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Orthogonalized linear combinations of atomic orbitals. II. Calculation of optical properties of polymorphs of silicon*

W. Y. Ching
Argonne National Laboratory, Argonne, Illinois 60439
and Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

Chun C. Lin
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

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By using the method of orthogonalized linear combinations of atomic orbitals developed recently, it is possible to obtain *ab initio* electronic wave functions of complex crystals like the two polymorphs of Si [Si III (*BC*-8) and Ge III (*ST*-12) structures] with basis-function sets of only moderate size. From these wave functions the dielectric functions (imaginary part) for these two Si polymorphs are obtained by computing the momentum matrix elements over the Brillouin zone. The present first-principles results are compared with previous works based on empirical methods. Possible implications on the optical-absorption properties of amorphous Si are discussed.

The method of linear combinations of atomic orbitals (LCAO) has been very successful[1] in obtaining accurate band structures for a variety of crystals, and in the study of interband optical transitions.[2-7] Because the crystal wave functions derived from an *ab initio* LCAO calculation are expressed as linear combinations of atomiclike functions centered at each lattice site and these atomiclike functions are usually expanded by Gaussian-type orbitals (GTO), the optical transition matrix elements can be easily obtained in closed forms. Therefore, with an efficient Brillouin-zone (BZ) integration scheme, accurate calculations of optical properties, which include the matrix-element effects, can be carried out. While such studies in simple crystals have reached a rather advanced stage, a first-principles calculation of the electronic and optical properties of complex crystals with many atoms (especially heavy atoms) per unit cell remains a formidable task. Instead, empirical or semiempirical methods have to be invoked. This is mainly because the basis-function set for a complex crystal becomes prohibitively large making the numerical work unduly excessive. In a recent paper[1] (which will be referred to as I), we have developed the orthogonalized-linear-combinations-of-atomic-orbitals (OLCAO) method for energy-band calculations. This method has been applied to several complex crystals[1,8-10] with great success. The essence of this method is to orthogonalize each valence Bloch sum to the core-state Bloch sums of all the other atoms in the unit cell so that the latter can be deleted from the final basis set resulting in a substantial reduction of the dimensionality of the secular equation. It was shown in paper I that in the case of Si III (*BC*-8) with eight atoms per unit cell in a body-centered-cubic structure, the energy levels obtained from the OLCAO calculation differ from those of the LCAO calculation (in which the core states are retained) by no more than 0.0008 a.u., while a great deal of saving in computer time is achieved. The method was then used to study the electronic structure of amorphous silicon (a-Si)[8] based on a quasiperiodic model of Henderson[11] with 61 atoms (H-61) in a simple cubic cell. The success of the OLCAO method for a "crystal" of such high complexity indicates that this method is a very promising one for first-principles calculations of electronic properties of disordered systems.

In paper I our OLCAO calculations were confined to the determination of energy levels. However, another important feature of the OLCAO technique is that because it involves much smaller basis sets as compared to the usual LCAO method, the computational procedure for such quantities as the momentum matrix elements is much simpler. This makes it feasible to perform theoretical calculations of the optical properties of many complex crystals from first principles. Accordingly, we present in this paper *ab initio* calculations of the optical matrix elements and the imaginary part of the dielectric functions [$\epsilon_2(\omega)$] for two polymorphs of Si [the Si III structure (*BC*-8) and the Ge III structure (*ST*-12)] using the wave functions derived from OLCAO band calculations. Comparison with some of the previous works obtained from empirical calculations[12-16] will be made.

The imaginary part of the dielectric function is given by[17]

$$\epsilon_2(\omega) = \frac{e^2}{3\pi m^2 \omega^2} \sum_{qm} \int \delta[E_q(\vec{k}) - E_m(\vec{k}) - \hbar\omega] \times |\langle \psi_q(\vec{k},\vec{r}) | \vec{p} | \psi_m(\vec{k},\vec{r}) \rangle|^2 d\vec{k}, \tag{1}$$

where ω is the photon frequency, $\vec{k}$ the wave vector, q and m the band indices, and $\vec{p}$ is the linear momentum operator. In the OLCAO method, we divide the usual Bloch sums into those of the core states ($b^c_{l\alpha}$) and those of non-core states ($b^n_{i\alpha}$) which include the valence states and the single Gaussians. Here α stands for the atomic sites in the primitive cell ($\alpha = 1, 2, \ldots, 8$ for *BC*-8 and $\alpha = 1, 2, \ldots, 12$ for *ST*-12), l runs through the core states ($1s, 2s, 2px, 2py, 2pz$ for Si), and i covers the valence orbitals ($3s, 3px, 3py, 3pz$) as well as the single Gaussians. We orthogonalize the non-core Bloch sums to all the core-state Bloch sums to form a set of orthogonalized Bloch sums ($b'^n_{i\alpha}$), i.e.,

$$b'^n_{i\alpha}(\vec{k},\vec{r}) = b^n_{i\alpha}(\vec{k},\vec{r}) + \sum_{l\gamma} a_{i\alpha,l\gamma} b^c_{l\gamma}(\vec{k},\vec{r}). \tag{2}$$

The one-electron crystal wave function is then expanded in terms of the orthogonalized Bloch sums as

$$\psi_q(\vec{k},\vec{r}) = \sum_{i\alpha} C^q_{i\alpha}(\vec{k}) b'^n_{i\alpha}(\vec{k},\vec{r}), \tag{3}$$

and the coefficients of expandion $C^q_{i\alpha}$ are obtained as the eigenvectors from the matrix diagonalization

$$|H'_{i\alpha,j\beta}(\vec{k}) - ES'_{i\alpha,j\beta}(\vec{k})| = 0, \tag{4}$$

where both the Hamiltonian matrix H' and the overlap matrix S' refer to the orthogonalized-basis space. The momentum matrix elements appearing in Eq. (1) can be reduced to, through the use of Eqs. (3) and (2), those with the unorthogonalized Bloch sums as basis, which can be computed easily.

While Ge is capable of existing in both the *BC*-8 and *ST*-12 structures, only the *BC*-8 structure has been discovered from high-pressure experiments for Si.[18,19] The band structure and density of states (DOS) of Si III (*BC*-8) derived from OLCAO calculations have been discussed in detail in paper I, those of the *ST*-12 structure were reported only briefly.[9] In these calculations, the crystal potential function is constructed from a superposition of atomic potentials of Si at each site with a Slater-type exchange approximation ($\alpha = \frac{2}{3}$). All the multicenter integrals occurring in the Hamiltonian matrix elements are evaluated exactly by the Gaussian technique and the summation of multicenter integrals over the lattice is carried to convergence. The construction of crystal potential and computation of matrix elements have been described in I. The lattice parameters used are the same as those of Ref. 15. In Fig. 1 we present the detailed band sturcture along the major symmetry lines of Si in the *ST*-12 structure. Using the eigenvalues for 126 nonequivalent $\vec{k}$ points in the BZ, we have calculated the DOS of *ST*-12 Si using the tetrahedron method[20] and the results are shown in Fig. 2. In general, as in the case of *BC*-8, the band structure in Fig. 1 is quite similar to that produced by the empirical pseudopotential method (EPM),[15] although subtle differences do exist especially in the unoccupied bands and the value of the band gap.

Using a minimal basis set ($3s$, $3px$, $3py$, $3pz$) in our calculation, we find an indirect band gap of 1.319 eV for *ST*-12 (as compared to 1.6 eV from Ref. 15). The top of the valence band is found to be at about 0.6 of ΓM_z from Γ and the bottom of the conduction band is at about 0.75 of ΓZ_x from Γ. Upon augmenting the basis function by one additional s-type and one p-type Gaussian orbital with exponent $\alpha = 0.18604$, the indirect band gap becomes 1.314 eV with little change in the general band structure. The subsequent optical calculations are based on the eigenvalues and eigenfunctions obtained from the calculation employing the minimal basis set.

With the eigenfunctions obtained from our band calculations, the optical transition matrix elements at any points in the BZ can be calculated. In order

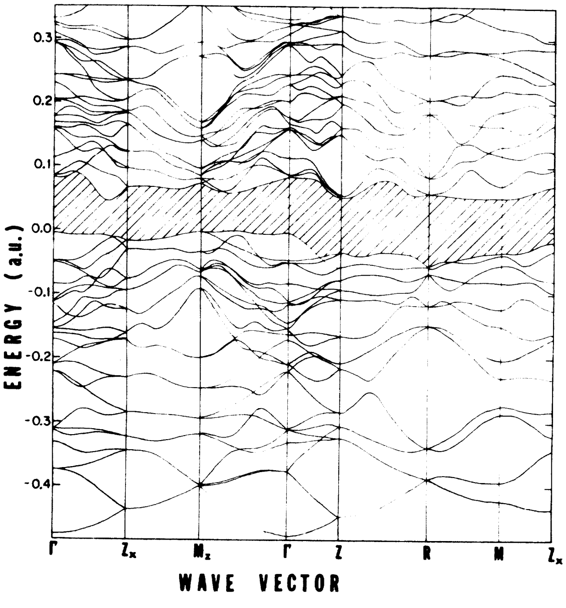

FIG. 1. Energy bands of *ST*-12 Si along various symmetry directions. The shaded area corresponds to the forbidden gap region. The energy of the top of the valence band is set to zero.

to assess the accuracy of the wave functions in the orthogonalized basis as compared to the ordinary LCAO basis, we have calculated the gradient matrix elements for many pairs of initial-final states at some general $\vec{k}$ points using wave functions generated by both methods. Typical results are listed in Table I for some representative pairs of bands. The agreement is excellent with differences in the fourth decimal place (atomic units) or less. Such small differences are certainly well within the accuracy of the minimal basis set itself and will show virtually no difference in the computed optical-absorption curves. Thus we can safely conclude that the wave functions obtained from the OLCAO method are as good as those from the LCAO method, yet a great deal of saving in computational cost is achieved. At an arbitrary $\vec{k}$ point in the BZ, both the matrix elements and the eigenfunctions are complex. The computational time for evaluating the momentum matrix elements increases rapidly with the number of basis functions which, in the case of the *BC*-8 structure, is 32 for the OLCAO basis, and 72 for the LCAO basis. Indeed, it takes 284 sec on the local Univac 1110 computer to calculate the momentum matrix elements for all pairs between valence and conduction bands at one $\vec{k}$ point using the LCAO wave functions, but takes only 66 sec for a similar calculation in the OLCAO case.

Having established the accuracy of the OLCAO wave functions, we proceed to calculate the optical matrix at 55 $\vec{k}$ points for the *BC*-8 structure and 70 $\vec{k}$ points for the *ST*-12 structure, each in their irreducible part of the BZ. Equation (1) is then evaluated by using numerical integration, i.e., the analytic linear energy tetrahedron method.[20] The matrix-element contribution from each tetrahedron microzone is taken to be the mean value of those at the four corners of the tetrahedron. We find the tetrahedron method more efficient than the usual Gilat-Raubenheimer method.[21]

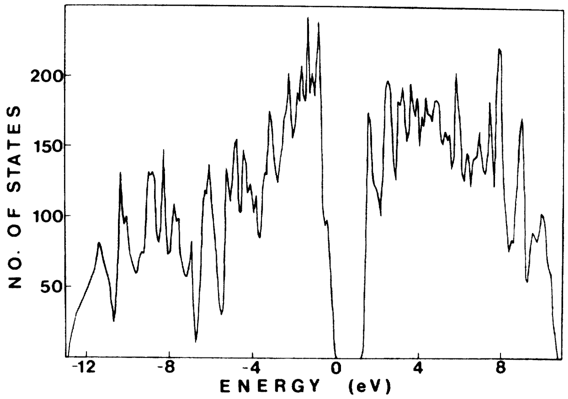

FIG. 2. Density of states of the conduction and valence bands of *ST*-12 Si in units of number of states per unit cell (12 atoms) per a.u. of energy. The energy of the top of the valence band is set to zero.

The $\epsilon_2(\omega)$ function can be regarded as the joint density of states (JDOS) weighted by the square of the transition matrix element at each $\vec{k}$ point in the BZ. In order to investigate the relative importance of the effects of each component on the optical absorption curve, we calculated separately the JDOS and ϵ_2 as functions of energy. The results are shown in Figs. 3 and 4, respectively, for the *BC*-8 and *ST*-12 structures. For both polymorphs, $\epsilon_2(\omega)$ peaks at a lower energy and more sharply than does the JDOS. For instance, ϵ_2 for the *ST*-12 structure peaks at 3.3 eV, whereas at this energy the JDOS is relatively small, being no more than 30% of its maximum value which occurs at about 11 eV. On the other hand ϵ_2 declines quite steeply above 4 eV and becomes very small upon reaching 11 eV. The vast difference in shape between the ϵ_2 and JDOS curves clearly depicts the matrix-element effects which give strong preference to the low-energy transitions. The ϵ_2 curve for the *BC*-8 structure rises from the onset energy rather gently up to about 2 eV and then shows an abrupt increase in the slope, ascending more drastically at higher energies. The same kind of

TABLE I. Comparison of the square of the gradient matrix element $M^2 = |\langle \psi_q(\vec{k},\vec{r}) | \vec{\nabla} | \psi_m(\vec{k},\vec{r}) \rangle|^2$ in a.u. for Si III at $\vec{k} = (2\pi/6a)(3,2,1)$ calculated by the LCAO method (including the core states) and by the OLCAO method. Here q_v and m_c are the band indices for some representative valence and conduction bands starting from the lowest valence band, and ΔE is the transition energy between the pair of bands (in eV).

		LCAO		OLCAO	
q_v	m_c	ΔE	M^2	ΔE	M^2
15	17	2.737	0.0595	2.735	0.0597
15	18	3.026	0.0124	3.025	0.0124
14	18	3.374	0.1355	3.372	0.1354
15	19	3.766	0.2523	3.765	0.2531
13	18	3.902	0.0671	3.900	0.0674
11	17	4.515	0.0366	4.516	0.0367
11	18	4.805	0.0296	4.806	0.0300
12	19	5.197	0.0244	5.197	0.0247
10	19	5.867	0.0034	5.870	0.0034
8	17	6.368	0.0110	6.376	0.0112
12	22	6.854	0.0063	6.853	0.0064
10	22	7.524	0.0188	7.526	0.0188
11	23	8.022	0.0016	8.024	0.0017
5	18	8.661	0.0046	8.666	0.0043
6	19	9.257	0.0088	9.259	0.0084
8	25	10.479	0.0086	10.487	0.0088
13	32	11.625	0.0025	11.619	0.0024
8	28	12.401	0.0002	12.408	0.0002
5	27	13.583	0.0004	13.587	0.0004
2	22	14.866	0.0002	14.883	0.0003

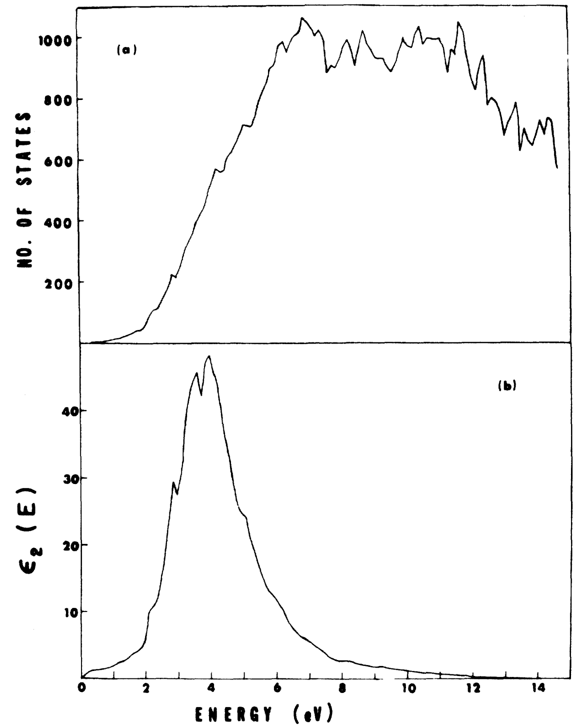

FIG. 3. (a) Joint density of states of BC-8 Si in units of number of states per unit cell (eight atoms) per a.u. of energy difference. (b) The imaginary part of dielectric function $\epsilon_2(E)$ of BC-8 Si.

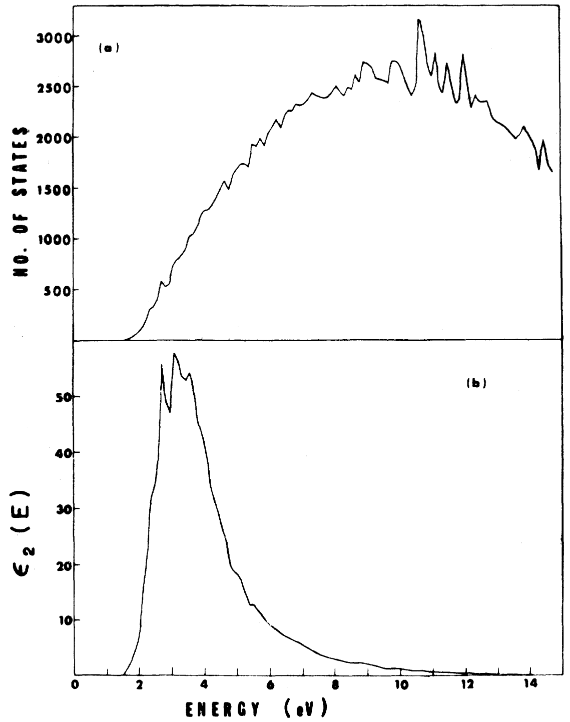

FIG. 4. (a) Joint density of states of ST-12 Si in units of number of states per unit cell (12 atoms) per a.u. of energy difference. (b) The imaginary part of dielectric function $\epsilon_2(E)$ of ST-12 Si.

abruptness is hardly evident in the ST-12 case. Upon examining the JDOS of these polymorphs, we see again a two-slope behavior for the BC-8 structure, but not for ST-12. Thus the slow-rising edge near the onset of $\epsilon_2(\omega)$ may be attributed to the similar behavior of the JDOS. As a result of it, the maximum value of $\epsilon_2(\omega)$ for BC-8 occurs at a higher energy than that for ST-12, in spite of the much larger threshold energy for the latter structure.

The ϵ_2 functions for the polymorphs of Si and Ge have been studied in detail using empirical methods.[13-16] It is of interest to compare the results of these empirical works with the present first-principles results based on a different method and potential. Specifically, we compare our results with those of the EPM calculation of Joannopoulous and Cohen.[16] Our OLCAO calculations give a smaller band gap than does the EPM for both the ST-12 structure (1.31 eV for OLCAO vs 1.6 eV from EPM) and the BC-8 structure (0.029 eV vs 0.4 eV); thus, a slight difference in the onset of the ϵ_2 curve is seen. Also the peak value of ϵ_2 in the present calculation is slightly higher than the EPM one for both structures. Nevertheless we find a very good overall agreement between the OLCAO and EPM results especially considering the vast difference in approach between the two methods. Furthermore, in both calculations ϵ_2 is found to exhibit a narrow peak as compared to the JDOS curve due to the effects of the momentum matrix elements.

An obvious extension of this work is to perform a similar theoretical analysis for a-Si. The importance of a basic understanding of the optical-absorption behavior of a-Si has been accentuated by the recent development of a-Si solar cells.[22] To represent the arrangement of the atoms in an a-Si sample, a number of continuous random tetrahedral network (CRTN) models have been proposed.[23] For our application the most attractive CRTN models are those with a quasiperiodic structure because for these cases the computational procedures for the electronic states of a-Si become identical, at least in principle, to those of crystalline solids. Thus based on the quasiperiodic model with 61 atoms in a simple-cubic unit cell proposed by Henderson[11](H-61), we have calcuated the energy spectrum and DOS of a-Si. While the valence-band DOS is in good agreement with experiment, there are indications that the deviation of the atomic position as given by the H-61 model from the perfect tetrahedral configuration is too large. Our calculations based on the H-61 model give no intrinsic band gap although the DOS near the Fermi level is quite low. However, whether an intrinsic band gap exists or not, as well as the question of the pattern of DOS near the Fermi level, may depend sensitively on the degree of distortion, and further studies are needed to get a more definitive answer. We have recently employed a quasiperiodic model with 54 atoms per unit cell constructed by Guttman[24] for a similar energy calculation. This model has generally somewhat smaller distortion than H-61, and gives an intrinsic gap of 0.7 eV. A great deal of systematic study to ascertain quantitatively how the electronic structure, particularly near the Fermi level, is influenced by various degrees of small local distortion, remains to be done. Once we have a model which can provide a more definitive answer concerning the band gap, it would be instructive to use the OLCAO technique to compute ϵ_2 for a-Si. Nevertheless, even in the absence of a first-principles calculation of ϵ_2 for a-Si, some conclusions concerning its optical properties can be drawn based on the results of this paper. In Ref. 8 we compare the experimental optical-transition strength of a-Si with the theoretical JDOS (using the H-61 model), since these two quantities would be proportional to each other if the momentum matrix elements were independent of the transition frequency. From Fig. 3(a) of Ref. 8, we see that the maximum of the theoretical JDOS occurs at 8 eV whereas the experimental optical-transition strength peaks at 4 eV. This discrepancy is now quite understandable because our analysis for the two polymorphs of Si indicates that the matrix elements have the effect of giving much higher preference to the low-energy transitions. Assuming the same kine of behavior for a-Si, we expect the inclusion of the matrix-element effects to shift the peak of the theoretical curve to a lower energy resulting in a better agreement with experiment.

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