussed below, the accuracy of the LDA self-energy correction in the OLCAO method depends to a large extent on the adequate convergence in the basis expansion of the LDA wave function. For that reason, all calculations reported in this paper use an extended basis set.

The atomic orbitals $\varphi_i(\mathbf{r})$ are expanded in terms of s, p or d types of Gaussian orbitals with a fixed set of exponentials which ranges typically from 0.12 to 500 000. The crystal potential and the charge density are constructed according to the LDA, and are linearly fitted to a set of atom-centered functionals consisting of an s type of Gaussians. The number of Gaussians used and the range of its exponentials depend on the type of atoms involved, and are chosen to achieve the most accurate representation for the charge density. An optimal choice of this Gaussian fitting set is very important in obtaining the accurate LDA result.

The overlap and Hamiltonian matrix elements between the Bloch sum $b_i(\mathbf{k},\mathbf{r})$ at each $\mathbf{k}$ point are evaluated in the real space. The lattice summation is carried out to sufficient convergence. The Bloch sums are properly orthogonalized so that the final secular equation does not involve core states:

$$b'_v(\mathbf{k},\mathbf{r}) = b_v(\mathbf{k},\mathbf{r}) - \sum_c \langle b_c(\mathbf{k},\mathbf{r})|b_v(\mathbf{k},\mathbf{r})\rangle b_c(\mathbf{k},\mathbf{r})\ , \tag{18}$$

where c,c' (v,v') represents the core (valence or noncore) orbitals and the primes indicate that the Bloch sum or wave function is core orthogonalized. The calculation is fully self-consistent with energy eigenvalues converge to less than 10^{-4} eV in 10–15 iterations for simple semiconductor crystals. A special $\mathbf{k}$-point sampling technique is used for summation over the Brillouin zone (BZ). For crystals studied in this paper, six special $\mathbf{k}$ points are sufficient to give well-converged LDA results.

After orthogonalization, the matrix element in (16) reduces to

$$\begin{aligned}\langle \Psi_{nk}(r)|V_X^{\mathrm{LDA}}|\Psi_{nk}(r)\rangle = \sum_{v,v'} C^{v*}_{nk} C^{v'}_{nk} \sum_\mu \exp(i\mathbf{k}\cdot\mathbf{R}_\mu) \Big[&\langle \varphi_v(\mathbf{r})|V_X^{\mathrm{LDA}}(\mathbf{r})|\varphi_{v'}(\mathbf{r}-\mathbf{R}_\mu)\rangle \\ &- \sum_c \langle \varphi_c(\mathbf{r})|\varphi_v(\mathbf{r})\rangle \langle \varphi_v(\mathbf{r})|V_X^{\mathrm{LDA}}(\mathbf{r})|\varphi_c(\mathbf{r}-\mathbf{R}_\mu)\rangle \\ &- \sum_c \langle \varphi_{v'}(\mathbf{r})|\varphi_c(\mathbf{r})\rangle \langle \varphi_c(\mathbf{r})|V_X^{\mathrm{LDA}}(\mathbf{r})|\varphi_{v'}(\mathbf{r}-\mathbf{R}_\mu)\rangle \\ &- \sum_{cc'} \langle \varphi_v(\mathbf{r})|\varphi_c(\mathbf{r})\rangle \langle \varphi_{c'}(\mathbf{r})|\varphi_{v'}(\mathbf{r})\rangle \langle \varphi_c(\mathbf{r})|V_X^{\mathrm{LDA}}(\mathbf{r})|\varphi_{c'}(\mathbf{r}-\mathbf{R}_\mu)\rangle \Big]\ . \end{aligned} \tag{19}$$

Relatively speaking, the calculation of the on-site exchange integral $\mathbb{C}$ [Eq. (13)] for the SI model and similar models employing bond orbitals to represent the electronic structure of the crystal is not precise. The main reason is the lack of rigorous correspondence between the bond orbitals in the two-band model and the actual crystal wave functions. Suppose $\phi_n(\mathbf{r}-\mathbf{R}_\mu)$ is a Wannier function centered at cell $\mathbf{R}_\mu$; the crystal wave function can be represented by

$$\Psi_{nk}(r) = N^{-1/2} \sum_\mu \exp(i\mathbf{k}\cdot\mathbf{R}_\mu)\phi_n(\mathbf{r}-\mathbf{R}_\mu)\ . \tag{20}$$

Comparing (20) with (17), it is apparent that $\sum_i C^i_{nk}\varphi_i(\mathbf{r}-\mathbf{R}_\mu)$ is a localized function but is $\mathbf{k}$ dependent. We can first define a $\mathbf{k}$-dependent on-site exchange integral as

$$\begin{aligned}\mathbb{C}(\mathbf{k}) &= \sum_i |C^i_{vk}|^2 |C^i_{ck}|^2 \\ &\quad \times \int |\varphi_i(\mathbf{r})|^2 \frac{1}{|\mathbf{r}-\mathbf{r}'|} |\varphi_i(\mathbf{r}')|^2 d\mathbf{r}\, d\mathbf{r}' \end{aligned} \tag{21}$$

and obtain $\mathbb{C}$ as the average value of $\mathbb{C}(\mathbf{k})$ summed over the BZ:

$$\mathbb{C}=\sum_{k}\mathbb{C}(\mathbf{k})W(\mathbf{k}) \,, \tag{22}$$

where $W(\mathbf{k})$ is the weighting factor of the special $\mathbf{k}$-point sampling.

In the present calculation, the atomic orbitals φ_i are expressed as s, p, or d types of Gaussian orbitals. Thus the calculation of (21) boils down to the evaluation of a series of exchange integrals between s, p, and d types of Gaussian orbitals which can be expressed in the analytic form. This is outlined in the Appendix.

IV. APPLICATION TO DIAMOND, Si, Ge, GaP, GaAs, AND ZnSe

We have successfully implemented the SI model to the OLCAO method, and have calculated the self-energy corrections to the LDA energy bands for six semiconductor crystals: diamond, Si, Ge, GaP, GaAs, and ZnSe. In the calculation for ZnSe, we treat the Zn 3d state as a valence state. As will be discussed below, the Zn 3d band is a localized narrow band in the VB region and should not be treated as a core state.

Tables I–VI list the LDA energy band levels at the three high-symmetry $\mathbf{k}$ points Γ, X, and L in the BZ before and after the self-energy correction. Some of the LDA results are slightly different from those of Huang and Ching[46] using the same method, mainly because of the slightly different fitting functions resulting in an improvement in the accuracy. Also listed for comparison are experimental data and results from other similar calculations. Our calculation differs from that of JSI in several respects. First, JSI used a pseudopotential method with a plane-wave basis set, while we use localized atomic orbitals for the basis set. Second, we estimate ε_0 based on the $\mathbf{k}$-averaged LDA gap and the plasmon frequency obtained from expression (14), while JSI used experimental values for ε_0. Third, we calculate the on-site exchange integrals according to expressions (21) and (22), using the actual LDA Bloch functions, while JSI used a rather crude estimation based on the bond orbital model. Furthermore, we find the convergence of $\mathbb{C}$ with respect to the number of special $\mathbf{k}$ points used is rather slow. In general, 44 special $\mathbf{k}$ points in the irreducible wedge of the BZ are needed to achieve a reasonable convergence. Since the self-energy correction based on the SI model has a simple analytic form, the computational time required for $\mathbb{C}$ is negligible compared to that required for the rigorous GW theory. In the present study for six crystals, the CPU time required for the self-energy correction is comparable to the LDA band calculation itself, which is acceptable.

From our calculated results listed in Tables I–VI, it is apparent that the implementation of the SI model to the OLCAO method is quite effective. The self-energy-corrected direct band gaps are within 0.3 eV of the experimental data for Si, and within 0.2 eV for the other five crystals. The improvement for the indirect gaps are less impressive, but still show a substantial improvement over the LDA result. For diamond, Si, Ge, and GaP, in which the minimal gaps are indirect, the differences from the measured values are 0.77, 0.47, 0.18, and 0.47 eV, respectively.

In calculations by JSI, the results for the self-energy correction are best for Si and GaAs, and relatively poor for Ge. The authors attributed this to the fact that, in Si and GaAs, the $\mathbf{k}$ variations for the top of the VB and the lowest CB are less strong, and as such a two-band model with a single effective gap is quite realistic. In Ge, the lowest CB near Γ is rather steep, with a negative gap of -0.19 eV, which may affect the self-energy correction. In contrast to JSI, we obtained the best result for Ge, and found the dependence of the model on the details of the LDA band structure to be less obvious. A possible reason for this is that, in our calculation, parameters such as E_g, $\mathbb{C}$, etc. are all BZ averaged using $\mathbf{k}$-weighted special points, and are thus less sensitive to the band structure in a local region such as near the Γ point.

Table VII lists the parameters used in our calculation,

TABLE I. Self-energy correction in diamond (energy in eV).

k	Band	LDA	Present	JSI (Ref. 39)	Hott (Ref. 33)	HL (Ref. 20)	Expt. (Ref. 33)
Γ	8	14.51	16.67	15.65	15.53	14.8	15.
	5–7	5.61	7.35	7.87	8.84	7.50	7.40
	2–4	0.0	0.0	0.0	0.0	0.0	0.0
	1	−21.46	−21.28	−22.09	−22.77	−23.0	−21.
X	5,6	5.24	6.77	6.67	7.86		6.0
	3,4	−6.36	−6.22	−6.52	−6.51		−5.
	1,2	−12.69	−12.58	−13.13	−13.43		−13.
L	7	9.52	11.42	11.07	11.66		
	5,6	8.73	10.41	10.62	11.85		
	3,4	−2.84	−2.79	−2.88	−2.78		−3.
	2	−13.47	−13.22	−14.00	−14.19	−14.4	−13.
	1	−15.51	−15.44	−16.05	−16.72	−17.3	−16.
E_{gap}	$\Gamma-X$	5.24	6.77	6.67	7.86		6.0
	$\Gamma-\Gamma$	5.61	7.35	7.87	8.84	7.5	7.4

TABLE II. Self-energy correction in Si (energy in eV).

k	Band	LDA	Present	JSI (Ref. 39)	Hott (Ref. 33)	HL (Ref. 20)	ZL (Ref. 30)	Expt. (Ref. 33)
Γ	8	3.11	4.39	4.06	3.55	4.08	4.32	4.15
	5–7	2.61	3.67	3.32	3.68	3.35	3.43	3.35
	2–4	0.00	0.00	0.00	0.00	0.00	0.00	
	1	−12.02	−11.99	−11.97	−12.38	−12.04	−12.30	−12.50±0.6
X	7,8	9.97	11.14	10.80	11.67			
	5,6	0.61	1.60	1.39	1.33	1.44	1.47	1.13
	3,4	−2.89	−2.86	−2.87	−2.99	−2.99	−3.02	−2.9
	1,2	−7.89	−7.89	−7.79	−8.15		−8.15	
L	8	8.07	9.06	8.22	8.90			
	6,7	3.46	4.47	4.08	4.38	4.24	4.30	3.91
	5	1.36	2.48	2.27	2.06	2.27	2.36	2.04±0.6
	3,4	−1.26	−1.26	−1.19	−1.15	−1.27	−1.28	−1.2±0.2
	2	−7.05	−7.00	−7.06	−7.39	−7.18	−7.28	−6.8±0.3
	1	−9.69	−9.69	−9.60	−10.04	−9.79	−9.98	−9.3±0.4
E_{gap}	Γ–X	0.61	1.60	1.39	1.33	1.44	1.47	1.13
	Γ–L	1.36	2.48	2.27	2.06	2.27	2.36	2.04
	Γ–Γ	2.61	3.67	3.32	3.68	3.35	3.43	3.35

and the on-site exchange integral $\mathbb{C}$ for the six crystals. We use the dielectric constants ε_0 obtained from E_g and ω_p from Eq. (14). JSI used experimental values for ε_0. From Eq. (7), E_g and ω_p, respectively, are the zero and the pole of the inverse dielectric function. These are precisely the key features in the screening interaction in semiconductors and insulators. The use of E_g and ω_p to estimate ε_0 in the self-energy correction is therefore at least internally consistent. Had we used the experimental values for ε_0 in our calculation, we would end up with an overcorrection for all six crystals. Table VII also shows our calculated on-site exchange integral $\mathbb{C}$, which is quite different from that of JSI. The on-site exchange integral is derived from a two-band model. For real materials with complicated band structures, $\mathbb{C}$ has no direct physical meaning. It is not surprising that different calculations lead to different $\mathbb{C}$ values. For comparison purpose, we also list the on-site exchange integrals for diamond and Si calculated by HS.[37] We are quite surprised to see that our $\mathbb{C}$ value for Si is markedly smaller than the other crystals. We are unable to explain the source of this large variation in Si. We speculate that it probably comes from

TABLE III. Self-energy correction in Ge (energy in eV).

k	Band	LDA	Present	JSI (Ref. 39)	Hott (Ref. 33)	HL (Ref. 20)	Expt. (Ref. 20)
Γ	6–8	2.81	3.19	3.03	3.60	3.04	3.01
	5	0.37	1.10	0.34	0.06	0.71	0.89
	2–4	0.00	0.00	0.00	0.00	0.00	0.00
	1	−12.59	−12.54	−12.82	−13.16	−12.86	−12.6
X	7,8	9.62	10.15	9.94	10.96		
	5,6	0.97	1.20	1.07	1.31	1.23	1.3±0.2
	3,4	−3.05	−2.96	−3.03	−3.26	−3.22	−3.15±0.2
	1,2	−8.71	−8.72	−8.91	−9.31	−9.13	−9.3±0.2
L	8	7.58	7.76	7.35	8.30	7.61	7.8±0.6
	6,7	4.07	4.39	4.14	4.73	4.33	4.3±0.2
	5	0.45	0.92	0.51	0.59	0.75	0.74
	3,4	−1.43	−1.39	−1.37	−1.36	−1.43	−1.4±0.3
	2	−7.47	−7.39	−7.64	−8.06	−7.82	−7.7±0.2
	1	−10.50	−10.51	−10.71	−11.12	−10.89	−10.6±0.5
E_{gap}	Γ–L	0.45	0.92	0.51	0.59	0.75	0.74
	Γ–Γ	0.37	1.10	0.34	0.06	0.71	0.89
	Γ–X	0.97	1.20	1.07	1.31	1.23	1.3

TABLE IV. Self-energy correction in GaP (energy in eV).

k	Band	LDA	Present	WGL (Ref. 32)	Expt. (Ref. 32)
Γ	6–8	4.04	4.38	4.50	4.6
	5	2.15	2.68	2.93	2.90
	2–4	0.00	0.00	0.00	0.00
	1	−12.39	−12.32	−12.64	−12.3
X	7–8	10.75	11.22		
	6	2.27	2.58	2.16	
	5	1.53	1.88	1.83	2.35
	3–4	−2.74	−2.66	−0.08	3.0
	2	−6.48	−6.41	−7.45	−6.8
	1	−9.48	−9.48	−9.68	−9.6
L	8	6.42	6.80		
	6–7	4.37	4.70		
	5	1.86	2.28	2.33	2.64
	3–4	−1.07	−1.03	−1.29	−0.9
	2	−6.81	−6.70	−7.36	−6.8
	1	−10.31	−10.29	−10.81	−10.8
E_{gap}	Γ–*X*	1.53	1.88	1.83	2.35
	Γ–*L*	1.86	2.28	2.33	2.64
	Γ–Γ	2.15	2.68	2.93	2.90

the differences in the nature of the wave functions near the band-gap region.

We should also point out that in the calculation of JSI (Ref. 39) they relied on Van Vetchten's fractional ionic character as an empirical parameter to estimate the on-site exchange integral. In multicomponent systems with a mixed type of bonding, such parameters would be difficult to determine. In our work, no empirical parameter or experimental data are used. All calculations are based on the LDA band structures. Thus the LDA band calculation and its self-energy correction are on the same footing. This is probably the reason that, while our $\mathbb{C}$ values are quite different from that of JSI, we still obtain quite satisfactory results for the self-energy correction.

As alluded to in Sec. II, the self-energy correction to the LDA band [Eq. (16)] is based on the premise that the LDA wave functions is very close to the quasiparticle wave function. An accurate and fully converged LDA wave function is the key to the correct self-energy correction. For example, in the case of diamond, if we use only the minimal basis consisting of 1*s*, 2*s*, and 2*p* orbitals, the self-energy-corrected band gap of 8.03 eV is actually direct. On using an expanded basis set, we obtained a self-energy-corrected indirect gap of 6.77 eV and a direct gap of 7.34 eV, which are in good agreement with experimental values of 6.0 and 7.4 eV, respectively.

Of the five crystals studied by JSI, ZeSe was the worst case, with a self-energy correction, overestimates the experimental gap value of about 1 eV. As can be seen from Table VI, our self-energy-corrected direct band gap for ZnSe appears to be very close to the experimental value of 2.82 eV. However, this is only a partial picture. At the *X* point, the two lowest CB's after the self-energy correction are lower than the experimentally determined ones by more than 1.0 eV. This is because the calculated LDA energies for these two CB's seem to be too low. Although the self-energy correction results in considerable improvement, it is not sufficient to be close to experimental values. At the *L* point, we have a LDA value for the middle VB of −4.97 eV, which is already very close to the experimental value of −5.08 eV. After the self-

TABLE V. Self-energy correction in GaAs (energy in eV).

k	Band	LDA	Present	JSI (Ref. 39)	Hott (Ref. 33)	WGL (Ref. 32)	ZL (Ref. 30)	Expt. (Ref. 33)
Γ	6–8	4.34	4.62	4.52	4.72	4.55		4.72
	5	1.28	1.42	1.43	0.93	1.42	1.22	1.52
	2–4	0.00	0.00	0.00	0.00	0.00		0.00
	1	−12.37	−12.29	−12.59	−12.94	−13.06		−13.1
X	7,8	10.58	10.57	10.96	11.79	11.06		
	6	2.04	2.48	2.32	2.24	2.26		2.58
	5	1.96	2.25	2.10	1.99	1.98		2.08
	3,4	−2.52	−2.68	−2.63	−2.89	−2.82		−2.80
	2	−6.44	−6.60	−6.78	−7.64	−7.12		−6.70
	1	−10.02	−10.10	−10.13	−10.28	−10.33		−10.75
L	8	8.36	8.77	8.35	8.95			
	6,7	5.23	5.55	5.35	5.63	5.40		
	5	1.50	1.63	1.78	1.40	2.72		1.85
	3,4	−1.08	−1.15	−1.11	−1.13	−1.21		−1.30
	2	−6.30	−6.52	−6.63	−7.41	−6.87		−6.70
	1	−10.72	−10.75	−10.89	−11.14	−11.29		−11.24
E_g	Γ–Γ	1.28	1.42	1.43	0.93	1.42	1.22	1.52
	Γ–*L*	1.50	1.63	1.78	1.40	1.72		1.85
	Γ–*X*	1.96	2.25	2.10	1.99	1.98		2.08

TABLE VI. Self-energy correction in ZnSe (energy in eV).

k	Band	LDA	Present	JSI (Ref. 39)	Expt. (Ref. 39)
Γ	6–8	6.37	6.55	7.77	7.33
	5	2.37	2.98	3.77	2.82
	2–4	0.00	0.00	0.00	0.00
	1	−12.74	−12.47	−12.26	−12.25
X	8	11.86	12.40	13.27	
	7	11.04	11.69	12.93	
	6	3.67	4.00	5.22	5.17
	5	3.45	3.45	4.59	4.54
	3,4	−2.06	−1.67	−1.71	−1.96
	2	−4.58	−4.31	−4.37	−4.96
	1	−11.70	−11.67	−10.95	−10.72
L	8	9.04	9.30	10.47	
	6,7	6.91	7.08	8.05	7.72
	5	3.05	3.45	4.70	3.96
	3,4	−0.82	−0.66	−0.62	−0.76
	2	−4.97	−4.30	−4.63	−5.08
	1	−11.96	−11.86	−11.32	−11.08
E_{gap}	$\Gamma-\Gamma$	2.37	2.98	3.77	2.82
	$\Gamma-L$	3.05	3.45	4.70	3.96

energy correction, this band energy is −4.30 eV, which deviates from the experimental value. (Similar sporadic examples of a negative effect for the self-energy correction at specific **k** points exist in other materials, but are not very obvious.) This may have more to do with the accuracy of the LDA result than the failure of the Sterne-Inkson model. All these difficulties with ZnSe may be related to the complexity of treating Zn 3*d* state, which is localized in real space but has significant hybridization with valence states at the same time.

In the Sterne-Inkson model, the self-energy correction to the LDA bands is **k** and energy dependent, which results from the matrix elements of V_X^{LDA} [Eq. (16)]. Therefore, comparison of the self-energy correction at different **k** points and at different energies can be viewed as a check of the model itself. Generally speaking, the correction at the BZ center or the Γ point is always better than at any other **k** points. This may reflect a somewhat local limitation of the model. Additional test calculations and analysis of the results are necessary to gain further insight.

Table VIII shows the convergence of the self-energy correction as a function of the number of special **k** points employed in the calculation. On the whole, the convergence is rather slow. To reach a convergence of 0.1 eV in the energy correction, at least 44 special **k** points are necessary. This relatively slow convergence of the self-energy correction with respect to the number of **k** points is probably related to the properties of the Wannier functions, since it takes crystal wave functions at many **k** points to construct a well-converged Wannier function.

TABLE VII. Parameters obtained in the calculation.

	E_g (eV)	$\hbar\omega_p$ (eV)	$\mathbb{C}$ (eV) Present	JSI (Ref. 39)	Hanke (Ref. 37)
Diamond	11.12	31.41	5.24	3.94	8.16
Si	4.00	16.60	0.58	1.67	5.72
Ge	4.00	15.61	4.25	1.56	
GaP	4.04	16.51	4.57		
GaAs	4.49	15.62	7.45	1.61	
ZnSe	5.43	15.57	7.97	1.86	

TABLE VIII. **k**-space convergence for the self-energy-corrected direct gaps (in eV).

		No. of **k** points			
Crystal	6 K	14 K	26 K	44 K	68 K
Diamond		7.61	7.28	7.35	
Si	3.74	3.69	3.67	3.67	
Ge		1.07	1.10	1.11	
GaP		3.16	2.91	2.76	2.68
GaAs		1.81	1.53	1.42	
ZnSe		2.83	2.95	2.98	

V. CONCLUSIONS

We have successfully implemented an approximate *GW* self-energy correction scheme to the OLCAO-LDA method of band-structure calculation, based on the Sterne-Inkson model. The on-site exchange integrals are evaluated using the LDA Bloch functions throughout the Brillouin zone. A **k**-weighted band gap E_g and a plasmon frequency ω_p determined by valence electron density are used to estimate the dielectric constant. This approach retains the first-principles nature for the self-energy correction. Test calculations are carried out on six semiconductor crystals: diamonds, Si, Ge, GaAs, GaP, and ZnSe. The results show the *GW*-corrected gap values to be generally within 10% of the experimental values. It is pointed out that an accurate and well-converged LDA wave function is crucial for an accurate self-energy correction. The model does have some limitations due to the approximations introduced in the Sterne-Inkson approach. However, the benefit of an efficient self-energy correction scheme with demonstrated improvement far outweigh its minor limitations. The first-principles approach to the SI model for self-energy correction presented in this paper will be more effective in wide-gap insulators, especially in those systems with complex crystal and bonding structures. In wide-gap insulators, VB and CB edges are usually quite flat and the wave functions correspondingly more localized. Such systems are more accurately described by a two-band model with a constant band gap than the covalently bonded semiconductors studied here. Indeed, preliminary calculation[49] for $LiNbO_3$ using the present scheme shows that the self-energy correction enlarges the LDA gap of 2.62 eV by 0.94 eV, and is in close agreement with the measured optical gap of 3.78 eV.[50] Application of this approach to more complex systems and other large gap insulators will be attempted in the near future.

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APPENDIX

From Eq. (21), the calculation of on-site exchange integral $\mathbb{C}$ involves the evaluation of the integral $\int|\phi_i(\mathbf{r})|^2[\mathbf{r}-\mathbf{r}']^{-1}|\phi_i(\mathbf{r}')|^2 d\mathbf{r}\,d\mathbf{r}'$ where the $\phi_i(\mathbf{r})$'s are atomic or atomiclike orbitals. $\phi_i(\mathbf{r})$ consists of symmetry-related Gaussians. Using the fact that

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|}=\frac{2}{\sqrt{\pi}}\int_0^\infty \exp(|\mathbf{r}-\mathbf{r}'|u^2)du\ ,$$

the above integral can be reduced to on-site exchange integrals of *s*, *p*, and *d* types of Gaussian orbitals.

For typical *s*-type Gaussian-type orbitals (GTO's), we have

$$\mathsf{S}\equiv\int e^{-(\alpha_A+\alpha_B)r^2}\frac{1}{|\mathbf{r}-\mathbf{r}'|}e^{-(\alpha_C+\alpha_D)r'^2}d\mathbf{r}\,d\mathbf{r}'$$
$$=\frac{2\pi^{5/2}}{(\alpha_A+\alpha_B)(\alpha_C+\alpha_D)(\alpha_A+\alpha_B+\alpha_C+\alpha_D)^{1/2}}\ .$$

For a typical *p*-type GTO, we have

$$\mathsf{P}\equiv\int x^2e^{-(\alpha_A+\alpha_B)r^2}\frac{1}{|\mathbf{r}-\mathbf{r}'|}x'^2e^{-(\alpha_C+\alpha_D)r'^2}d\mathbf{r}\,d\mathbf{r}'$$
$$=\frac{\pi^{5/2}}{3(\alpha_A+\alpha_B)^2(\alpha_C+\alpha_D)^2(\alpha_A+\alpha_B+\alpha_C+\alpha_D)^{1/2}}$$
$$+\frac{3\pi^{5/2}}{10(\alpha_A+\alpha_B)(\alpha_C+\alpha_D)(\alpha_A+\alpha_B+\alpha_C+\alpha_D)^{5/2}}\ .$$

For a typical *d*-type GTO, we have

$$\mathsf{D}\equiv\int x^2y^2e^{-(\alpha_A+\alpha_B)r^2}\frac{1}{|\mathbf{r}-\mathbf{r}'|}x'^2y'^2e^{-(\alpha_C+\alpha_D)r'^2}d\mathbf{r}\,d\mathbf{r}'$$
$$=\frac{\pi^{5/2}}{15(\alpha_A+\alpha_B)^3(\alpha_C+\alpha_D)^3(\alpha_A+\alpha_B+\alpha_C+\alpha_D)^{1/2}}+\frac{3\pi^{5/2}}{70(\alpha_A+\alpha_B)^2(\alpha_C+\alpha_D)^2(\alpha_A+\alpha_B+\alpha_C+\alpha_D)^{5/2}}$$
$$+\frac{\pi^{5/2}}{8(\alpha_A+\alpha_B)(\alpha_C+\alpha_D)(\alpha_A+\alpha_B+\alpha_C+\alpha_D)^{9/2}}\ .$$

If C_A are the coefficients of expansion of $\phi_i(\mathbf{r})$ in terms of a GTO with exponential α_A, we have

$$\int|\phi_i(\mathbf{r})|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}|\phi_i(\mathbf{r}')|^2d\mathbf{r}\,d\mathbf{r}'=\sum_{A,B,C,D}C_AC_BC_CC_D\times\begin{cases}\mathsf{S} & \text{for } i=s \text{ type}\\ \mathsf{P} & \text{for } i=p \text{ type}\\ \mathsf{D} & \text{for } i=d \text{ type.}\end{cases}$$

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