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Calculation of optical excitations in cubic semiconductors. I. Electronic structure and linear response

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The electronic structures and the linear optical dielectric functions of 18 cubic semiconductors are studied by the first-principles orthogonalized linear-combination-of-atomic-orbitals (OLCAO) method in the local-density approximation. The crystals studied include the group-IV semiconductors C, Si, and Ge; the III-V compounds AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb; and the II-VI semiconductors ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe. Results are presented for the band structures, for the density of states, and for the real and imaginary parts of the linear dielectric functions for photon energies up to 12 eV. The results are compared with other existing calculations and experimental data. Some interesting correlations and trends among the 18 semiconductors studied are pointed out, and possible problems with the optical excitation calculation are discussed. These results provide the groundwork for the calculation of nonlinear optical properties on these crystals using the full band-structure approach in the two papers to follow. It is argued that optical excitations in semiconductors can be efficiently carried out using the OLCAO method without resorting to empirical methods or model studies. The present calculation gives band gaps larger than the well-converged result of first-principles pseudopotential calculations. The consequence of this difference on the optical properties is discussed.

I. INTRODUCTION

The subject of optical excitations in elemental and compound semiconductors has been the focus of many experimental and theoretical studies for a long time.[1–6] Rarely are the linear response and the nonlinear excitation treated at the same time and on equal footing. Moreover, detailed measurements or rigorous calculations were usually carried out for one or a few semiconductors at a time, limiting the scope of any correlated analysis aimed at a coherent overall picture. In this series of three papers, we present our first-principles study of optical excitations in 18 elemental, III-V and II-VI semiconductors. The crystals studied are C, Si, Ge, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb, ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe. Diamond was included because of our interest in the nonlinear optical properties of other C-related compounds and α-Sn was excluded because it is generally considered as a semimetal rather than a semiconductor. In the first paper, we discuss the results of electronic structure and the linear dielectric functions as calculated by the self-consistent orthogonalized linear-combination-of-atomic-orbitals (OLCAO) method. Since reasonably accurate linear dielectric function is a prerequisite for nonlinear optical studies, it is necessary to focus at first on the methodology of the electronic-structure calculation and to assess the quality of linear optical results for the semiconductors. In the two following papers,[7,8] results on the nonlinear optical calculations, namely, the second and the third harmonic generations in these crystals, will be presented. We hope that such a comprehensive study based on rigorous quantum-mechanical calculation will provide a more coherent understanding of the optical excitations in bulk semiconductors.

There are numerous previous theoretical investigations of the linear dielectric functions of semiconductors.[9–41] Earlier work was generally based on the empirical methods, with limited accuracy. In recent years, extensive application of density-functional theory[42–44] in the local-density approximation (LDA) and local-spin-density approximation (LSDA) (Ref. 45) made accurate first-principles calculations of electronic structures of many semiconductors a rather routine task. LDA itself is an approximation that is valid only for a homogeneous electron system in the ground states and it is generally assumed that in a real crystal, the somewhat uneven electron distribution can be locally represented by its density. However, in the case of optical excitation, one has to confront the serious problem of using the eigenvalues of the unoccupied states obtained from the LDA calculation as approximate excitation energies similar to the Koopman's theorem in the Hartree-Fock theory. There have been many tenuous efforts to go beyond the LDA theory to account for these effects in real crystals in order to obtain results in closer agreement with experimental measurements. However, in the present paper, we confine ourselves strictly to the results obtained within the context of the LDA theory and a very specific computational scheme, and focus our attention on the possible correlations and trends among different semiconductors, and on the practicality of using the same approach to study the nonlinear optical properties.

The plan for this paper is rather straightforward. The method of calculation is succinctly summarized in Sec. II. The calculated band structures and the density of states (DOS) for the 18 semiconductors are presented in Sec. III. The results on the linear optical properties are

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presented in Sec. IV. These results are further discussed in Sec. V. The last section is a brief conclusion.

II. THE OLCAO BAND-STRUCTURE METHOD

The OLCAO method is one of the very competitive modern methods used for electronic-structure calculation in solids. Since the details of the method have been described in many publications,[46] it suffices to summarize the essential elements of this method, which are listed below.

(1) The method is an all-electron method based on the density-functional theory in the LDA or the LSDA.

(2) Correction for the correlation effect is added, usually in the form of the Wigner-interpolation formula,[47] but other variations are also possible.

(3) The crystal wave functions are expanded in terms of Bloch functions constructed from the atomic or atomic-like orbitals centered at each atomic site. The orbitals are labeled by the principal quantum number and the orbital quantum number of the atom (and the spin quantum number in the case of spin-polarized calculation). A minimal basis consists of all atomic orbitals, occupied or unoccupied, up to the shell of the principle quantum number of the highest occupied valence electron. For an extended basis, additional orbitals of the next empty shell may be added. Further augmentation of the basis set to increase the variational freedom can be achieved by adding individual single Gaussians.

(4) Each atomic wave function is expressed as a linear combination of s-type, p-type, d-type (or f-type, if necessary) Gaussian-type orbitals (GTO's) with a fixed set of exponentials. The choice of these exponentials depends on the size of the atom and the ionic nature of the crystal, and is generally guided by pure atomic calculations[48] or more likely by past experience. The range is usually from a minimum of 0.12 to a maximum of 2 500 000 in a set of about 14–26 GTO.

(5) The potential and the charge density of the crystal are constructed in the direct space according to the LDA or the LSDA. They are linearly fitted as sums of atom-centered s-type GTO's of varying numbers of terms. For high-precision calculations (usually involve calculations of total energies), additional Gaussians in the fitting function may be placed at strategically located positions in the crystal. The accuracy of the calculation depends critically on the accuracy of the fitted functions and this is monitored by comparing the actual number of valence electrons in the crystal with the number of integrated charge from the fitted functions.

(6) The two-center overlap and the three-center Hamiltonian (consisting of kinetic energy, Coulomb, and the exchange-correlation terms) matrix elements at each $\mathbf{k}$ point in the Brillouin zone (BZ) are calculated in the $\mathbf{r}$ space. A direct lattice sum extending to nonzero interaction integrals is performed. The use of GTO's in both the basis functions and the fitting functions facilitates the analytical evaluation of multicenter integrals in the matrix elements.

(7) An orthogonalization to the core procedure[49] is applied to eliminate the core states from the final secular matrix. (As a rule of thumb, an atomic state with orbital energy lower than the oxygen 2s level is considered a core state.) The orthogonalized secular equation at each $\mathbf{k}$ point is diagonalized to obtain the energy eigenvalues and eigenvectors. The orthogonalization process for reducing the size of the matrix equation is a very important feature of the method for its effective application to complex systems, or to problems that require wave functions at a large number of sampling $\mathbf{k}$ points without being computationally prohibitive.

(8) A self-consistent iterative procedure is instituted in which the new potential and charge-density functions are reconstructed from the crystal wave functions. A convergence criterion is established, usually in the form of relative change in the potential function or in the energy eigenvalues. Twelve to twenty iterations are usually needed to obtain a fully converged result at which the energy eigenvalues change by less than 0.0001 eV. For semiconductors, only a small number of special $\mathbf{k}$ points in the BZ are needed to achieve very good convergence with respect to the number of $\mathbf{k}$ points for the BZ integration.

(9) After the self-consistency is reached, the energy eigenvalues and vectors are recalculated at a large number of regularly spaced $\mathbf{k}$ points in the irreducible portion of the BZ to be used for calculations of optical excitations or other physical observables. In general, a linear analytic tetrahedron method[50,51] or similar scheme for numerical integration over the BZ is employed.

(10) Relativistic correction within the OLCAO scheme has been properly formulated and tested.[52] However, it was not implemented in the present study.

Calculation of the linear optical properties of solids using the OLCAO method has also been described before.[46] The method has been successfully applied to a large number of insulating crystals, including some with very complex crystal structures.[53–67] Very recently, the same method has been applied to study the linear optical properties of all the existing polymorphic forms of silicon dioxide with much more complicated crystal structures.[65] In our approach, the frequency-dependent optical properties are calculated in the random-phase approximation (RPA) based on the electron-gas result of many-particle perturbation theory,[68] but using the electronic structure obtained from the LDA theory. Baroni and Resta[29] had discussed the improvement in the RPA within the framework of the density-functional theory in the LDA. They obtained a bulk dielectric constant for Si in very good agreement with experiment. Their approach, which involves the screening of the wave-vector-dependent dielectric matrix, is more rigorous but is computationally far more demanding. We must stress that in the present work for the calculation of linear and nonlinear optical excitation, LDA calculation refers strictly to the electronic structure only, and does not involve any additional correction for the RPA.

The interband optical-conductivity tensor using the Kubo Greenwood formula[69] is as follows:

$$\sigma_{xx}(\omega)=\frac{2\pi e^2}{m\Omega\hbar\omega}\frac{\Omega}{(2\pi)^3}\times\int d\mathbf{k}\sum_{n,l}|\langle\psi_n(\mathbf{k},\mathbf{r})|\mathbf{P}_x|\psi_l(\mathbf{k},\mathbf{r})\rangle|^2\times f_l(\mathbf{k})[1-f_n(\mathbf{k})]\times\delta[E_n(\mathbf{k})-E_l(\mathbf{k})-\hbar\omega]\,, \quad (1)$$

where $\hbar\omega$ is the photon energy, $f_l(\mathbf{k})$ the Fermi distribution function. The Cartesian components of the momentum matrix elements (MME) in (1), taken between the occupied valence-band (VB) state l with energy $E_l(\mathbf{k})$ and the unoccupied conduction-band (CB) state n with energy $E_n(\mathbf{k})$, are properly evaluated from the eigenfunctions. The MME is found to be strongly $\mathbf{k}$ dependent and must be evaluated at each sampling $\mathbf{k}$ point. The integration over the BZ is carried out by using the linear analytic tetrahedron method. Once the interband conductivity σ is calculated, it can be converted to the imaginary part of the dielectric function $\varepsilon_2(\omega)$ via $\sigma(\omega)=4\pi\varepsilon_2(\omega)/\omega$. The real part of the dielectric function $\varepsilon_1(\omega)$ is obtained from the imaginary part using the Kramers-Kronig relation. Other frequency-dependent linear optical constants such as reflectance spectra, the electron-energy-loss spectra, or the refractive index, etc., can be readily obtained from the complex dielectric function.

It is well known that the LDA theory is only appropriate for the ground-state properties of the solid. This is reflected most commonly in the fact that the band gap of a semiconductor calculated using the LDA theory is usually underestimated.[70] Correction for band gaps in semiconductors beyond the LDA theory had been attempted by many groups.[71–77] Different schemes were developed to address this problem in order to bring the calculated gap value closer to the experimental value. Quasiparticle calculation in the *GW* approximation[78] addresses the gap problem from a more fundamental point of view and the results in several semiconductors appear to be in very good agreement with experiment.[75–77] The self-interaction correction (SIC) scheme aims at the elimination of the incomplete cancellation of the electron self-interaction in the Hartree term of the LDA theory. The SIC leads to the lowering of the VB states, thereby enlarging the gap while totally ignoring the effects on the CB states.[79–81] This approach has considerable success in addressing the problem of gap underestimation in wide-gap insulators.[79–81,68] Carlsson[74] had shown that corrections to the CB and VB are equally important for semiconductors. Simpler correction procedures[75,76] appear to yield equally good results for enlarging the gap sizes in semiconductors. It is not clear at this stage which approach is more appropriate and computationally expedient; it may take several corrections to address the gap problem. In the nonlinear optical calculation, we plan to use the simplest approach by applying a "scissor operator" in which the CB states are given a rigid shift so as to match the measured gap value. This is fully justified for the present level of study, since quasiparticle calculations show a more or less uniform shift in the CB without a substantial change in the CB wave functions,[71,72] and the variation of the gap correction for transitions to different CB states seems to be small.[76] A more refined self-energy-effect correction requires not only adding a scissor operator to the usual LDA Hamiltonian, but also renormalizing the velocity operator for the transition matrix elements.[40,41]

For covalently bonded semiconductors, many-body effects beyond the one-electron theory also become important for optical excitations. The most important ones are the local-field effect and the excitonic effect.[19,40,41,82–87] Both effects also affect the gap states and the nature of carrier excitations in semiconductors.[87] Theoretical approaches to studying the effects of bond excitons on the optical properties of semiconductors are generally based on phenomenological models.[82–84,88] We ignore all these effects in the present calculation.

III. ELECTRONIC STRUCTURES

In a previous paper,[89] the band structures, the DOS, and the effective masses of 32 semiconductors with diamond, zinc-blende, wurtzite, rocksalt, and trigonal structures were studied using the OLCAO method. However, that calculation was not self-consistent and minimal basis functions were employed. The key point of that work was to adjust the Slater exchange-correlation parameter[90] in the potential such that, in conjunction with a minimal basis, the correct experimental band gaps were reproduced. All the interaction integrals were calculated to the furthest neighbors necessary. This method gives quite accurate VB and lower CB states with only a simple 8×8 matrix diagonalization for cubic semiconductors, and does not involve any other adjustable parameters. The method also provides wave functions that can be used for studying other properties. The *semi-ab-initio* method was designed to be a compromise between rigorous self-consistent calculations and the much simpler empirical studies. With a purely empirical method such as the bond orbital method[18,23] or the empirical tight-binding method (ETB),[22] it is difficult to have decent CB states and therefore impossible to obtain good results for optical excitations at higher photon frequencies. Indeed, Moss, Ghahramani, Sipe, and van Driel (the Toronto Group) had adopted this *semi-ab-initio* approach to studying the nonlinear optical properties of a number of cubic semiconductors and their interfaces.[91–96] It is also fair to say that our present study of the linear and nonlinear optical properties of 18 semiconductors using the first-principles OLCAO method is mainly motivated by the work of the Toronto Group who used the ETB and the *semi-ab-initio* methods.

While the *semi-ab-initio* approach is simple and effective for a number of useful studies in semiconductors such as with superlattices[97,98] and crystalline defect,[99] and for the study of the electronic structures of various polycrystalline phases of SiO_2,[100] it would be inherently more satisfying if all the calculations could be carried out as accurately as possible within the LDA formalism and the adopted computational scheme. The rapid advance of the computing technology and the fast development of the methodologies associated with the first-principles cal-

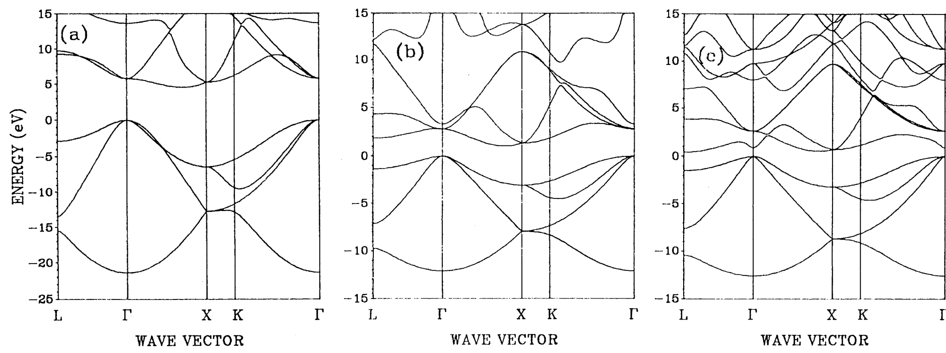

FIG. 1. Band structure of (a) C, (b) Si, and (c) Ge.

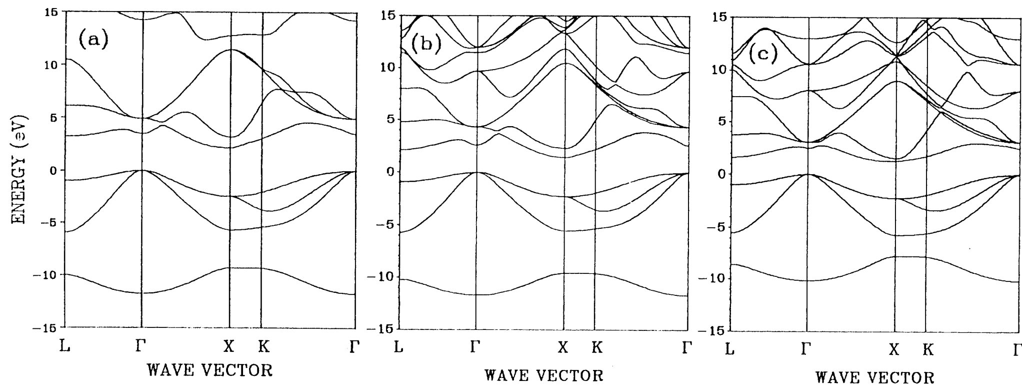

FIG. 2. Band structure of (a) AlP, (b) AlAs, and (c) AlSb.

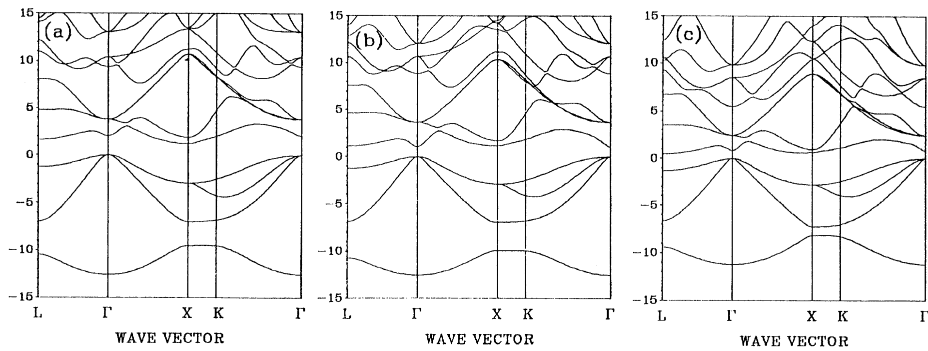

FIG. 3. Band structure of (a) GaP, (b) GaAs, and (c) GaSb.

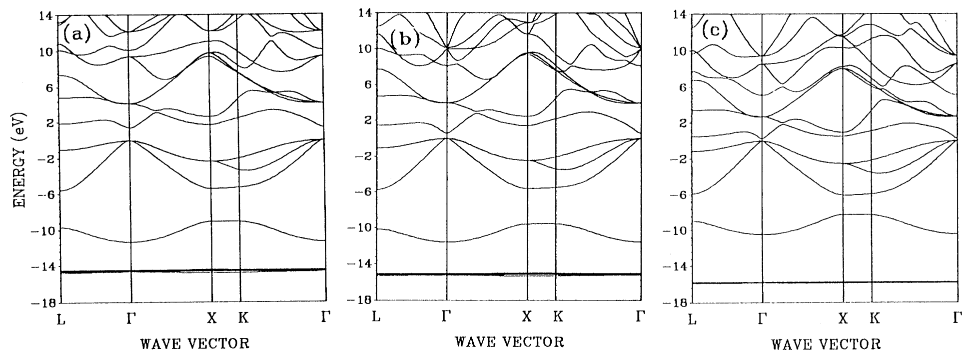

FIG. 4. Band structure of (a) InP, (b) InAs, and (c) InSb.

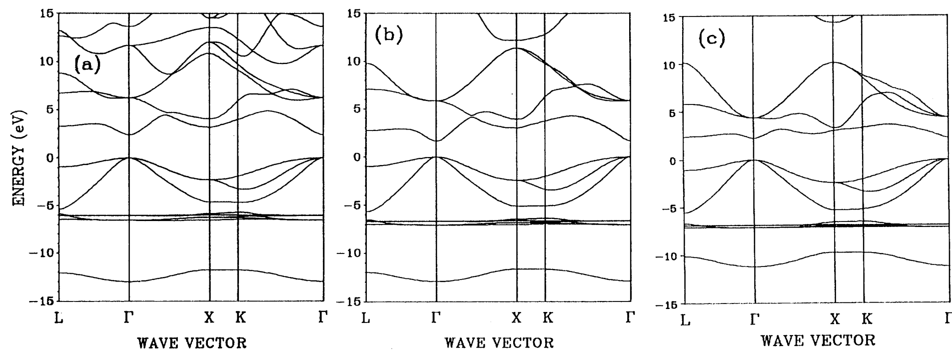

FIG. 5. Band structure of (a) ZnS, (b) ZnSe, and (c) ZnTe.

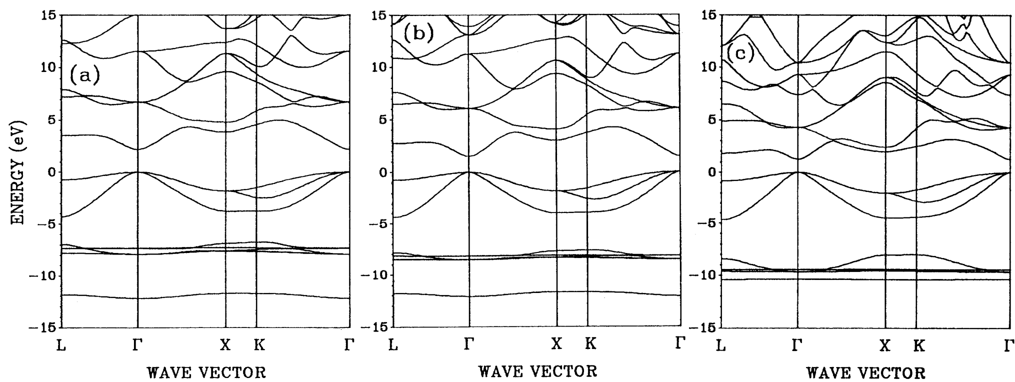

FIG. 6. Band structure of (a) CdS, (b) CdSe, and (c) CdTe.

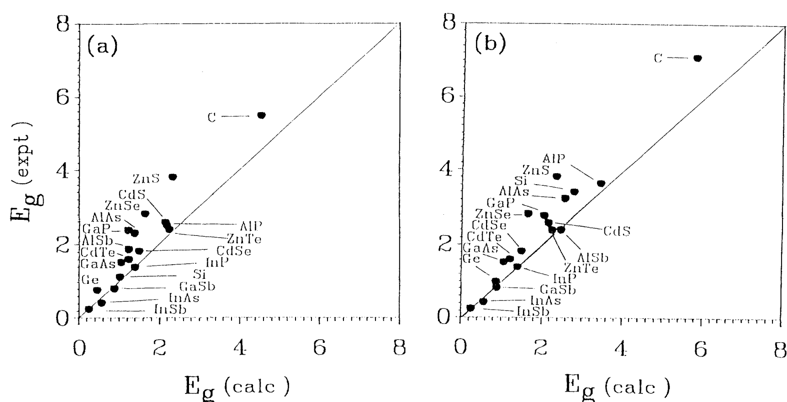

FIG. 7. Calculated vs experimental band gap E_g: (a) minimum gap; (b) direct gap at Γ.

culations made the *semi-ab-initio* approach obsolete. The usual arguments for the use of empirical models are no longer valid. The present study of 18 cubic semiconductors using the fully self-consistent OLCAO method with extended basis sets demonstrates the effectiveness of the currently used first-principles techniques.

The calculated self-consistent band structures of the group-IV semiconductors diamond, Si, and Ge are presented in Fig. 1. For the III-V compounds, the band structures for the Al series (AlP, AlAs, AlSb) are presented in Fig. 2, the Ga series (GaP, GaAs, GaSb) in Fig. 3, and the In series (InP, InAs, InSb) in Fig. 4. For the II-VI compounds, the band structures of ZnS, ZnSe, and ZnTe are shown in Fig. 5 and those of CdS, CdSe, and CdTe in Fig. 6. These band structures are of comparable quality to other first-principles LDA calculations, with the exception that the values of the band gaps may be slightly different. It is *not* our intention here to make a detailed analysis of the individual band structure in the present paper. These band-structure results only serve as the starting point for our investigation of the linear and nonlinear optical properties in these crystals. The calculated band gaps for most of these crystals are smaller than the experimental values,[101] as would be expected from the LDA calculations. For InAs, the calculated gap is actually slightly larger (by 0.13 eV) than the measured gap, and for InSb the calculated gap of 0.24 eV is the same as the measured one. This is true for both the minimal gap E_g and the direct gap E_0 at Γ. The direct band gap at Γ is of prime importance for both linear and nonlinear optical excitations. It is one of the most important parameters in the empirical type of study. In Fig. 7,

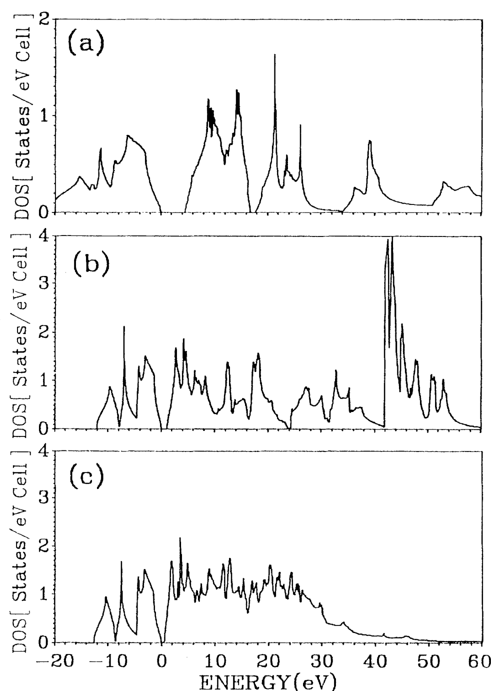

FIG. 8. DOS of (a) C, (b) Si, and (c) Ge.

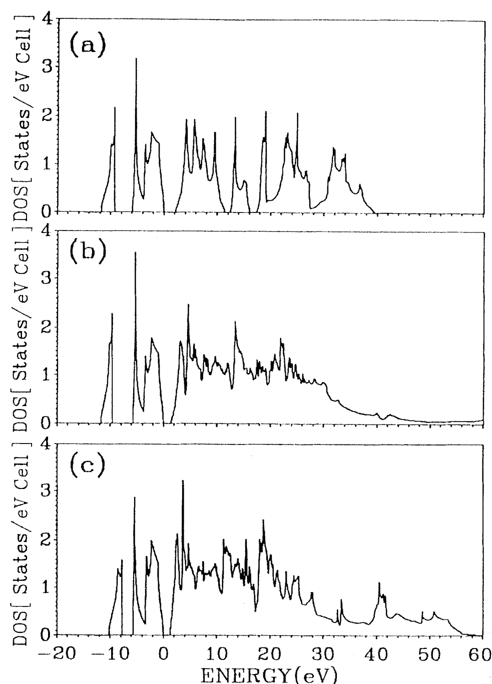

FIG. 9. DOS of (a) AlP, (b) AlAs, and (c) AlSb.

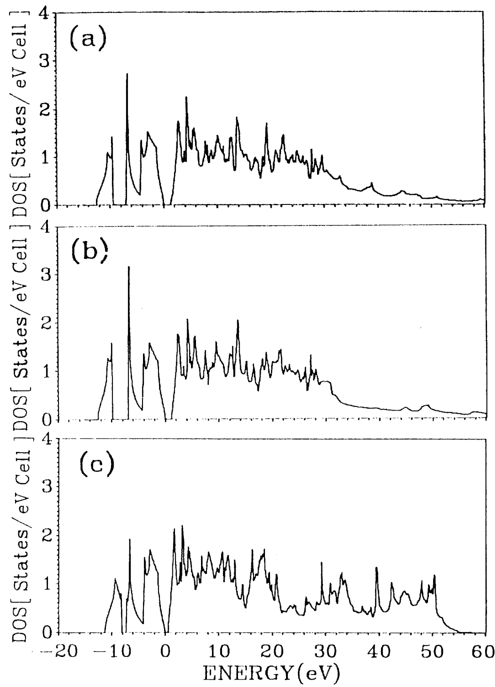

FIG. 10. DOS of (a) GaP, (b) GaAs, and (c) GaSb.

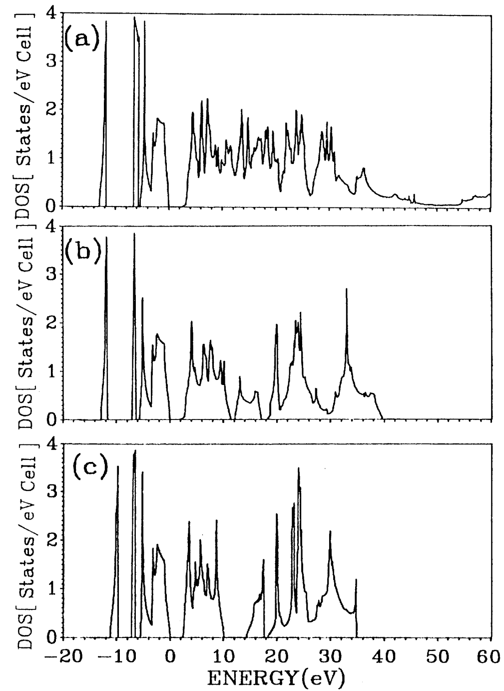

FIG. 12. DOS of (a) ZnS, (b) ZnSe, and (c) ZnTe.

we plot the calculated band gaps against the measured values for the 18 semiconductors. We have noticed that our OLCAO band gaps are generally larger and, therefore, in closer agreement with the measured data than those obtained by other methods. For example, well-converged state-of-the-art pseudopotential plane-wave calculations give gap values for Ge, GaAs, GaSb, and ZnS of 0.0, 0.5, 0.1, and 1.82 eV compared to our values of 0.44, 1.04, 0.80, and 2.34 eV for the same crystals.[102] We will discuss this point later, in Sec. VI. The calculated gap values are summarized in Table I. Also listed are the lattice constants used in our calculation.

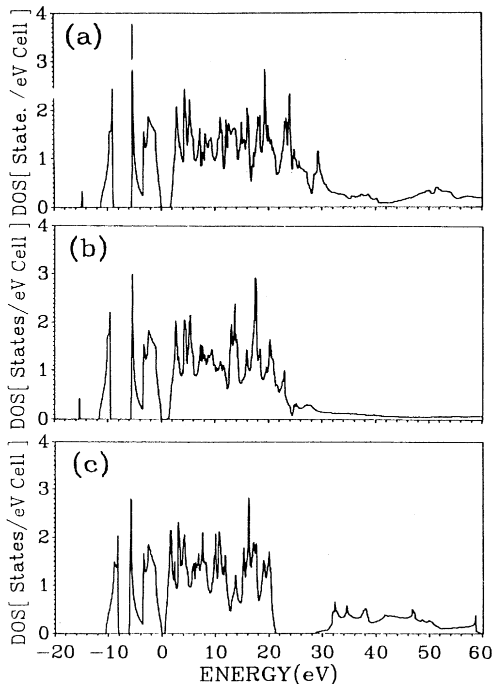

FIG. 11. DOS of (a) InP, (b) InAs, and (c) InSb.

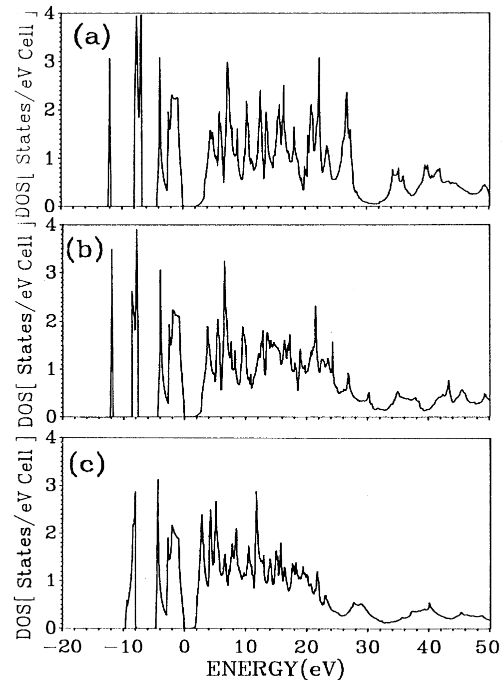

FIG. 13. DOS of (a) CdS, (b) CdSe, and (c) CdTe.

The DOS of the 18 semiconductors corresponding to the band structures shown in Figs. 1–6 are presented in Figs. 8–13. The DOS are calculated using the linear analytic tetrahedral method[50,51] based on the energy eigenvalues at the 505 regularly spaced **k** points in the $\frac{1}{48}$ of the fcc BZ. Use of a smaller mesh of 89 **k** points produces no discernible change in the DOS spectra. In these DOS diagrams, the CB DOS up to 60 eV above the gap are presented. In most published work on the electronic structure of semiconductors, usually no more than 10 eV of the CB DOS were presented. As will become evident in paper II,[7] the higher CB states turn out to be extremely important for nonlinear optical calculations. The extended basis set used in the present self-consistent OLCAO calculation enables us to obtain sufficiently accurate high-CB states, which would not be possible with the *semi-ab-initio* minimal basis approach or with the empirical approach.

For the group-IV elements, the DOS of diamond is noticeably different from those of Si and Ge, since C can hardly be viewed as a semiconductor with its large gap. For the III-V compounds, the VB DOS are all very similar, while there are substantial differences in the CB DOS especially in the high-energy range. Similar comments can be applied to the DOS of the II-VI semiconductors. The VB widths for the II-VI compounds are much narrower than those of III-V compounds, reflecting the increased ionicity in the former. The highly localized bands in Figs. 5, 6, and 7 correspond to the semi-core-like *d* electrons in these crystals.

IV. LINEAR OPTICAL PROPERTIES

The linear optical properties of cubic semiconductors have been studied by many groups in recent years.[14–41] We find that there were very few theoretical calculations for the Al series in the III-V compounds and the Cd series in the II-VI compounds. Chelikowsky and Cohen made systematic studies of 11 semiconductors including CdTe using nonlocal pseudopotentials as early as 1976.[15] More recent studies include those of Wang and Klein (WK),[19] who used a method (linear-combination-of-Gaussian-orbitals method) very similar to ours for Si, Ge, GaP, GaAs, ZnS, and ZnSe. Among other more comprehensive studies, Moss *et al.*[22] used the ETB method to study the linear optical response in ten group-IV and III-V semiconductors by including interactions up to third-nearest neighbors. Forouhi and Bloomer[31] used

TABLE I. Calculated linear optical properties of cubic semiconductors.

Crystal	lattice constant (Å)	E_g (eV) (expt.) direct	indirect	$\varepsilon_2(\omega)$ peak positions (eV) E_1	E_2	E_1'	$\varepsilon(0)$ Calc.	(Expt.)
Group IV								
C	3.567	5.79 (7.1)	4.54 (5.47)		4.8		4.34	(5.7)[a]
Si	5.431	2.77 (3.4)	1.01 (1.13)	3.3	4.5	5.6	9.03	(11.4)[b]
Ge	5.658	0.85 (0.98)	0.44 (0.76)	2.1	3.9	5.2	12.31	(15.3)[b]
III-V compounds								
AlP	5.462	3.44 (3.63)	2.17 (2.50)	4.3	5.4	7.0	5.63	(8.0)[c]
AlAs	5.66	2.56 (3.22)	1.37 (2.3)	3.5	4.4	5.6	6.81	(8.16)[d]
AlSb	6.135	2.46 (2.38)	1.23 (1.87)	2.8	3.8	4.7	7.21	(10.2)[e]
GaP	5.451	2.04 (2.77)	1.22 (2.38)	3.1	4.6	5.9	9.29	(9.1)[f]
GaAs	5.654	1.04 (1.52)		2.9	4.4	5.9	11.21	(10.9)[e]
GaSb	6.095	0.80 (0.81)		1.9	3.6	4.8	11.42	(14.4)[e]
InP	5.869	1.39 (1.39)		3.0	4.5	5.7	7.92	(9.6)[e]
InAs	6.036	0.55 (0.42)		2.6	4.3	5.7	10.02	(12.3)[e]
InSb	6.479	0.24 (0.24)		1.8	3.3	4.5	13.51	(15.7)[e]
II-IV compounds								
ZnS	5.409	2.34 (3.80)		4.3	5.9	7.3	5.63	(5.2)[g]
ZnSe	5.668	1.65 (2.82)		3.8	5.8	7.8	5.56	(5.9)[h]
ZnTe	6.089	2.24 (2.39)		3.6	5.4	6.9	5.24	(7.3)[i]
CdS	5.83	2.15 (2.58)		4.3	6.4	7.9	5.05	(5.2)[j]
CdSe	6.084	1.48 (1.82)		3.6	5.3	7.2	5.68	(5.8)[h]
CdTe	6.48	1.24 (1.60)		2.7	4.2	5.4	9.02	(7.2)[i]

[a]Reference 106.
[b]Reference 107.
[c]Reference 108.
[d]Reference 109.
[e]Reference 110.
[f]Reference 111.
[g]Reference 112.
[h]Reference 113.
[i]Reference 114.
[j]Reference 115.

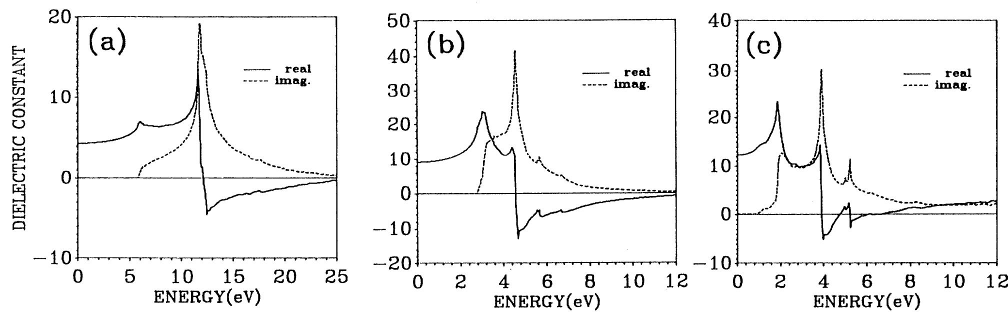

FIG. 14. The real [$\varepsilon_1(\omega)$, solid line] and the imaginary [$\varepsilon_2(\omega)$, dashed line] parts of the dielectric function for (a) C, (b) Si, and (c) Ge.

a parametrized scheme by fitting to the measured data to produce the optical spectra of about ten group-IV and III-VI semiconductors and also that of SiO_2 and SiC. With the exception of WK, these approaches were different from the present first-principles approach, in which the only experimentally measured data used are the lattice constants. More recently, Levine and Allan[40,41] had studied the linear responses in Si and Ge by applying a scissor operator to represent the self-energy correction, which yields excellent results for the dielectric response of semiconductors. However, none of the previous studies included as many crystals as the present study. A comprehensive study including as many crystals as possible is important for correlated studies and for the observation of general trends.

The calculated dispersion curves for the linear optical response for the 18 crystals whose band structures have just been presented in Figs. 1–6 are shown in Figs. 14–19. Both the real and the imaginary parts of the dielectric functions are plotted. The general agreement between the calculated spectra and the available measured ones[103–105] has been reasonable. The experimental curves are not reproduced in Figs. 14–19 because their inclusion tends to diminish the visual clarity of the results, and also, not all crystals have the measured data for inclusion. The range of frequency for display in our result is about 12 eV, except for diamond and the Cd series. For C, the major absorption peak is near 12 eV, much higher than in other crystals, and for the Cd compounds, there are substantial optical-absorption structures above 12 eV. Our most significant finding is that the spectra for each series are remarkably similar (with the exception of diamond in the group-IV semiconductors). It turns out that this is not the case with the frequency-dependent nonlinear optical susceptibilities[7,8] because of the important role of the higher CB states in the nonlinear optical excitations. In the empirical type of calculations, the $\varepsilon_2(\omega)$ curves in the same series can have large variations in structures,[22] an obvious artifact resulting from the inaccurate CB states.

Like the fundamental band gap, the dielectric constant in the static limit, $\varepsilon(0)$, is a very important physical quantity for semiconductors. The ability of LDA theory to predict the correct $\varepsilon(0)$ value in semiconductors has been a subject of major interest. Generally speaking, the LDA result for $\varepsilon(0)$ is much closer to experimental values than those obtained by empirical calculations.[18,22] However, a considerable discrepancy remains that may require theoretical treatment beyond the LDA theory. In Fig. 20, we plot the calculated $\varepsilon(0)$ values against the measured values for all the 18 semiconductors. The experimental data are taken from Refs. 106–115. The overall agreement is quite satisfactory. Of the 18 crystals, five are very close to the experimental data (GaP, GaAs, ZnSe, CdSe, and CdS) and two (ZnS and CdTe) overestimate the experimental data. The $\varepsilon(0)$ values for the remaining 12 crystals underestimate the experimental values. It should be pointed out that the LDA calcula-

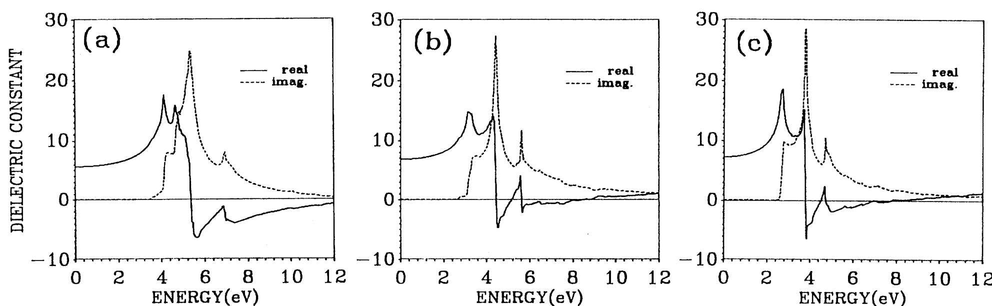

FIG. 15. The real [$\varepsilon_1(\omega)$, solid line] and the imaginary [$\varepsilon_2(\omega)$, dashed line] parts of the dielectric function for (a) AlP, (b) AlAs, and (c) AlSb.

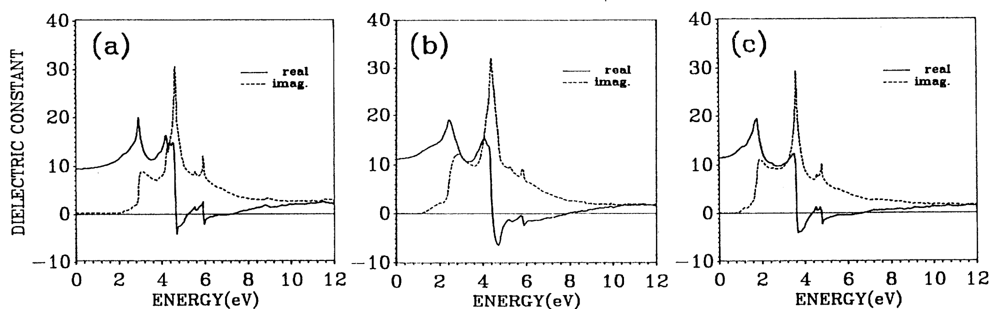

FIG. 16. The real [$\varepsilon_1(\omega)$, solid line] and the imaginary [$\varepsilon_2(\omega)$, dashed line] parts of the dielectric function for (a) GaP, (b) GaAs, and (c) GaSb.

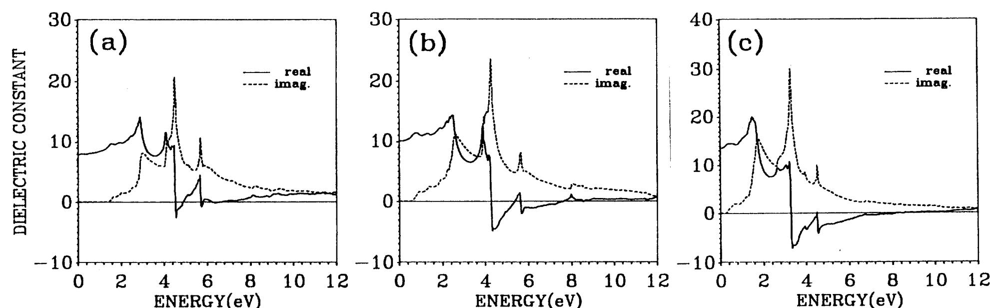

FIG. 17. The real [$\varepsilon_1(\omega)$, solid line] and the imaginary [$\varepsilon_2(\omega)$, dashed line] parts of the dielectric function for (a) InP, (b) InAs, and (c) InSb.

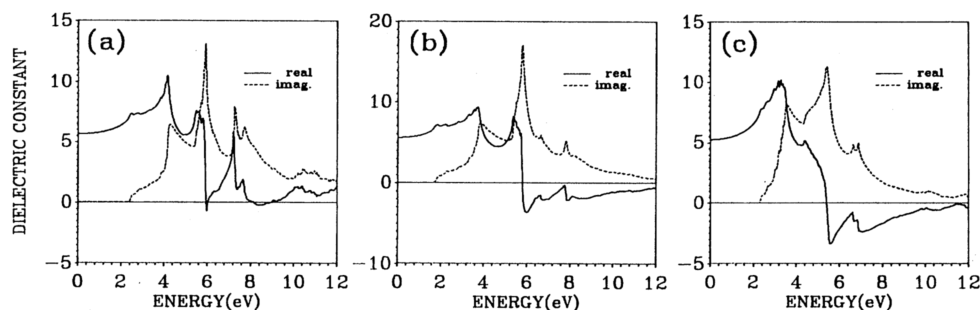

FIG. 18. The real [$\varepsilon_1(\omega)$, solid line] and the imaginary [$\varepsilon_2(\omega)$, dashed line] parts of the dielectric function for (a) ZnS, (b) ZnSe, and (c) ZnTe.

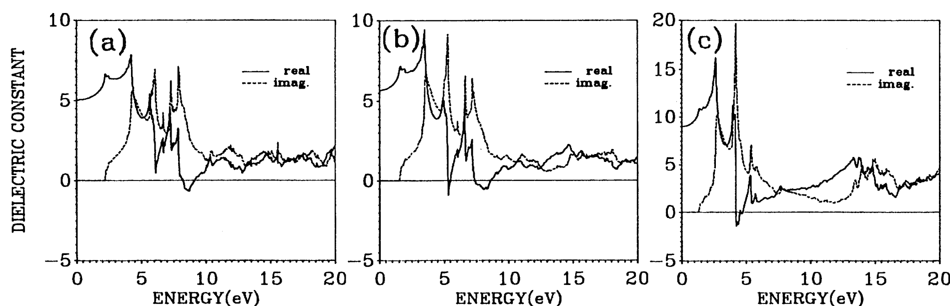

FIG. 19. The real [$\varepsilon_1(\omega)$, solid line] and the imaginary [$\varepsilon_2(\omega)$, dashed line] parts of the dielectric function for (a) CdS, (b) CdSe, and (c) CdTe.

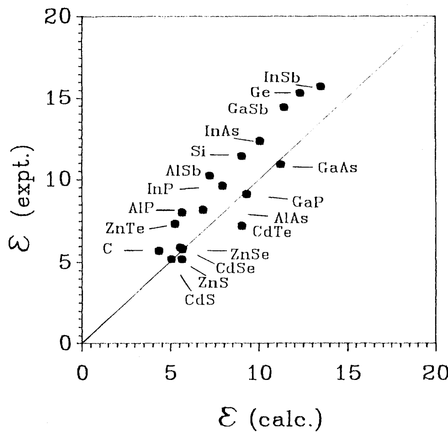

FIG. 20. Calculated vs experimental values of ε(0) for the cubic semiconductors.

tions generally tend to overestimate the ε(0) value, depending on the degree of underestimation of the gap. Since the gap underestimation in the present work tends to be less than other first-principles calculations, the calculated ε(0) values are correspondingly smaller. This point will be discussed later, in Sec. IV. The calculated ε(0) values for all 18 crystals are also listed in Table I.

The $\varepsilon_2(\omega)$ curves for the 18 semiconductors shown in Figs. 14–19 are characterized by two major structures, E_1 and E_2, arising from the critical-point transitions, and another smaller peak E_1' at a higher energy. The positions for the E_1, E_2, and E_1' peaks from our calculation are listed in Table I. WK had made detailed comparison of dielectric spectra with the experimental data for the six representative semiconductors from group-VI (Si, Ge), III-V (GaP, GaAs), and II-VI (ZnS, ZnSe) compounds. Detailed analysis of the structures in $\varepsilon_2(\omega)$ was identified with transitions between bands at critical points or along symmetry lines in the BZ. Both the critical-point transitions and the BZ volume effect were found to be important in shaping the structures. WK had also simulated the effect of self-energy correction by including a phenomenological relaxation time τ in an empirical scheme in their calculation. The relaxation time describes the lifetime broadening effect. The self-energy correction was carried out by introducing an empirical parameter λ following the work of Janak, Williams, and Moruzzi for metals[116] such that $\varepsilon(\omega) = 1/(1+\lambda)\varepsilon[\omega/(1+\lambda)]$ where λ's were chosen by aligning the central E_2 peak with the experiment. Both of these corrections did not change the spectra in any fundamental way. Since our linear optical results for Si, Ge, GaP, GaAs, ZnS, and ZnSe are very similar to WK in the sharp limit ($\tau \rightarrow 0$), and since the experimental data are available for only some of these crystals, we choose not to make any detailed crystal-by-crystal comparison as in WK. Rather, we will summarize our major results as follows: (1) like WK and other first-principles calculations, our results show that E_1 peaks are underestimated and E_2 peaks are overestimated. Inclusion of excitonic effects may partially improve the agreement; (2) the onset transitions, which correspond to the direct gaps at Γ, and the positions of the peak structures from our calculation are very close to those obtained by WK. The small difference reflects the slight deviation in the band structures because of the different ways the self-consistent potential was derived, and possibly, a different range of Gaussian decaying exponents in the basis functions; (3) our E_2 peaks are generally of smaller amplitude than WK and, therefore, in closer agreement with experiment. This, however, does not indicate any fundamental improvement over WK and is most likely due to the somewhat different ranges of the basis functions.

Aspnes and Stundna (AS) (Ref. 103) measured the optical properties of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV using spectroscopic ellipsometry. Pseudodielectric functions for the above eight semiconductors with no corrections made for surface overlayer or the substrate damage effect were obtained. They had emphasized the importance of sample preparation, surface, and substrate effects in the experimental determination of linear optical properties of bulk semiconductors. They had argued that for the same sample, the optical constants for bulk semiconductor using different experimental techniques should not differ by more than a few percent. The pseudodielectric functions presented by AS are in good overall agreement with our calculated spectra. The E_1 peaks in their result for Ge, GaAs, GaSb, and the In compounds show double structures presumably due to the spin-orbit coupling effect, which is not included in our calculation. In Table II, we compare the peak positions for E_1, E_2, and E_1' from our calculation with the values obtained by AS. The E_1' peaks for GaP, GaAs, InP, and InAs in Ref. 103 were not available because the maximum photon energy used was 6 eV. The overall agreement for the eight semiconductors is fairly good, taking into the consideration that our LDA calculation underestimates the gap values and therefore have lower peak positions.

There is less experimental and theoretical information for the Cd series. Our results on CdTe is reasonably close to Alouani, Brey, and Christensen[32] using the linear-muffin-tin-orbital (LMTO) method, with the exception

TABLE II. Comparison of calculated peak positions in $\varepsilon_2(\omega)$ with that of Aspnes and Studa (Ref. 103) (in parentheses). The values of E_1' for GaP, GaAs, InP, and InAs were not available because of the photon energy limitation.

Crystal	E_1 (eV)	E_2 (eV)	E_1' (eV)
Si	3.3 (3.4)	4.5 (4.2)	5.6 (5.3)
Ge	2.1 (2.3)	3.9 (4.2)	5.2 (5.5)
GaP	3.1 (3.7)	4.6 (5.0)	5.9 (–)
GaAs	2.9 (3.1)	4.4 (4.8)	5.9 (–)
GaSb	1.9 (2.1)	3.6 (4.0)	4.8 (5.3)
InP	3.0 (3.2)	4.5 (4.7)	5.7 (–)
InAs	2.6 (2.6)	4.3 (4.4)	5.7 (–)
InSb	1.8 (1.9)	3.3 (3.9)	4.5 (5.2)

that the E_1' peak in their calculation appears to be quite weak. On the whole, the spectra for the Cd compounds up to 8 eV resemble that of the Zn series, but substantial absorptions are also present at frequencies above 10 eV. This is related to the more complex CB structures in the Cd compounds shown in Fig. 6.

V. DISCUSSION

In Fig. 21, we plot the calculated values of minimum gap E_g with the $\varepsilon(0)$ for the 18 crystals whose electronic structures and linear optical properties were just presented. Both the calculated and the measured values for $\varepsilon(0)$ are shown. There is a general trend that for $E_g < 2.0$ eV, a smaller gap corresponds to a larger $\varepsilon(0)$ value. This trend is not evident for crystals with $E_g > 2.0$ eV. It has been recognized[19,40,41,73] that precise $\varepsilon(0)$ values in semiconductors depend on several competing factors. The LDA theory generally overestimates $\varepsilon(0)$ because of the underestimation of the gap; the local-field effect tends to reduce $\varepsilon(0)$, at least in Si; and the excitonic effects, which should be present in all these crystals, will increase $\varepsilon(0)$.[19] It is therefore quite difficult to separate these effects in each crystal. Godby, Schluter, and Sham[73] had investigated the $\varepsilon(0)$ in semiconductors by replacing LDA-exchange-correlation potential with a nonlocal self-energy operator in the spirit of the *GW* approximation,[78] and found that the agreement with experiment is actually even worse than the LDA result because the self-energy effects were not included correctly. The work of Levine and Allan[40,41] indicates that adding a scissor operator to the usual LDA Hamiltonian and simultaneously modifying the velocity operator improves the agreement with experiment drastically. For Si and Ge, their method improved the linear dielectric constant by almost 50% over the "naive" model. Their work underscores the importance of having a correct gap to obtain good linear and nonlinear optical constants. Whether or not this is the case with all other semiconductors remains to be seen.

As discussed earlier, our OLCAO-LDA results give a somewhat larger gap and correspondingly smaller $\varepsilon(0)$ values than some other first-principles LDA calculations. Although our gap values are in better agreement with experiment, thus facilitating the optical calculations, it should not be interpreted as a better result. One of the possible reasons for a larger gap in our calculation could be due to the insufficiently complete basis set in the present OLCAO calculation. However, test calculations on GaAs show further augmentation of basis set leading to only a very small reduction in the band gap. A desirable but more time-consuming approach is to obtain a more converged OLCAO-LDA result and then applying the scissor operator. In this work, we did not explore this route because we intend to concentrate on the overall trends of the linear and nonlinear optical properties for a large number of crystals rather than a very precise calculation for a single material. Also, the scissor operator has to be used irrespective of the actual calculated gap sizes. It is more likely that the difference in the calculated gap values comes from the different computational approaches to the electronic structure; especially with the functional form in which the potential is represented and the spatial extent of the basis function. A pseudopotential plane-wave approach can give quite different crystal wave functions than the present all-electron approach because of the different treatments of core polarization. Also, a method with some shape approximation to the potential function such as the LMTO method[32,33,116] will give somewhat different results especially with the covalently bonded semiconductors with open structures. Erwin, Pederson, and Pickett[117] had carefully tested the accuracy of the linear-combination-of-Gaussian-orbitals (LCGO) method against the linearized augmented-plane-wave method in three different systems: diamond, vanadium, and the diamond/Ni [001] interface with exactly the same potential functions. They have obtained almost identical results for the two methods. Their calculated values of $E_g = 4.79$ eV and $E_0 = 5.57$ eV for diamond are quite close to our result of 4.54 and 5.79 eV, respectively. The small difference can be attributed to the different forms of the basis functions (LCAO vs LCGO) and the different numerical procedures for the self-consistency. An interesting case is the α-quartz. The electronic structure calculated by the self-consistent-field–OLCAO method with a full basis set similar to this work[65] gave an indirect minimal gap of 5.59 eV and a direct gap of 5.91 eV at Γ. This is very close to the well-converged first-principles pseudopotential calculation of Binggeli *et al.*,[118] who obtained an indirect band gap of 5.8 eV. More recently, Allan has claimed[119] to have obtained the most accurate pseudopotential calculation to date on α-SiO_2 with an indirect gap of 5.602 eV and a direct gap of 5.925 eV at Γ. This is almost identical to the values obtained by the OLCAO calculation. It is highly desirable to carry out similar comparative tests for other crystals under very carefully controlled conditions.

The present calculation neglects relativistic effects, especially the spin-orbital coupling which definitely will affect the gap and the $\varepsilon(0)$ values for semiconductors involving fourth- or fifth-row elements of the Periodic Table. For those crystals with large Z atoms, WK (Ref. 19) had found that the inclusion of the relativistic effects

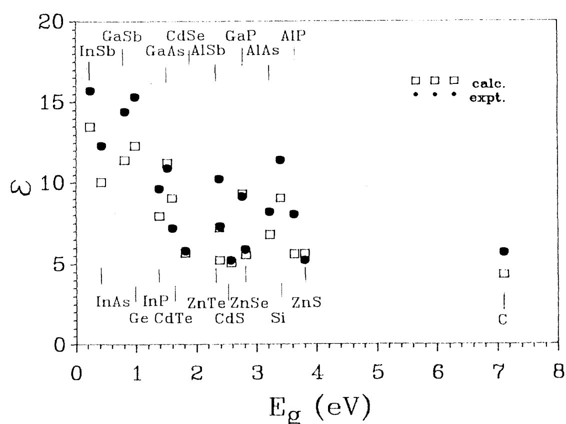

FIG. 21. Calculated and experimental $\varepsilon(0)$ vs experimental gap.

actually worsens the agreement of the gap values with the measurement. The inclusion of these effects probably will also reduce our gap values and increase the $\varepsilon(0)$ values for some crystals by an estimated 5–10 %. However, the present work focuses more on complete coverage of the large number of semiconductors, and on providing a reference base for the much more complicated calculation of nonlinear optical excitations. Inclusion of relativistic corrections greatly complicates the calculation and makes such an endeavor computationally unfeasible. With these considerations, we feel the use of the simpler form of the LDA calculation is justified.

There are several effects in semiconductors that are beyond the usual LDA treatment of electronic theory and affect the optical excitations. Apart from the band-gap underestimation, the other most important one is the local-field effect. In a crystal, the local field at the ion (or the atom) site is different from the average field within the cell. This will induce charge polarization to the ions which, in turn, contributes to the fields at other ion sites. The mutual interaction of the fields among the ions implies that the problem has to be solved in a self-consistent manner.[83] Louie, Chelikowsky, and Cohen find significant increase in the $\varepsilon_2(\omega)$ values at higher energies in Si due to the local-field effect.[17]

The second effect of considerable importance is the excitonic effect. In semiconductors and also in large-gap insulators, an excited electron in the CB and the hole left behind in the VB give rise to excitonic states near the band edge. Transitions to the excitonic states can greatly affect the optical properties of semiconductors near the absorption threshold, depending largely on electron-hole concentration. Extensive research work exists in this area.[87,88] The theoretical approach used is generally empirical in nature, relying very much on experimentally measured parameters, and is usually confined to bands near the top of the VB and the bottom of the CB. A first-principles type of treatment for the excitonic effect in semiconductors is extremely difficult because the ground state obtained from the LDA calculation is no longer adequate and the matrix elements of transition must be evaluated between site-specific many-particle states constructed as the linear-combination-of-single-particle states.

Another important effect not included in the present calculation is the electron-phonon interaction, which may be significant at higher temperatures. Many optical data involve extrapolations near the threshold region. Phonon-assisted transitions may introduce weak absorption tails in the low-frequency region where direct transition may not be possible. Most likely the effect of phonon-assisted transition may be negligible in the energy range of electronic excitation. There has been some recent work on the study of temperature dependence of optical absorptions in semiconductors, taking into consideration phonon-assisted transitions.[39] In the present study of optical excitations in semiconductors, we assume that we are dealing with the interaction of light with a covalently bonded medium without the complication of the exciton formation and without phonon emission and absorption. It is possible that in future studies, excitonic effects may be added to the LDA results based on some plausible models.

VI. CONCLUSIONS

The electronic structures and the linear optical properties of 18 cubic semiconductors are calculated by the first-principles OLCAO method based on the LDA formulation. The assumption that the excited states of the crystal are taken from the eigenstates of the ground-state Hamiltonian in the sense of Koopman's theory works reasonably well. The overall agreement of our calculation with experimental data and other first-principles calculations is quite satisfactory. Our calculated gap values are found to be larger and therefore in closer agreement with experiments than the well-converged pseudopotential calculations. This disagreement is probably due to the limited basis expansion in the present calculation or other aspects of differences in the computational approaches. Further improvement within the present simpler form of LDA formalism is possible. For example, we may further optimize the use of atomic orbitals used in the basis expansion and in the fitting functions for the charge density and potential, or by implementing some simpler procedures for gap correction. However, we must stress that most of the problems have to be addressed by more sophisticated treatments beyond the local-density theory and the one-electron model in general.

The present study forms a solid starting point for the calculations of nonlinear optical properties in the same 18 semiconductors in the two papers to follow. Our comprehensive study shows that a straightforward, accurate OLCAO-LDA calculation can provide a reasonably accurate description of optical excitations in semiconductors. Since no adjustable parameters, fitted or experimental (other than the fundamental gap treated by scissor operator), enter into our calculations, this first-principles LDA-OLCAO approach can be effectively applied to systems whose properties or structures are less well known without resorting to empirical or semiempirical methods. This greatly increases the versatility and the range of application of the theoretical tool to materials of practical interest.

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