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Orthogonalized linear combinations of atomic orbitals: Application to the calculation of energy bands of Si III†

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The method of linear combinations of atomic orbitals has been modified by orthogonalizing Bloch sums of the valence states to those of the core states so that the latter can be deleted from the basis-function set in order to reduce the size of the secular equations. In case the overlap of the core wave functions between different atoms is small, the expansion coefficients in the orthogonalization process are simply related to the overlap matrix elements. This methods of orthogonalized linear combinations of atomic orbitals (OLCAO) is applied to Si III which has eight atoms in a primitive cell, and its accuracy is verified by comparing the OLCAO results with those obtained by directly including the core wave functions in the basis set. Our calculations give a band gap of 0.029 eV for Si III and the density of states for Si III is found to be substantially different from that of the ordinary silicon crystals. The small band gap provides an explanation for the drastic decrease of electric resistivity at high pressure and the metallic behavior of highly compressed silicon.

I. INTRODUCTION

The method of linear combinations of atomic orbitals (LCAO), or the tight-binding method, for band-structure calculations has been shown to be very successful in recent years.[1,2] The essential key to the success of this method is the ability to calculate the multicenter integrals accurately and efficiently. The crystal potential is usually calculated from a superposition of free-atom charge densities using local-exchange approximation. Self-consistency can be achieved by an iterative process.[3,4] The method has been applied to crystals of different varieties[4-12] and has been demonstrated as capable of yielding very accurate energy bands.

In the LCAO method the basis functions are Bloch sums of localized functions centered at the atomic sites, i.e.,

$$b_i(\vec{k},\vec{r})=\sum_{\nu} e^{i\vec{k}\cdot\vec{R}_\nu}\phi_i(\vec{r}-\vec{R}_\nu)\,, \tag{1}$$

where $\vec{R}_\nu$ is a translational vector. Traditionally these localized functions are taken as the wave functions of the free atoms, including both the core and valence states. For ease of computation, the atomic orbitals are usually expanded in terms of Gaussian-type orbitals (GTO). Another choice of basis functions is to simply use each individual GTO for ϕ_i to form a set of single-Gaussian Bloch sums. This gives a larger basis set and more accurate band energies because of the increased variational freedom. The single-Gaussian basis is particularly well adapted for simple systems such as light alkali metals,[2,10,13] but becomes less practical for heavier crystals because of excessively large secular equations. Another approach is to take the ϕ_i's as some linear combinations of Gaussians which are qualitatively similar to the atomic wave functions but include to some degree the distortion of the atomic orbitals by the crystal. Methods for generating these linear combinations, sometimes referred to as contracted Gaussians or optimized orbitals, have been described.[14] These optimized orbitals give better band structures than do the true atomic orbitals.[14] For higher accuracy a few single-Gaussian Bloch sums can be added to the optimized-orbital set. Basis sets consisting of mixture of optimized orbitals and single Gaussians offer a great deal of flexibility in providing accurate band structures with a relatively small number of functions.

For more complex crystals with several heavy atoms (N) per unit cell, the size of the basis set increases with N times the number of localized orbitals chosen for each atom. From the computational standpoint, it is important to reduce the number of the localized orbitals without adversely affecting the energies. For heavy-atom crystals, a considerable portion of the basis functions is associated with the core states which are often not of prime interest in energy-band work. However, if one simply excludes the core states from the basis set, the calculated levels may fall well below the correct values as the linear variational method always attempts to reproduce the lowest states (in this case, the core states) instead of the valence states. Even for a favorable case (Si), the neglect of the core functions causes a nonlinear downward shift of the valence band by 0.2–2.8 eV.[15] This difficulty, however, can be circumvented if one orthogonalizes the valence Bloch sums to all the core-state ones, and retains only the orthogonalized valence Bloch sums in the basis set. A drastic reduction of the dimensionality of the secular equation can be accomplished, making it practical to apply the LCAO method to complex crystals. This is, in spirit, similar to the method of orthogonalized plane waves (OPW),[16] but the detailed formulation is quite different. A much larger basis set is required for the OPW method as compared to the orthogonalized-LCAO (OLCAO) method.

In Sec. II, the method of OLCAO is formulated from the basic framework of the LCAO method. Application of the OLCAO method to the case of Si III is made in Sec. III. Si III is a polycrystalline phase of Si recovered from high pressure experiments and was found to be far more metallic than ordinary silicon.[17,18] It has a body-center-cubic structure containing eight atoms in a primitive cell.[19] The results of band calculation using the OLCAO method are compared with those based on the usual LCAO method with core states included. Discussions of the band structure of Si III are given in Sec. IV.

II. ORTHOGONALIZED LCAO METHOD

Consider a complex crystal with N atoms per primitive cell. Without loss of generality, we assume the N atoms to be of the same type. Generalization to atoms of different type is trivial. In the LCAO method, a Bloch sum basis function may be characterized by the particular localized function ϕ_i and its associated atomic site (α) in a primitive cell, the position of which is designated by $\vec{\rho}_\alpha$, i.e.,

$$b_{i\alpha}(\vec{k},\vec{r}) = \sum_{\nu} e^{i\vec{k}\cdot\vec{R}_\nu}\phi_i(\vec{r}-\vec{\rho}_\alpha-\vec{R}_\nu)\,, \qquad \alpha=1,2,\ldots,N, \tag{2}$$

where $\phi_i(\vec{r}-\vec{\rho}_\alpha-\vec{R}_\nu)$ is the ith localized function centered at the αth atom in the νth cell. For a given one-electron Hamiltonian, one uses these basis functions to obtain the Hamiltonian and overlap matrix elements, $H_{i\alpha,j\beta}$ and $S_{i\alpha,j\beta}$, and then solve the secular equation

$$|H_{i\alpha,j\beta}(\vec{k}) - S_{i\alpha,j\beta}(\vec{k})E| = 0\,, \tag{3}$$

to find the energies. The localized functions ϕ_i are now taken as atomiclike orbitals (such as the true atomic orbitals or the optimized orbitals) corresponding to the core and valence states of the constituent atoms, with possible supplement of single Gaussians. We partition the Bloch sums into those of the core states ($b^c_{i\alpha}$) and those of noncore states ($b^n_{i\alpha}$) which include the valence states and the single Gaussians. For the case of silicon, the core states are readily identified as 1s, 2s, and 2p, although for heavier atoms the division between core and valence states is less distinct. We shall return to this point at the end of this section. By orthogonalizing the noncore Bloch sums to all the core-state Bloch sums, a new set of basis functions are obtained, e.g.,

$$b'^{n}_{i\alpha}(\vec{k},\vec{r}) = b^n_{i\alpha}(\vec{k},\vec{r}) + \sum_{l,\gamma} a_{i\alpha,l\gamma}\, b^c_{l\gamma}(\vec{k},\vec{r})\,, \tag{4}$$

where the summation over l and γ cover all the core states and all the atoms in the unit cell. The orthogonality condition requires

$$\langle b'^{n}_{i\alpha}(\vec{k},\vec{r})\,|\,b^c_{j\beta}(\vec{k},\vec{r})\rangle = 0. \tag{5}$$

In principle, a series of simultaneous equations must be solved to determine the coefficient a's in Eq. (4). If, however, the overlap between the core functions of different atoms can be neglected, i.e.,

$$\langle b^c_{i\alpha}(\vec{k},\vec{r})\,|\,b^c_{j\beta}(\vec{k},\vec{r})\rangle = 0 \quad \text{for } \alpha\neq\beta\,, \tag{6}$$

then the orthogonalization coefficients assume a very simple form

$$a_{i\alpha,l\gamma} = -\langle b^n_{i\alpha}(\vec{k},\vec{r})\,|\,b^c_{l\gamma}(\vec{k},\vec{r})\rangle\,. \tag{7}$$

We now change over to the orthogonalized Bloch sums as basis functions with i covering only the noncore states. The matrix elements in this new representation, denoted as $H'_{i\alpha,j\beta}$ and $S'_{i\alpha,j\beta}$, are related to the unprimed ones by the appropriate transformation associated with Eq. (4). With the core states removed, the size of the secular equations is reduced.

If the core-function overlap is not negligible, Eq. (7) is no longer applicable and the orthogonalization coefficients have to be determined by solving a system of linear equations. Alternatively one can identify as core states only those for which Eq. (6) applies and put those states having appreciable interatomic overlap into the noncore group, so as to retain Eq. (7). For Si III the interatomic core overlap is quite small and our results in the next section indeed show that Eq. (7) is valid.

III. APPLICATION TO Si III

A. Crystal potential and basis functions

Si III is a metastable phase of Si recovered from high-pressure experiments. The crystal structure has been determined from x-ray diffraction patterns.[19] The positions of the eight atoms in a primitive cell as measured from the center of a cube with $a=6.636$ Å are $(0.1, -0.1, 0.1)a$, $(-0.1, 0.1, -0.1)a$, $(0.1, 0.1, -0.4)a$, $(-0.1, -0.1, 0.4)a$, $(-0.1, 0.4, 0.1)a$, $(0.1, -0.4, -0.1)a$, $(0.4, 0.1, 0.1)a$, and $(-0.4, -0.1, -0.1)a$.

Si III is an ideal case for the application of the OLCAO method. It has a fairly complex crystal structure containing eight atoms per primitive cell to make it a suitable candidate to test the orthogonalization technique. On the other hand it is still within our available computing capability to include all the core states in the band calculation so that we can compare the OLCAO with the LCAO results. Furthermore the very large abrupt decrease in electric resistance of Si at high pressure[17] has attracted much attention, and may be related to a transition to a metallic state.[20,21] Theoretical prediction of pressure-induced changes of the lattice type and the accompanying variation in band structure to explain these observations is of prime interest. Because of its slightly distorted tetrahedral-coordination structure, Si III also has been studied recently in relation to amorphous Si.[22] Because of the complexity of these polytypes, empirical methods were used in the previous theoretical efforts such as the calculations for Ge III and Ge IV by Henderson and Ortenburger[23] and the empirical pseudopotential work of Ref. 22. Hence a first-principles calculation of the band structure of Si III is very desirable.

The crystal potential in the one-electron Hamiltonian is expressed as a superposition of spherical atomiclike potentials $V_a(r)$ centered at each Si site. Evaluation of the multicenter integrals is greatly simplified if $V_a(r)$ is curve-fitted to the functional form of

$$V_a(r) = -\frac{Z}{r} e^{-Cr^2} + \sum_m \xi_m e^{-b_m r^2}. \tag{8}$$

A typical multicenter integral appearing in the Hamiltonian matrix elements involves the product of a Gaussian at site A, another at B, and $V_a(r)$ centered at C. The integrals associated with the first term of Eq. (8) can be expressed in terms of the error function and those associated with the second member can be evaluated analytically.

It has been customary to use the overlapping atomic potential (OAP) model as the first approximation to the crystal potential, i.e., approximate $V_a(r)$ by the potential of a free Si atom computed from the Hartree-Fock wave function with a Slater-type local exchange.[24] Before proceeding to Si III, we have performed some test calculations for the *ordinary silicon crystal* in order to check the adequacy of the OAP model. Using an atomic potential with the exchange parameter α set to $\frac{2}{3}$, we have calculated the OAP band structure of the ordinary silicon crystal by a basis set of eleven s-type and nine p-type single-Gaussian Bloch sums. The results are in good overall agreement with those of Stukel and Euwema[25] obtained by a self-consistent-field (SCF) calculation with the OPW method.[26] Our calculated band gap (indirect) is 1.14 eV as compared to 1.10 eV given by Stukel and Euwema, and 1.13 eV from experiment.[27] For the band calculation we find it advantageous to discard the very long-range component of the atomic potential. The resulting band structure shows virtually no change (less than 0.0005 a.u.) from the previous one. On the other hand, suppression of the long-range tail has the benefit of bringing the vacuum level much closer to the experimental value and significantly reducing the computational work. This atomic potential is used to construct the OAP model for Si III. The parameters of the Gaussian fit [Eq. (8)] are as follows: $Z = 14$, $C = 11.49932$, $b_m = 378.19607$, 71.18895, 18.38183, 4.09387, 1.52868, 0.45629, 0.13739 with the corresponding $\xi_m = 6.22033$, 14.46129, 31.95406, −9.65245, −0.40900, −1.87997, −0.47627.

To select the localized functions ϕ_i, we resort to the method of contracted Gaussians. Following the procedure of Ref. 14, we solve the secular equation with $\vec{k} = 0$ for the ordinary Si crystal using eleven s-type and nine p-type single Gaussian Bloch sums as basis functions. According to the weightings of these Bloch sums in the eigenvector corresponding to a 1s core state, we construct a linear combination of the Gaussians (centered at the same site) which is referred to as a contracted Gaussian and is taken as the 1s "optimized orbital." Similarly we obtain the 2s and 2p optimized orbitals in the same manner. For the 3s and 3p states one may use respectively the Γ_{1v} and Γ'_{25v} eigenfunctions to form contracted

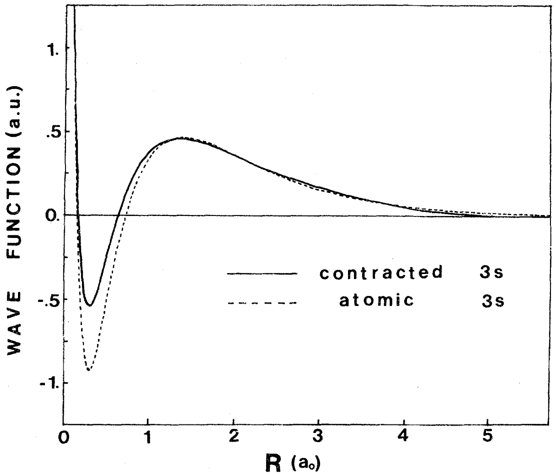

FIG. 1. Comparison of the 3s optimized contracted-Gaussian orbital with the true atomic orbital.

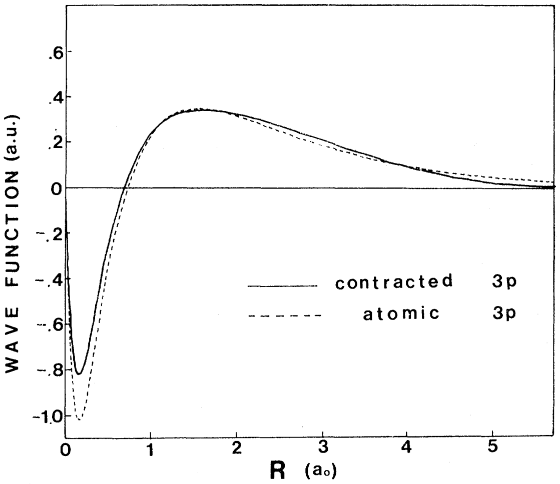

FIG. 2. Comparison of the $3p$ optimized contracted-Gaussian orbital with the true atomic orbital.

Gaussians. However, because the bottom of the conduction band of the ordinary Si crystal is at $\vec{k}=(2\pi/a)$ (0.85, 0, 0), it is also natural to base the contraction procedure on the single-Gaussian solution at this $\vec{k}$ point. Thus we choose a weighted average between the two sets of contracted Gaussians based on $\vec{k}=0$ and $\vec{k}=(2\pi/a)$ (0.85, 0, 0) as our $3s$ and $3p$ optimized orbitals; the weighting was selected so as to produce a band gap close to 1.14 eV. The $1s$, $2s$, and $2p$ optimized orbitals are very similar to the true atomic functions.[28] In Figs. 1 and 2 are shown respectively the $3s$ and $3p$ optimized contracted-Gaussian orbitals which are seen to be qualitatively similar to their atomic counterparts but of slightly shorter range. When this set of $1s, \ldots, 3p$ optimized orbitals is used as basis functions, we obtain a band structure of the ordinary Si crystal which agrees with the results of the single-Gaussian basis set to within typically 0.007 a.u. For our work on Si III, this set of optimized orbitals will be adopted.

B. Band calculations

With the OAP approximation for the crystal potential and the $1s, \ldots, 3p$ optimized orbitals described in the preceeding section, we have calculated the band structure of Si III using both the OLCAO and LCAO schemes. The basis set contains 72 functions with the core states included and 32 functions without. The agreement is excellent; the two sets of energies differ by no more than 0.0008 a.u. For illustration we compare the energy levels of the Γ and H points determined by the two schemes in Table I. For states near the

TABLE I. Comparison of energies (in a.u.) of the conduction (upper group) and valence (lower group) states of Si III at the Γ and H points calculated by the LCAO method (including core states) and by the OLCAO method. Reference point is set at the top of the valence bands. The numeral 2 inside a parentheses indicates double degeneracy.

Γ		H	
LCAO	OLCAO	LCAO	OLCAO
0.3179	0.3178	0.2533(2)	0.2532(2)
0.3142(2)	0.3140(2)	0.1711(2)	0.1710(2)
0.2926(2)	0.2926(2)	0.1594(2)	0.1593(2)
0.2842	0.2841	0.1593	0.1591
0.2735	0.2732	0.1399(2)	0.1398(2)
0.1924	0.1924	0.1355	0.1356
0.1884(2)	0.1884(2)	0.1351	0.1350
0.1630	0.1629	0.1271	0.1270
0.1587(2)	0.1586(2)	0.1215(2)	0.1214(2)
0.0881(2)	0.0881(2)	0.1089	0.1090
0.0875	0.0875	−0.0022	−0.0023
−0.0408	−0.0407	0.0(2)	−0.0001(2)
−0.0571(2)	−0.0571(2)	−0.0008	−0.0009
−0.1536(2)	−0.1540(2)	−0.0959	−0.0959
−0.1538	−0.1542	−0.0961(2)	−0.0961(2)
−0.1978(2)	−0.1982(2)	−0.1470(2)	−0.1471(2)
−0.2488(2)	−0.2488(2)	−0.1478	−0.1479
−0.2495	−0.2495	−0.2285	−0.2281
−0.3139	−0.3142	−0.3345(2)	−0.3353(2)
−0.3222(2)	−0.3220(2)	−0.3347	−0.3354
−0.3223	−0.3221	−0.4054	−0.4057
−0.4913	−0.4920	−0.4055(2)	−0.4059(2)

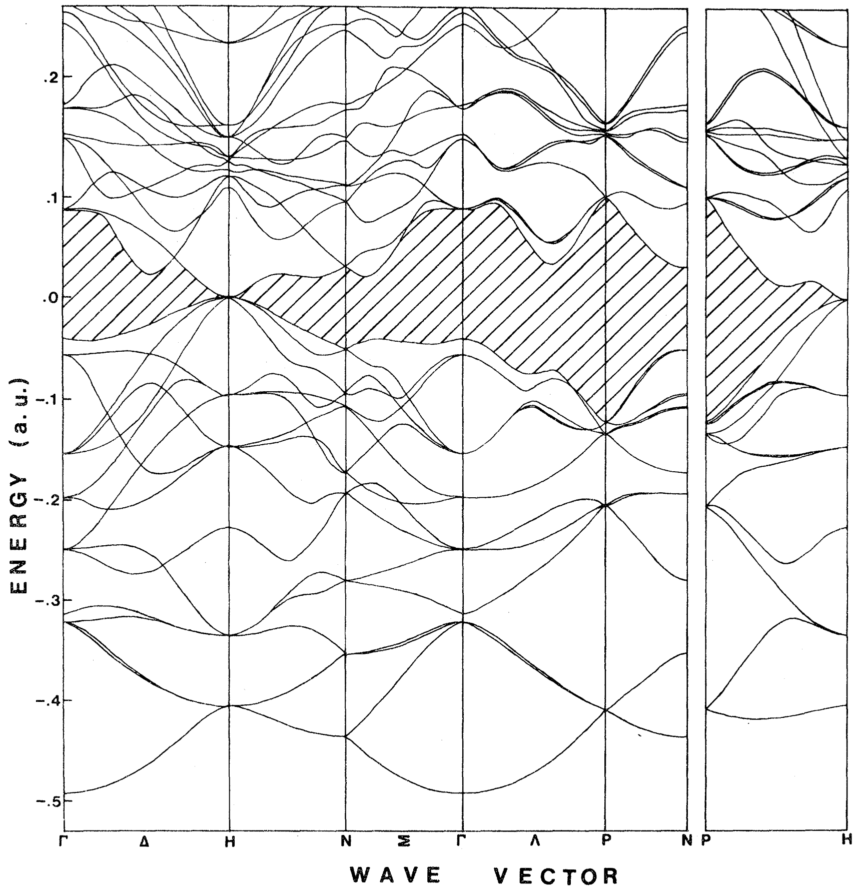

FIG. 3. Energy bands of Si III along various symmetry directions. The shaded area corresponds to the forbidden gap region. The energy of the top of the valence band is set to zero.

Fermi levels where the electronic states are of most importance, the difference is even smaller, less than 0.0002 a.u. This confirms the validity of neglecting interatomic core overlap.

Figure 3 shows the energy bands of Si III calculated by using the OLCAO method along several symmetry lines. A band structure of Si III has been previously reported by Joannopoulos and Cohen using the empirical pseudopotential method (EPM).[22] Our valence-band structure is in fairly good agreement with the EPM work, but substantial differences exist for the conduction states with respect to both the general shape and the width of the bands. The EPM calculation gives a direct band gap of about 0.4 eV at the *H* point while our results show a negative gap of about 0.04 eV at the same $\vec{k}$ point, i.e., the bottom of the conduction band is lower than the top of the valence band. The discrepancy between the results of EPM and of ours is not too surprising in view of the difference in approach. Although a negative gap is not incompatible with the experimental observation that the resistivity of Si III is much smaller than that of ordinary Si,[18] one must bear in mind that our energy bands are obtained by using a basis set with $1s, \ldots, 3p$ orbitals only, and the uncertainty of the energy values due to the use of such a limited basis set, may very well exceed 0.04 eV. The question of band gap will be examined further in Sec. III C by means of extended-basis calculations.

The density of states (DOS) for Si III is calculated by using the analytic tetrahedron linear energy method.[29,30] In the present case, 55 regularly spaced $\vec{k}$ points in $\frac{1}{48}$ of the Brillouin zone yields 128 tetrahedrons of equal volume. The gradient of energy which is required in the DOS calculation can be simply expressed in terms of energies at the four corners of the tetrahedron microzone. In Fig. 4 we present our calculated DOS. The general feature is rather different from that of ordinary Si. The leading peak near the upper edge of the valence band of Si III is much sharper and the two lower peaks of ordinary Si are split into a series of smaller peaks. Our DOS curve for the valence band agrees well with that of the EPM calculation.

C. Band gap by extended-basis calculations

Since the band gap of −0.04 eV which we obtained in Sec. III B, may be smaller than the uncertainty

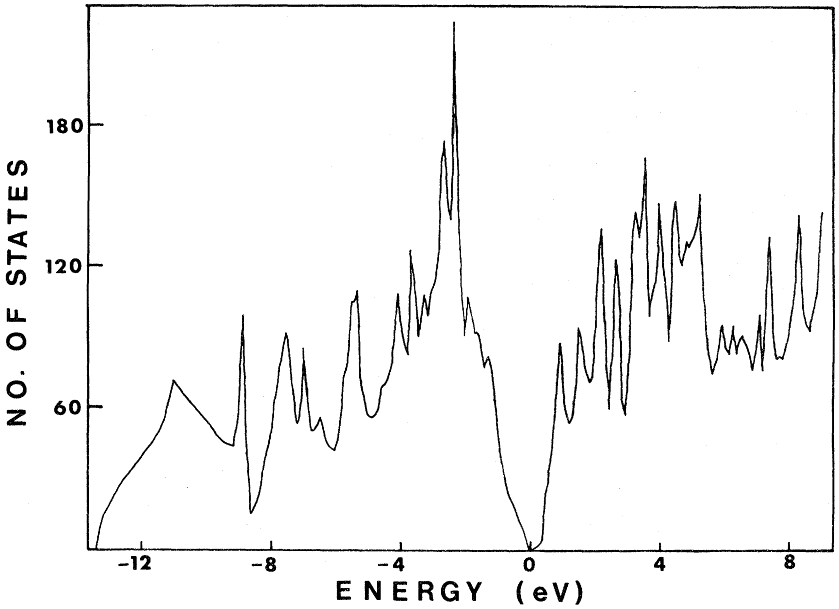

FIG. 4. Density of states of the conduction and valence bands of Si III. The energy of the top of the valence band is set to zero.

associated with using a limited set of atomiclike orbitals to determine the eigenvalues of a given crystal Hamiltonian, it is desirable to augment the basis set and examine the variations of the energies near the gap. To this end we supplement the optimized-orbital basis functions by a series of single-Gaussian Bloch sums corresponding to the long-range members of the GTO constituents. For the H point where the band gap occurs, we have calculated the level energies using several different combinations of single-Gaussian supplement. Let us label the GTO's of exponents 0.186 040, 0.257 644, 0.503 922, and 1.452 21 by subscripts 1, 2, 3, and 4, respectively, so that s_1 represents an s-type single-Gaussian Bloch sum of exponent 0.186 040. In Fig. 5 we show the two highest valence-band levels and the lowest conduction-band level (at the H point) for the following sets of added single Gaussians: (a) s_1, s_2, p_1, and p_2; (b) s_1, s_2, s_3, p_1, p_2, p_3; (c) s_1, s_2, s_3, s_4, p_1, and p_2; (d) s_1, s_2, s_3, s_4, p_1, p_2, and p_3; (e) s_1, s_2, s_3, p_1, p_2, p_3, and p_4. In all the calculations we have included the core states in the basis set. Figure 5 indicates that the valence states undergo a larger decrease in energy due to the added variational freedom than does the conduction state and as a result the band gap turns positive with the extended bases. The valence states and conduction state appear to have reached convergence with four (s_1, s_2, p_1, p_2) and six (s_1, s_2, s_3, p_1, p_2, p_3) additional single Gaussians respectively. Using the extended basis set with s_1, s_2, s_3, p_1, p_2, and p_3, we have recalculated the band energies at the Γ, H, N, and P points which

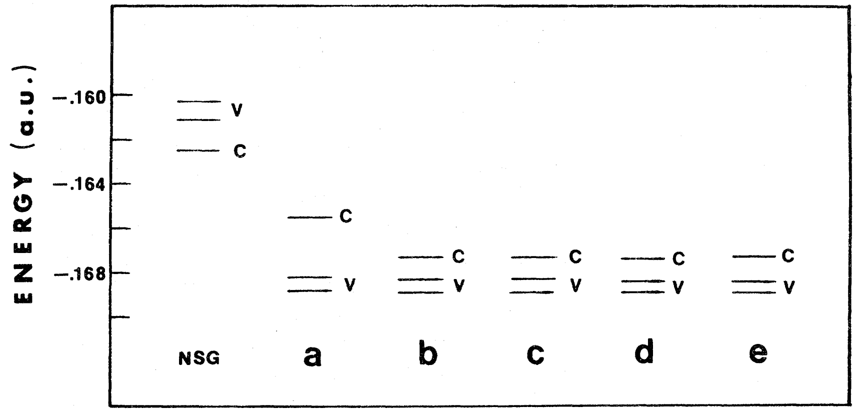

FIG. 5. Variations of the energies of the two highest valence-band levels and the lowest conduction-band level (at the H point) with increasing variational freedom due to inclusion of additional single-Gaussian Bloch sums in the basis set. The columns labeled a, b, c, d, and e correspond to five different sets of added single Gaussians as explained in Sec. III C. NSG in the first column stands for "no single Gaussians added."

TABLE II. Energies (in a.u.) of the conduction (upper group) and valence (lower group) states of Si III at four high-symmetry points calculated by an extended basis set (Sec. III C). Reference point is set at the top of the valence band. The numeral 2 inside a parentheses indicates double degeneracy.

Γ	*H*	*N*	*P*
0.3111	0.2298(2)	0.3233	0.3283
0.3016(2)	0.1731(2)	0.3194	0.3229(2)
0.2861(2)	0.1585	0.2857	0.3000
0.2792	0.1582(2)	0.2783	0.1651
0.2763	0.1408	0.2699	0.1648(2)
0.1972	0.1251	0.2546	0.1622
0.1917(2)	0.1224(2)	0.1952	0.1610(2)
0.1569	0.1197(2)	0.1888	0.1487(2)
0.1543(2)	0.1139	0.1594	0.1020
0.0852	0.1107	0.1504	0.1013(2)
0.0844(2)	0.0011	0.1049	0.0977
		0.1041	
		0.0943	
		0.0934	
		0.0325	
		0.0304	
−0.0499	0.0(2)	−0.0552	−0.1248(2)
−0.0618(2)	−0.0005	−0.0560	−0.1260(2)
−0.1517(2)	−0.0990(2)	−0.0592	−0.1335
−0.1522	−0.0998	−0.0960	−0.1338(2)
−0.1974(2)	−0.1514(2)	−0.1120	−0.1344
−0.2470(2)	−0.1519	−0.1126	−0.2071(2)
−0.2476	−0.2316	−0.1724	−0.2072
−0.3124	−0.3315	−0.1730	−0.2075
−0.3236(2)	−0.3316(2)	−0.1929	−0.4063(4)
−0.3237	−0.4039	−0.1933	
−0.4872	−0.4040(2)	−0.2797(2)	
		−0.3533	
		−0.3534	
		−0.4329(2)	

are summarized in Table II. The shift of the level spacings due to the improvement by single Gaussians is generally less than 0.1 eV, therefore the DOS curves in Fig. 4 are little affected and the band diagrams in Fig. 3 are still essentially correct within the reading accuracy of the graphs.

For the OAP model of the one-electron Hamiltonian adopted in Sec. III A, we obtain a band gap for Si III as 0.029 eV. We would expect the band gap to decrease somewhat if the energy calculation were carried out to self-consistency, since this trend is found in ordinary silicon and other tetrahedral semiconductor crystals.[25,31] Nevertheless, the gap value of 0.029 eV is consistent with the observed behaviors of electrical conductivity of Si III.

IV. CONCLUSIONS

We have introduced the technique of orthogonalization to the LCAO method in order to remove core-state basis functions, and applied it to calculate the band structure of Si III. The results obtained by the OLCAO procedure are as accurate (to within 0.0008 a.u.) as when the core states are directly included. Although extra matrix manipulation is required in the orthogonalizing process, this is more than compensated by the substantial reduction in size of the final secular equations. For example at a general $\vec{k}$ point in the Brillouin zone, it takes about 36 sec on the local Univac 1110 computer to obtain the eigenvalues and eigenvectors of Si III when the core states are included (dimension 72), but takes only 8 sec using the orthogonalization scheme (dimension 32). The saving in computer time would be even more impressive for more complicated systems where the secular equations may have a dimensionality well over 100. The OLCAO method opens a way to obtain accurate energy levels based on a first-principles approach for cases which were previously limited by computing capacity for matrix diagonalization such as amorphous solids and crystals of complex structure or involving heavy atoms. The reduction of the dimensionality of the Hamiltonian eigenvectors by the OLCAO method offers a great deal of advantage for calculation of such quantities as optical absorption, Compton profile, charge density, and self-consistency potential which require accurate crystal wave functions.

Recently, Bonifacic and Huzinaga[32] proposed a method for generating a model potential to simulate the effects of the core electrons so as to prevent the collapse of the valence states when the core basis functions are deleted. This scheme has been successfully applied to a Hartree-Fock calculation of energy bands of diamond by Euwema and Greene.[33] The construction of the model, however, requires adjustment of some parameters. In this regard, the model-potential approach is quite different from the method of orthogonalization. The latter involves only the assumption that the admixture of the valence orbitals in the crystal core states is negligible, and it entails no parametrization. For the Hartree-Fock calculation of diamond, comparison of the eigenvalues of the valence and low conduction bands obtained by the model potential with those obtained by including the $1s$ core shows a rms deviation of 0.006 a.u.

Our calculated DOS of Si III differs significantly from that of the ordinary Si crystal. Using extended basis-function sets, we obtain the band gap of Si III as 0.029 eV (at the H point). Because of the small gap, increase of pressure may greatly affect the electric conductivity and even possibly cause the band gap to vanish. Indeed a strong dependence of the conductivity of Si III on shear, exposure time, and temperature has been found experimentally.[18] The small gap of Si III also provides an explanation for the experimental observation that the resistivity decreases by a factor of 10^5 or 10^6 upon compression from 20 kbar to 150–160 kbar and at the high-pressure region the resistivity of compressed silicon is similar to that of aluminum.[18] However, additional experimental works on Si III are needed in order to make a more comprehensive comparison between the theoretical band structure and experiments.

ACKNOWLEDGMENT

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