PHYSICAL REVIEW B VOLUME 15, NUMBER 4 15 FEBRUARY 1977

# New method for calculating Hartree-Fock energy-band structures in solids using a linear combination of atomic orbitals basis: Application to diamond*

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(Received 6 January 1976)

A new technique for solving the one-electron Schrödinger equation of crystals using a linear combination of atomic orbitals (LCAO) basis set is presented. The main feature is the use of a Fourier transform, to write all the quantities of interest in terms of the form factors of the atomic orbitals. This leads to a formulation quite similar to the orthogonalized-plane-wave (OPW) method. An obvious advantage is to avoid the calculation of many-center integrals. Another point is that summations are now truncated in reciprocal space. This procedure is found to be more convergent than the usual truncations in real space. Application to diamond in a full self-consistent Hartree-Fock treatment leads to excellent agreement with previously reported results. The optimized atomic orbitals have their exponent increased by 30% with respect to their free-atom value, leading to a good value for the $F_{222}$ x-ray scattering factor. The conduction band is also calculated within an improved OPW approximation, where the plane waves are orthogonalized not only to the core functions but also to the valence-band states. The convergence is found to be quite good (only 15 plane waves are necessary) and the results significantly better for the higher conduction-band states than when using a LCAO basis.

## INTRODUCTION

Solutions of the Hartree-Fock equations with nonlocal exchange have been reported for several insulators by many authors. The first of these is the tight-binding calculation of the valence bands of KCl by Howland.[1] Much later, an augmented-plane-wave (APW) Hartree-Fock (HF) method[2] has been used by Dagens and Perrot to calculate the band structure of rare gases[2] (Ar,Ne), alkali fluorides, and chlorides.[3] Nevertheless, these and similar calculations[4] use free-atom HF wave functions, and are consequently not self-consistent. At the same time, a quite different procedure has developed: the great difficulty of solving the eigenproblem with the exact HF operator led some authors to approximate it by homogeneous-gas approximations,[5] the exchange-correlation $X\alpha$ operator in particular.[6] In compensation, the calculations can then be performed self-consistently. Unfortunately, when these operators are used to calculate crystalline charge densities, discrepancies between calculation and experiment are systematically observed. This is expected mostly in semiconductors crystallizing in open structures, such as diamond, in which essentially covalent bonds determine the main features of the electronic structure. In effect, these calculations use generally a muffin-tin potential (augmented plane wave, Korringa-Kohn-Rostoker) and, in such materials, the volume inside the muffin-tin spheres is too small a fraction of the total crystal volume. Regions of high-valence electron density are thus described by a constant potential, which makes the approximation not good. Nevertheless the $X\alpha$ method has also been used with a linear combination of atomic orbitals (LCAO) Bloch basis set for diamond.[7] But in this case the variations of band gaps and valence bandwidth with a small variation of the exchange factor $\alpha$ are large. This makes the results somewhat unreliable. In chlorides, there exists the orthogonalized-plane-wave (OPW) calculation with Slater's exchange of Kunz for LiCl, NaCl, KCl, and the augmented-plane-wave calculation by De Cicco for KCl.[8] Disagreements with experiment are also observed.

The first fully self-consistent HF calculation has been reported by Kunz[9] in LiCl, using the Kunz mixed basis formalism.[10] Several authors have then followed a similar procedure.[11] The method was applied successfully to other insulators.[12] In semiconductors, the first complete HF calculation has been carried out by Euwema, Whilite, and Suratt[13] for diamond, followed by Pantelides, Mickish, and Kunz.[14] These calculations use fairly complicated sets of Gaussian functions to describe the electronic orbitals, but the results are in very good agreement with experiment for the bulk properties of the diamond.

The purpose of this paper is to present a different method to calculate the HF valence bands in crystals. An illustration is given for diamond. In all the previous methods the one-electron Schrödinger equation is solved in real space.[15] Then the calculation of many two-, three-, and even four-electron-center integrals in the Coulomb and exchange energy must be worked out to get the true eigenvalues. The reason is that the valence-band orbitals spread over a volume larger than the Wigner-Seitz zone. In this paper we set up the one-electron Schrödinger equation in reciprocal space. The Fourier transform of the valence-band orbitals being more localized than in real space, the convergence is easier to obtain. This equation is solved for diamond, as an example. Because of the covalent bonding of the material, hybridized $sp^3$ orbitals have been chosen as a basis of wave functions. They are built from Slater-type orbitals. However, the coefficients in the exponentials are allowed to be different from the atomic ones and are considered as variational parameters of a trial wave function to reach self-consistency. The Hartree-Fock equation which we must solve in our formulation is similar to the secular equation met in OPW and pseudopotential methods. In other words, the suitable Fourier transformations lead to energies which can be cast into a form similar to that met in a nearly-free-electron picture. This formalism can thus be considered as a generalized Hartree-Fock pseudopotential method, using an atomic-orbital basis for the pseudo wave function, instead of a plane-wave basis.

The Hartree-Fock conduction band is calculated by two methods. First, we derive LCAO results as a by-product of our valence-band calculation. Second, we use an OPW method slightly modified to improve convergence. The point is that the plane waves are orthogonalized not only to the core wave functions, but also to the valence wave functions found above. This results in an extra term in the Hamiltonian, which smoothes the pseudopotential and restricts the number of plane waves required.

This paper is divided into five parts. In Sec. I we present the Hartree-Fock formalism used to determine the ground-state energies of crystals. In Sec. II this formalism is applied to diamond. In Sec. III the improved OPW method is described and used to determine the HF conduction band of diamond. In Sec. IV the computational results are given. They are then discussed in Sec. V, where possible extensions of this work are also investigated.

## I. HARTREE-FOCK FORMALISM

To improve clarity, let us first derive the formalism for the one-electron Hamiltonian with a local potential $W(\vec{r})$. We use a LCAO method; i.e., we expand the wave function in terms of atomic orbitals $\varphi^\alpha(\vec{r}-\vec{R}_j)$, $\alpha$ being the orbital index, $\vec{R}_j$ being a lattice vector connecting the origin to the $j$th atom. The Bloch sum corresponding to such orbitals is then

$$\psi_{\vec{k}}^\alpha(\vec{r}) = c_{\vec{k}}^\alpha \sum_j e^{i\vec{k}\cdot\vec{R}_j}\varphi^\alpha(\vec{r}-\vec{R}_j), \tag{1.1}$$

where $c_{\vec{k}}^\alpha$ is a normalization factor. Using Bloch's theorem, we can write

$$\psi_{\vec{k}}^\alpha(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}^\alpha(\vec{r}), \tag{1.2}$$

where $u_{\vec{k}}^\alpha$ is periodic and thus can be expanded in a Fourier series. This leads for $\psi_{\vec{k}}^\alpha$ to the expression

$$\psi_{\vec{k}}^\alpha(\vec{r}) = \frac{c_{\vec{k}}^\alpha}{\Omega}\sum_{\vec{K}} g^\alpha(\vec{k}+\vec{K})e^{i(\vec{k}+\vec{K})\cdot\vec{r}}, \tag{1.3}$$

where $\Omega$ is the unit cell volume, K are reciprocal-lattice vectors, and $g^\alpha(\vec{q})$ is the Fourier transform of the atomic orbital

$$g^\alpha(\vec{q}) = \int e^{-i\vec{q}\cdot\vec{r}}\varphi^\alpha(\vec{r})\,d^3r. \tag{1.4}$$

The factor $c_{\vec{k}}^\alpha$ chosen so as to normalize $\psi_{\vec{k}}^\alpha$ in Eq. (1.3) is given by

$$|c_{\vec{k}}^\alpha|^2 = \Omega \Big/ N\sum_{\vec{K}} |g^\alpha(\vec{k}+\vec{K})|^2. \tag{1.5}$$

We are now able to determine the matrix elements of the Hamiltonian $H$ between two such Bloch states which turn out to be given by

$$\begin{aligned}\langle \psi_{\vec{k}}^{\alpha'}|H|\psi_{\vec{k}}^\alpha\rangle &= \Big(\sum_{\vec{K}} |g^{\alpha'}(\vec{k}+\vec{K})|^2\Big)^{-1/2}\Big(\sum_{\vec{K}} |g^\alpha(\vec{k}+\vec{K})|^2\Big)^{-1/2} \\ &\quad\times\Big(\sum_{\vec{K}}(|\vec{k}+\vec{K}|^2+W_0)[g^{\alpha'}(\vec{k}+\vec{K})]^*g^\alpha(\vec{k}+\vec{K}) \\ &\quad+\sum_{\substack{\vec{K},\vec{K}'\\ \vec{K}\neq\vec{K}'}} W_{\vec{K}'-\vec{K}}[g^{\alpha'}(\vec{k}+\vec{K}')]^*g^\alpha(\vec{k}+\vec{K})\Big).\end{aligned} \tag{1.6}$$

It is clear that this equation involves terms similar to those which appear in OPW theory. It is then ideally suited to a comparison of the two methods. The quantities $W_{\vec{K}}$ are the Fourier components of the local potential or pseudopotential. The main difference is the appearance of the quantities $g^\alpha(\vec{k}+\vec{K})$. They ensure a very rapid convergence when $\varphi^\alpha(\vec{r})$ decreases slowly in space, which is the case for all $sp$ bonded systems. We can then hope that Eq. (1.6) represents a quite practical computational scheme.

The situation becomes slightly more complicated when dealing with a nonlocal potential. Such is the case for the exchange term in the Hartree-Fock (HF) approximation. In effect, the HF matrix element between $\psi_{\vec{k}}^{\alpha'}$ and $\psi_{\vec{k}}^\alpha$ can be expressed in real space as

$$\langle\psi_{\vec{k}}^{\alpha'}|H|\psi_{\vec{k}}^{\alpha}\rangle=-\int\psi_{\vec{k}}^{\alpha'}(\vec{r})^{*}\nabla^{2}\psi_{\vec{k}}^{\alpha}(\vec{r})-2Z\sum_{n}\int\frac{\psi_{k}^{\alpha'}(\vec{r})^{*}\psi_{k}^{\alpha}(\vec{r})}{|\vec{r}-\vec{R}_{n}|}d^{3}r+2\sum_{j,\vec{k}'}\int\frac{\psi_{\vec{k}}^{\alpha'}(\vec{r})^{*}\psi_{\vec{k}}^{\alpha}(\vec{r})|\Psi_{j\vec{k}'}(\vec{r}')|^{2}}{|\vec{r}-\vec{r}'|}d^{3}r\,d^{3}r'$$

$$-2\sum_{j,\vec{k}'}\delta_{s_{\alpha},s_{j}}\delta_{s_{\alpha'},s_{j}}\int\frac{\Psi_{\vec{k}}^{\alpha'}(\vec{r})^{*}\Psi_{j\vec{k}'}(\vec{r})\Psi_{j\vec{k}'}(\vec{r}')^{*}\psi_{\vec{k}}^{\alpha}(\vec{r}')}{|\vec{r}-\vec{r}'|}d^{3}r\,d^{3}r'. \qquad (1.7)$$

Here use is made of rydberg units. The first term is the kinetic energy; the second term is the Coulomb energy due to the interaction with the nuclei; the third one is the Coulomb interaction with the electron clouds, and the last one corresponds to the exchange term. The Kronecker symbol means that spins must be identical in the exchange part. All sums $\sum_{j,\vec{k}'}$ are taken over filled states whose Bloch functions are $\Psi_{j\vec{k}'}$. $j$ is the index of occupied quantum states at a given wave vector $\vec{k}$. $Z$ is the atomic number of the atoms in the crystal.

To put Eq. (1.7) into a form similar to Eq. (1.6), the expansion of $\psi_{\vec{k}}^{\alpha}$ and $\psi_{\vec{k}}^{\alpha'}$ in Fourier series as in Eq. (1.3) is clearly required. However, this is not sufficient because Eq. (1.7) also contains the Bloch functions $\Psi_{j\vec{k}}$ of the filled states. These are not Bloch sums corresponding to one given atomic orbital, but linear combinations of such sums. Nevertheless, they can also be put in the form

$$\Psi_{j\vec{k}}(\vec{r})=\frac{c_{j\vec{k}}}{\Omega}\sum_{\vec{K}}e^{i(\vec{k}+\vec{K})\cdot\vec{r}}g_{j}(\vec{k}+\vec{K}), \qquad (1.8)$$

where $g_j$ is the corresponding combination of the atomic form factors. This quantity can also be considered as the form factor of the Wannier function associated to the $j$th eigenfunction.

With these definitions Eq. (1.7) can be written as follows:

$$\langle\psi_{\vec{k}}^{\alpha'}|H|\psi_{\vec{k}}^{\alpha}\rangle=\sum_{\vec{K},\vec{K}'}A_{\vec{K}',\vec{K}}^{\alpha,\alpha'}(\vec{k})\Big[|\vec{k}+\vec{K}|^{2}\delta_{\vec{K},\vec{K}'}-\frac{8\pi}{\Omega}LZ\frac{F(\vec{K}-\vec{K}')}{|\vec{K}-\vec{K}'|^{2}}$$

$$+\frac{1}{\pi^{2}}\sum_{j}\int d^{3}k'\sum_{\vec{K}_{1}}B_{j}(\vec{k}',\vec{K},\vec{K}',\vec{K}_{1})\left(\frac{1}{|\vec{K}-\vec{K}'|^{2}}-\frac{1}{2}\,\frac{1}{|\vec{k}-\vec{k}'+\vec{K}'-\vec{K}_{1}|^{2}}\right)\Big] \qquad (1.9)$$

with

$$A_{\vec{K}',\vec{K}}^{\alpha,\alpha'}=g^{\alpha'}(\vec{k}+\vec{K}')^{*}g^{\alpha}(\vec{k}+\vec{K})\Big/\left[\left(\sum_{\vec{K}}|g^{\alpha'}(\vec{k}+\vec{K})|^{2}\right)\left(\sum_{\vec{K}}|g^{\alpha}(\vec{k}+\vec{K})|^{2}\right)\right]^{1/2}$$

$$B_{j}(\vec{k}',\vec{K},\vec{K}'\vec{K}_{1})=g_{j}(\vec{k}'+\vec{K}_{1})^{*}g_{j}(\vec{k}'+\vec{K}_{1}+\vec{K}-\vec{K}')\Big/\sum_{\vec{K}}|g_{j}(\vec{k}+\vec{K})|^{2} \qquad (1.10)$$

In this expression $\vec{K},\vec{K}',\vec{K}_1$ are reciprocal-lattice vectors and the integrals with respect to $\vec{k}'$ extend over the Brillouin zone in insulators or semiconductors where the valence bands are completely filled. The terms are in the same order as in Eq. (1.7). We have considered in Eq. (1.9) the possibility of having several (namely, $L$) atoms per unit cell. That is why we have introduced the structure factor $F(q)$ defined by

$$F(\vec{q})=\frac{1}{L}\sum_{l}e^{i\vec{q}\cdot\vec{r}_{l}}. \qquad (1.11)$$

The sum runs over all the positions $\vec{r}_l$ of the atoms in a unit cell. In Eq. (1.9), only correlations[16] and spin-orbit effects[17] are neglected.

At this point we can compare our method of evaluating matrix elements from Eq. (1.9) to the standard procedure where the summations are made in real space. When working in real space one is faced to the problem of evaluating many-center integrals. These are quite numerous and some of them must be calculated in an approximate manner (the three- and four-center integrals).[13] Finally, the series are truncated at some point. On the contrary the full use of the translational symmetry leads to expression (1.9), where all such integrals are taken into account. The sum is now over the reciprocal-lattice vectors. This presents two kinds of advantages: firstly there are no more many-center integrals to compute and secondly the convergence is more rapid in reciprocal space when the atomic functions decrease slowly in real space, which is the case for all $sp$ bonded systems.

It is clear that our method can be used to obtain any desired degree of accuracy. It is also necessary to truncate the series in reciprocal space but we have checked that only few reciprocal vectors have to be included to obtain correct convergence. In order to save computing time we have applied the method to diamond only considering high symmetry axes and treating the valence-band wave functions as combinations of bonding orbitals. This will be detailed in Sec. II.

## II. BASIS FUNCTIONS FOR THE VALENCE BAND OF DIAMOND

Mainly, two reasons have prevailed for our choice of diamond rather than any other semiconductor. Firstly this is the only case where the exact HF band structure has been calculated,[13] allowing us to test our model. Secondly, the carbon atom is a light element, with only 1$s$, 2$s$, and 2$p$ occupied atomic states, which makes the calculation easier. We have taken Slater-type atomic orbitals as a basis set, i.e.:

$$\begin{aligned} 1s &= (\alpha^3/\pi)^{1/2} e^{-\alpha r}, \\ 2s &= (\beta_s^5/3\pi)^{1/2} r e^{-\beta_s r}, \qquad (2.1) \\ 2p_x &= (\beta_p^5/\pi)^{1/2} x e^{-\beta_p r} \end{aligned}$$

and similar expressions for $2p_y$ and $2p_z$ orbitals. In a carbon atom, the coefficients $\alpha$, $\beta_s$, and $\beta_p$ are, in atomic units:

$$\alpha = 5.7, \quad \beta_s = \beta_p = 1.625. \qquad (2.2)$$

Nevertheless, in the crystal, the electrons are not expected to remain longer in the atomic states, because of the interaction with the surrounding atoms. We must then allow the orbitals to relax, letting the parameters $\beta_s$ and $\beta_p$ be different in the crystal and in an isolated atom. The relaxed crystal orbitals will be those for which the values of the parameters minimize the cohesive energy. Furthermore, the hermiticity of the Hamiltonian implies that the eigenstates must be orthogonal. Such is the case between 1$s$ and 2$p$ orbitals owing to symmetry considerations. But the 2$s$ state in Eq. (2.1) is not orthogonalized to the 1$s$ state. This can be achieved by the same method as in the OPW formalism. Instead of the 2$s$ orbital in Eq. (2.1), we can then choose

$$2s = \frac{(\beta_s^5/3\pi)^{1/2} r\, e^{-\beta_s r} - \lambda(\alpha^3/\pi)^{1/2} e^{-\alpha r}}{(1-\lambda^2)^{1/2}}, \qquad (2.3)$$

$$\lambda = \frac{8\sqrt{3}(\alpha^3\beta_s^5)^{1/2}}{(\alpha+\beta_s)^4}.$$

The value of $\lambda$ has been chosen so that $\langle 2s | 1s\rangle = 0$. We shall discuss the opportunity to take such a value of $\lambda$ in Sec. V. It is well known that the tetrahedral symmetry of diamond implies the hybridization of the 2$s$ and 2$p$ orbitals. In the tight-binding model, suitable basis functions are then the $sp^3$ orbitals

$$\begin{aligned} \chi_0 &= \tfrac{1}{2}(s+p_x+p_y+p_z), \quad \chi_2 = \tfrac{1}{2}(s-p_x+p_y-p_z), \qquad (2.4) \\ \chi_1 &= \tfrac{1}{2}(s+p_x-p_y-p_z), \quad \chi_3 = \tfrac{1}{2}(s-p_x-p_y+p_z). \end{aligned}$$

In this paper, we shall treat the crystal in its ground state as if it were a huge molecule where each bond is localized. The wave function for one such bond will be approximately built out of the previous $sp^3$ hybrid orbitals, oriented around each atom in such a way that the orbitals which are paired together point directly towards each other. Then, the bonding orbitals deduced from Eq. (2.4) are

$$\chi_j'(\vec{r}) = \frac{1}{[2(1+S)]^{1/2}}[\chi_j(\vec{r}+\vec{\tau}_0) + \chi_j(-\vec{r}+\vec{\tau}_0-\vec{b}_j)]. \qquad (2.5)$$

$j$ indexes the four orbitals, the vectors $\vec{b}_{j=1,3}$ are the first lattice vectors

$$\begin{aligned} \vec{b}_0 &= (0,0,0), \\ \vec{b}_1 &= \tfrac{1}{2}a(0,0,1), \\ \vec{b}_2 &= \tfrac{1}{2}a(1,0,1), \qquad (2.6) \\ \vec{b}_3 &= \tfrac{1}{2}a(1,1,0), \end{aligned}$$

where $a$ is the lattice parameter. $S$ is the overlap integral between paired $sp^3$ orbitals. Two methods of describing the unit cell are used in international tables, we have chosen here the case where the origin is taken at the middle of a bond, with atoms at $\pm\vec{\tau}_0$ with $\vec{\tau}_0 = \frac{1}{8}a(1,1,1)$.

Unfortunately, the basis (2.5) is not orthonormalized, since

$$\langle \chi_i' | \chi_{j\neq i}' \rangle = S_1 = \frac{2\beta' + \gamma}{2(1+S)}. \qquad (2.7)$$

$\beta'$ and $\gamma$ are overlap integrals between $sp^3$ orbitals pointing towards different directions shown in Fig. 1. The wave functions $V_j(\vec{r})$ must then be defined by

$$V_i = \chi_i' + \sum_{j\neq i} c_{ji}\chi_j', \qquad (2.8)$$

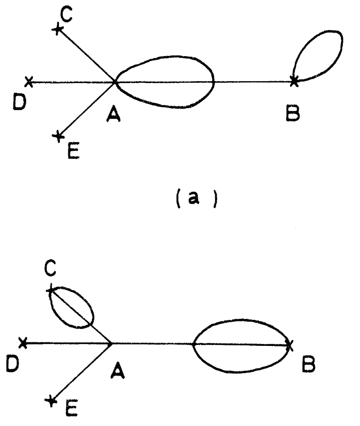
where the $c_{ji}$ coefficients are chosen so that $\langle V_i | V_{j\neq i}\rangle = 0$. Since the $c_{ji}$ are the same order of magnitude than $S_1$, we can write

$$\langle V_i | V_{j\neq i}\rangle = S_1 + c_{ij} + c_{ji} + O(S_1^2). \qquad (2.9)$$

So, we shall take $c_{ji} = c_{ij} = -\frac{1}{2}S_1$, which implies that the basis (2.8) is orthogonal to second order in $S_1$. For the atomic values in Eq. (2.2), $S_1 = 0.11$, so that the first order is a good enough approximation:

$$V_i = \chi_i' - \frac{S_1}{2}\left(\sum_{j\neq i} \chi_j'\right). \qquad (2.10)$$

The fact that the functions $V_i$ are orthogonal is



(a)

(b)

FIG. 1. Diagrammatic representation of the overlap integrals which must be calculated. Letters indicate lattice sites. Quantity $\beta'$ in this text is the overlap integral between $sp^3$ orbitals centered on first-neighboring atoms, and pointing towards different directions (a). Quantity $\gamma$ is the overlap integral between orbitals centered on second-neighboring atoms (b).

important, because it implies that they are a unitary transformation of the Wannier functions. In Eq. (1.7), the crystal potential involves the calculation of

$$\sum_{j\vec{k}'} |\Psi_{j\vec{k}'}(\vec{r}')|^2 \text{ and } \sum_{j,\vec{k}'} \Psi_{j,\vec{k}}(\vec{r})\Psi_{j\vec{k}'}(\vec{r}').$$

*A priori*, this would require the knowledge of the Wannier functions for a general point $\vec{k}'$ in the Brillouin zone, which is impossible. Nevertheless the usual closure relation in quantum mechanics shows that these sums are invariant under a unitary transformation of the basis functions. They can thus be calculated by replacing the exact Wannier functions $U_i$ by the functions $V_i$. This is a consequence of the scalar character of the Hamiltonian operator. In all the numerical calculations we have then replaced the $g_j(k)$ form factors appearing in the quantities $B_j$ of Eq. (1.9) by the Fourier transform of the functions $V_i$. The error is only of second order in $S_1$ and can be neglected.

Now, to avoid a complete diagonalization of the Hamiltonian matrix, we shall consider only high-symmetry directions. Along the [100] axis we can build directly the total wave function $\Psi_{j\vec{k}}$ in terms of the elementary Bloch functions $\psi_{\vec{k}}^{\alpha}$ only from symmetry considerations, with the use of group theory. In the [111] direction, however, there are two bands associated with the same one-dimensional representation $\Lambda_1$, so that a $2\times 2$ matrix must be diagonalized to get the eigenvalues. Even in this case this is of a great simplification because the computation of any matrix element in Eq. (1.9) is rather long. Let us now illustrate the calculations for the case when $\vec{k}$ is in the [100] direction. This is of particular interest because we should find the minimum of the conduction band along this axis.

We can set up the symmetrized wave function $\Psi_j^i$ belonging to the $i$th row of the $j$th irreducible representation $\Delta_j$ of the wave-vector group for $\vec{k}$ in the direction [100] by the use of the basis function generating machine due to Van Vleck[18]:

$$\Psi_j^i = \sum_R [M_j(R)]_{ii}^* R\psi_{\vec{k}}^{\alpha}. \tag{2.11}$$

The summation runs over all the elements $R$ of the spatial group $O_h^7$, which also belong to the wave-vector group. $M_j(R)$ is the matrix associated to the operation $R$ in the $j$th representation. This well-known procedure does not require further comments. Attention should only be paid to the fact that the $O_h^7$ group is not symmorphic. So, nonprimitive translations are associated to the operations of the point group $O_h$ to build the operations $R$ in Eq. (2.11). The matrix elements $[M_j(R)]_{ii}$ and the operations $R$ themselves are found in the literature.[19] The LCAO's which are symmetry orbitals and factor the secular equation are then

$$U_{i=0,3} = \frac{1}{2\sqrt{N_i}}(V_0 - \tau_{4-i}^x V_1 - \tau_{4-i}^y V_2 - \tau_{4-i}^z V_3),$$

$$N_0 = 1 + 3S_1; \quad N_{i\neq 0} = 1 - S_1. \tag{2.12}$$

$N_i$ is a normalization factor. $\tau_{4-i}^{x,y,z}$ are the components of the vectors defined by

$$\begin{aligned} \vec{\tau}_1 &= (1,1,-1), \quad \vec{\tau}_3 = (-1,1,1), \\ \vec{\tau}_2 &= (1,-1,1), \quad \tau_4 = (-1,-1,-1). \end{aligned} \tag{2.13}$$

Here, the four Wannier functions $U_j$ and the corresponding symmetrized wave functions $\Psi_i$ are distinguished by one index instead of two, in order to improve clarity. Thus, $U_0$ is a basis function of the irreducible representation $\Delta_1$, $U_1$ is a basis function of $\Delta_2$, while $U_2$ and $U_3$ are orthogonal basis functions of the twofold degenerate representation $\Delta_5$. The Wannier functions in Eq. (2.12) have been determined by identification of $\Psi_i$ with the expression given in Eq. (1.1), with $U_i$ in place of $\varphi^{\alpha}$. In effect, the wave-vector group being not symmorphic, any direct calculation of the Wannier functions $U_i$ is not straightforward and cannot be achieved by means of Eq. (2.11).

The determination of the Fourier transform of $U_i$, $g_i(\vec{q})$, is now very easy. The Fourier transform of $s$ and $p$ Slater orbitals have been calculated in Appendix A. From Eqs. (A6) and (A7), we can deduce that the Fourier transform of $\chi_j'(\vec{r})$ and $\chi_j(\vec{r})$ are, respectively, $\chi_j'(q)$ and $\chi_j(\vec{q})$ given by

$$\chi_j'(q) = \frac{1}{[2(1+S)]^{1/2}} [e^{i\vec{q}\cdot\vec{\tau}_0}\chi_j(\vec{q}) + e^{-i\vec{q}\cdot(\vec{\tau}_0-\vec{b}_j)}\chi_j(\vec{q})^*],$$

$$\chi_j(q) = -\frac{4\pi\lambda\alpha^2}{(\alpha^2+q^2)^2}\left(\frac{\pi\alpha}{1-\lambda^2}\right)^{1/2} + \frac{4\beta_s^2(3\beta_s^2-q^2)}{(\beta_s^2+q^2)^3}\left(\frac{\pi\beta_s}{3(1-\lambda^2)}\right)^{1/2} + i\,\frac{16\beta_p^3(\pi\beta_p)^{1/2}}{(\beta_p^2+q^2)^3}\,\vec{q}\cdot\vec{\tau}_{4-j} \tag{2.14}$$

the quantities $g_j(q)$ are linear combinations of the $\chi_j'(q)$ and are thus analytic. Nevertheless, the coefficients of these combinations include overlap integrals like $S$, $\beta'$, and $\gamma$ which must be calculated. This problem is solved in Appendix B.

## III. BASIS FUNCTIONS FOR THE CONDUCTION BAND

The simplicity of the $(1s)^2$ cores of carbon have inspired the first OPW calculations on diamond, done by Herman,[20] and further developments are due to Kleinman and Phillips.[21] More recent studies have been performed.[22] The success of this method presumably relies on the applicability of the Phillips cancellation theorem.[23] However, the absence of $p$ core states means that the kinetic energy of the valence $p$ electrons is not cancelled.[24] In other words, the repulsive pseudopotential arising from the orthogonality of the plane waves to the $(1s)$ atomic orbitals is not seen by the valence states and the states of the conduction band stemming from the $\Gamma_{15}$ point which have a $p$-type symmetry. That is why many plane waves are needed to describe these eigenfunctions. It is much more advisable, now, to make the plane waves orthogonal not only to the $1s$ band but also to the valence bands. The cancellation for the conduction bands is thus complete and the convergence of the OPW method greatly improved. This idea, however, is not new and has been first used by Redei.[25] Unfortunately, the errors in this article have involved incorrect results.

We can define a normalized set of orthogonalized plane waves $\Phi(\vec{k},\vec{G})$ by the equation

$$\Phi(\vec{k},\vec{G}) = \left(1-\sum_j|\lambda_j|^2\right)^{-1/2}\left(\frac{1}{(N\Omega)^{1/2}}e^{i(\vec{k}+\vec{G})\cdot\vec{r}} - \sum_j\lambda_j(\vec{k},\vec{G})\Psi_{j\vec{k}}(\vec{r})\right). \tag{3.1}$$

$\vec{G}$ is a vector of the reciprocal lattice and the summation runs over all occupied states $j$. The orthogonality coefficients $\lambda_j$ are defined in the same way as in Eq. (2.8):

$$\lambda_j(\vec{k},\vec{G}) = (N/\Omega)^{1/2}(c_{j\vec{k}})^* g_j(\vec{k}+\vec{G})^*. \tag{3.2}$$

The wave function of the conduction band, $\Psi_{\vec{k}}^c(\vec{r})$ can be developed in the OPW basis

$$\Psi_{\vec{k}}^c(\vec{r}) = \sum_{\vec{G}} A(\vec{k},\vec{G})\Phi(\vec{k},\vec{G}). \tag{3.3}$$

This eigenfunction is defined by the condition

$$H|\Psi_{\vec{k}}^c\rangle = E_c(\vec{k})|\Psi_{\vec{k}}^c\rangle. \tag{3.4}$$

$H$ is the Hartree-Fock Hamiltonian and $E_c(\vec{k})$ is the eigenvalue. The scalar product of Eq. (3.4) by $\Phi(\vec{k},\vec{G})$ leads to a set of linear equations for $A(\vec{k},\vec{G})$. Nonvanishing solutions are obtained when the secular equation is fulfilled

$$\det\left[\left(\frac{1-\sum_j|\lambda_j(\vec{k},\vec{G}')|^2}{1-\sum_j|\lambda_j(\vec{k},\vec{G})|^2}\right)^{1/2}\left(\frac{1}{N\Omega}\langle e^{i(\vec{k}+\vec{G}')\cdot\vec{r}}|H|e^{i(\vec{k}+\vec{G})\cdot\vec{r}}\rangle - E_c(\vec{k})\delta(\vec{G},\vec{G}') + \sum_j[E_c(\vec{k})-E_j(\vec{k})]\lambda_j(\vec{k},\vec{G})\lambda_j(\vec{k},\vec{G}')\right)\right]=0. \tag{3.5}$$

The last term is a nonlocal pseudopotential matrix element. $E_j(\vec{k})$ are the eigenvalues of the occupied states. The solutions of Eq. (3.5) are the eigenvalues $E_c(\vec{k})$. The diagonalization of the effective Hamiltonian for these values gives the degeneracy of the bands together with the wave vectors.

## IV. COMPUTATION

Under the form [given in Eq. (1.9)], the summations over the reciprocal-lattice vectors are still slowly convergent. The reason is that Eqs. (1.9) and (3.5) include summations over all occupied states and in particular the $1s$ states. Since the $1s$ states are very localized, their Fourier transforms

$$g_{1s}(\vec{q}) = (2\pi\alpha)^{1/2}\cos(\vec{q}\cdot\vec{\tau}_0)[8\pi\alpha^2/(\alpha^2+q^2)^2] \tag{4.1}$$

spread over large $q$. The contribution of such states must then be calculated separately. Neglecting $q$ with respect to $\alpha$, the contribution of one $1s$ state to the Coulomb electron energy is

$$\frac{1}{\pi^2}\sum_{\vec{K},\vec{K}'}\frac{A^{\alpha,\alpha'}_{\vec{K},\vec{K}'}(\vec{k})}{|\vec{K}-\vec{K}'|^2}\int d^3k'\,\frac{\sum_{\vec{K}_1}\cos[(\vec{k}'+\vec{K}+\vec{K}_1)\cdot\vec{\tau}_0]\cos[(\vec{k}'+\vec{K}'+\vec{K}_1)\cdot\vec{\tau}_0]}{\sum_{\vec{K}}\cos^2[(\vec{k}+\vec{K})\cdot\vec{\tau}_0]}\,. \tag{4.2}$$

Replacing the products of cosine terms by their average values, the above integrand $B_{1s}$ becomes

$$\tfrac{1}{2}\cos[(\vec{K}-\vec{K}')\cdot\vec{\tau}_0]/(1/2)$$

so that the expression (4.2) takes the form

$$\frac{1}{\pi^2}\sum_{\vec{K},\vec{K}'}\frac{A^{\alpha,\alpha'}_{\vec{K},\vec{K}'}(\vec{k})}{|\vec{K}-\vec{K}'|^2}\,\frac{8\pi^3}{\Omega}\cos[(\vec{K}-\vec{K}')\cdot\vec{\tau}_0]\,. \tag{4.3}$$

Since there are four $1s$ states, the contributions from $1s$ states to the Coulomb energy is four times this quantity and the total Coulomb energy can be written

$$\sum_{\vec{K},\vec{K}'}\frac{A^{\alpha,\alpha'}_{\vec{K},\vec{K}'}(\vec{k})}{|\vec{K}-\vec{K}'|^2}\left[\frac{1}{\pi^2}\left({\sum_j}'\int d^3k'\sum_{\vec{K}_1}B_j(\vec{k}',\vec{K},\vec{K}',\vec{K}_1)\right) - \frac{8\pi}{\Omega}L(Z-2)F(\vec{K}-\vec{K}')\right], \tag{4.4}$$

the prime sign in $\sum_j'$ means that the summation runs over all occupied states except the $1s$ states.

Comparing Eqs. (4.4) and (1.9), we can see that our approximation lies in a complete screening of the nucleus charge $Z$ of the carbon atom by $1s$ electrons. The effective charge of the nucleus is then $Z-2=4$.

On the contrary, any significant contribution of $1s$ states to the exchange energy does not occur, because of the denominator $|\vec{k}-\vec{k}'-\vec{K}_2|^2$, which becomes large for values of $|\vec{K}_2|=|\vec{K}_1-\vec{K}'|$ in the range $0\ll|\vec{K}_2|\ll\alpha$.

Another type of contribution to the energy comes from the $1s$ part in $2s$ orbitals [see Eq. (3.3)]. Since the mixing coefficient $\lambda$ is small, this effect is negligible except for the kinetic energy. In effect, the coefficient $|\vec{k}+\vec{K}|^2$ in Eq. (1.9) greatly enhances the contribution of $1s$ states for large $K$. With the functions in Eq. (2.12), this contribution, calculated directly in real space is

$$E^0_{\text{kin}}=\frac{\lambda^2\alpha^2}{8(1-\lambda^2)}\,\frac{1+2S_1}{1+S}\,,$$
$$E^1_{\text{kin}}=\frac{5\lambda^2\alpha^2}{8(1-\lambda^2)}\,\frac{1-6S_1}{1+S}\,. \tag{4.5}$$

$E^0_{\text{kin}}$ is the expression for the band $\Delta_1$ stemming from $\Gamma_1$ and $E^1_{\text{kin}}$ is the expression for the other valence bands stemming from $\Gamma_{25'}$.

Similar calculations must be performed for the conduction band. The resulting element deduced from Eq. (3.5) is:

$$\begin{aligned}H_{\vec{K}_1,\vec{K}_3}=[N(K_1,K_3)]^{1/2}\Bigg[&|\vec{k}+\vec{K}_1|^2\delta(\vec{K}_1,\vec{K}_3)\\&+\frac{1-\delta(\vec{K}_1,\vec{K}_3)}{\pi^2}\,\frac{1}{|\vec{K}_1-\vec{K}_3|^2}\left(\sum_{\vec{K}'}\int d^3k'\,T(\vec{k}',\vec{K}',\vec{K}_1,\vec{K}_3)-\frac{16(Z-2)\pi^3}{\Omega}\cos[(\vec{K}_1-\vec{K}_3)\cdot\vec{\tau}_0]\right)\\&-\frac{1}{2\pi^2}\int d^3k'\sum_{\vec{K}'}\frac{T(\vec{k}',\vec{K}',\vec{K}_1,\vec{K}_3)}{|\vec{k}-\vec{k}'-\vec{K}'|^2}+{\sum_j}'\frac{g_j(\vec{k}+\vec{K}_3)^*g_j(\vec{k}+\vec{K}_1)}{\sum_{\vec{K}}|g_j(\vec{k}+\vec{K})|^2}[E_c(\vec{k})-E_j(\vec{k})|\\&-4\left(\frac{8\pi}{\alpha a}\right)^3\cos[(\vec{k}+\vec{K}_1)\cdot\vec{\tau}_0]\cos[(\vec{k}+\vec{K}_3)\cdot\vec{\tau}_0][E_c(\vec{k})-E_{1s}]\Bigg]\,.\end{aligned} \tag{4.6}$$

$a$ is the lattice parameter and $N(\vec{K}_1,\vec{K}_3)$ is the factor appearing in Eq. (3.5) arising from the normalization of the orthogonalized plane wave. Its expression is

$$N(\vec{K}_1,\vec{K}_3)=\left(1-\sum_j\frac{|g_j(\vec{k}+\vec{K}_3)|^2}{\sum_{\vec{K}}|g_j(\vec{k}+\vec{K})|^2}\right)\times\left(1-\sum_j\frac{|g_j(\vec{k}+\vec{K}_1)|^2}{\sum_{\vec{K}}|g_j(\vec{k}+\vec{K})|^2}\right)^{-1}. \tag{4.7}$$

Usually this term is neglected. Such is not the case when we orthogonalize the plane waves to the valence states. $T$ is defined by

$$T(\vec{k}',\vec{K}',\vec{K}_1,\vec{K}_3)={\sum_j}'\frac{g_j(\vec{k}'+\vec{K}'+\vec{K}_1)\,g_j(\vec{k}'+\vec{K}'+\vec{K}_3)^*}{\sum_{\vec{K}}|g_j(\vec{k}'+\vec{K})|^2}\,; \tag{4.8}$$

the prime in the summations means that they run over valence states, the $1s$ states being excluded. The last term is the pseudopotential due to the orthogonalization of the plane waves to $1s$ states, calculated separately. Equation (4.6) is nothing but the expansion of the matrix element in Eq. (3.5) in terms $g_j(\vec{q})$, but in this form the computations could be easily achieved.

The integration over the Brillouin zone has been replaced by the summation over the ten symmetry independent zone points in $\frac{1}{48}$ of the first Brillouin zone determined by Chadi and Cohen[26] and the equivalent points. They build a 256 point mesh of the Brillouin zone, which ensures a good convergence.

The computations were done with $a = 3.57$ Å.[27] Rather than a truncation of the summations over reciprocal-lattice vectors in Eqs. (1.9) and (4.6), we have truncated the Fourier transform of the atomic orbitals. This method proved to be much more convergent, because it results in a compensation between the errors made in calculating the numerators and denominators of Eqs. (1.9) and (4.6). We have truncated these Fourier transforms to the first reciprocal-lattice vectors, keeping only $g_j(\vec{k}+\vec{K})$ for $\vec{K}$ belonging to the $\langle 111 \rangle$ set. The summations are then finite and can be carried out. The convergence has been tested only on the kinetic energy (it was as good as 1%), because the other terms are much more complicated. The calculations of the cohesive energy require the knowledge of the valence-band eigenvalues at many points in the Brillouin zone and such a computation was not achieved. We have thus chosen the parameters $\beta_s$ and $\beta_p$ so as to minimize the Hartree-Fock eigenvalues at the $\Gamma$ point. This was achieved for

$$\beta_s = \beta_p \simeq 2.1 \,. \tag{4.9}$$

In other words the relaxed orbitals in the crystal are contracted by 30% with respect to the atomic configuration. The top of the valence band is then at an energy equal to $E(\Gamma_{25'}) = 0.07$ Ry with respect to the vacuum, which is in very good agreement with previous results.[13] Such an agreement was also met for the shape of the bands calculated by Euwema *et al.*[13] and reported by Brener.[28] We have plotted in Fig. 2 the uncorrelated HF energy bands computed in the [100] and [111] directions.

For the conduction band, we have truncated our basis $\phi(\vec{k},\vec{G})$ by allowing only $|\vec{G}|^2 = 0$, 3, and 4 in units of $(2\pi/a)^2$. The eigenvalues are then obtained by the diagonalization of a $15 \times 15$ complex matrix, i.e., a $30 \times 30$ real matrix. It was necessary to take into account the (2,0,0) wave vectors $G$ only to have a good picture of the conduction band stemming from $\Gamma_{2'}$. To give a physical explanation to this result, we have plotted in Fig. 3 the energy bands for the empty diamond lattice and the symmetries of the various plane-wave states. We can see that a wave function with the $\Gamma_{2'}$ symmetry can be built with the $G = (1,1,1)$ vectors, but also another one with the (2,0,0) vectors, [from Fq. (2.11)]. These two functions, having the same symmetry, can be coupled by the crystal potential, and they must be taken into account. On the contrary, no wave functions with the sym-

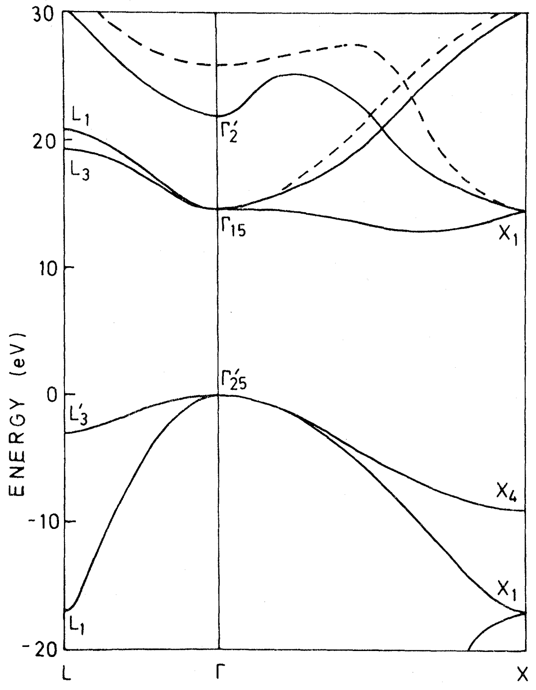


FIG. 2. Uncorrelated Hartree-Fock energy bands for diamond. Valence bands were calculated by the LCAO method. For the conduction bands, dashed curves were calculated with the LCAO method, and solid curves by OPW.

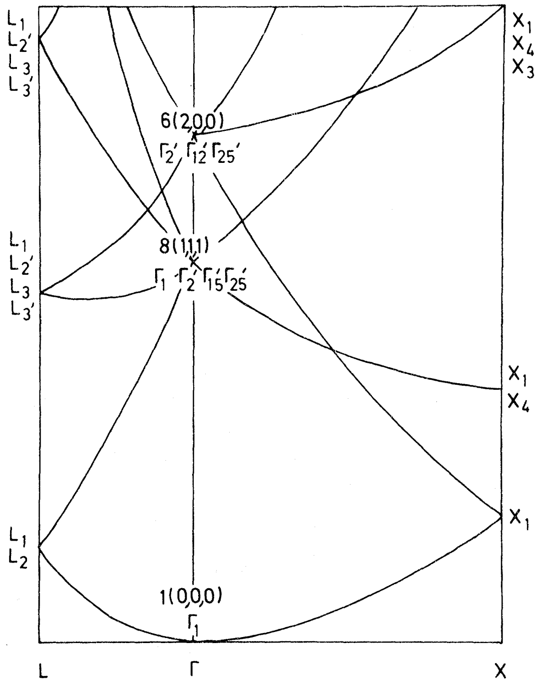


FIG. 3. Energy bands of the diamond lattice in the free-electron limit and symmetries of the various plane-wave eigenstates having wave vector (in units of $2\pi/a$) [0, 0, 0] , [1, 1, 1] , and [2, 0, 0] .

metry $\Gamma_{15}$ can be built with (2,0,0) vectors, and the other bands stemming from this point then have a too largely different energy to have effects on the energy gap. This is why the two first conduction bands are already well depicted by considering only (1,1,1) reciprocal vectors. The results are in fairly good agreement with those of Ref. 13 concerning the conduction bands $\Delta_1$, $\Lambda_1$, and $\Lambda_3$. The shape of twofold-degenerate conduction band $\Delta_5$ is slightly different. Nevertheless, the energy difference between the eigenvalues in Ref. 13 and this paper for such states does not exceed 3 eV, away from the $\Gamma_{15}$ point. The disagreement for the $\Delta_{2'}$ states is larger, and a departure of 6 eV can be observed from the conduction band $\Delta_{2'}$ in Ref. 13, at the point $\vec{k}=(0.5,0,0)$. We find an energy at the $\Gamma_{2'}$ point that is 4 eV lower than in Ref. 13. All these features are illustrated in Fig. 2.

It is interesting to compare these conduction bands with those we should have deduced from a tight-binding method. With this aim in mind we have calculated that the eigenvalues of the Hamiltonian in Eq. (1.9) with the $g_i(q)$ corresponding to antibonding orbitals

$$\chi_j'(\vec{r})=[2(1-S)]^{-1/2}[\chi_j(\vec{r}-\vec{\tau}_0)-\chi_j(-\vec{r}+\vec{\tau}_0-\vec{b}_j)] \tag{4.10}$$

instead of the bonding orbitals in Eq. (2.5). The only changes with respect to the valence-band calculations are:

$$S_1=(\gamma-2\beta')/[2(1-S)]$$

instead of Eq. (2.7) and

$$\chi_j'(\vec{q})=[2(1-S)]^{-1/2}[e^{i\vec{q}\cdot\vec{\tau}_0}\chi_j(\vec{q})-e^{-i\vec{k}\cdot(\vec{\tau}_0-\vec{b}_j)}\chi_j^*(\vec{q})] \tag{4.11}$$

instead of Eq. (2.13). The results are then in very good agreement with those of Ref. 13, not only for the conduction bands stemming from the level but also for the band stemming from $\Gamma_{2'}$. This is consistent with the fact that the earlier HF calculation of both conduction and valence bands in Ref. 13 were done in a LCAO method, in that the wave functions were built with atomic functions.(described by Gaussian lobes) and not with plane waves.

The disagreement between OPW and tight-binding calculations which then appears, firstly for the $\Delta_5$ conduction band, and more significantly for the band stemming from $\Gamma_{2'}$, is thus a measurement of the delocalization of the electrons. This effect is only important at energies higher than the $\Gamma_{15}$ level by 5 eV. This is the order of magnitude of the energy gap $E_g$ when correlations are taken into account. Otherwise it should be noted that at energies in the conduction band as high as the energy difference between bonding and antibonding states $E_g$, the wave functions are no longer pure bonding or antibonding states. The failure of the tight-binding method and the covalence concept at such energies is then not surprising.

## V. DISCUSSION

We have shown in the previous paragraph that the HF valence bands and, at least the first conduction band, are roughly identical to those obtained by a previous calculation.[13] Brener has calculated the energy bands deduced from these HF bands when the correlations are considered.[28] The results are then in very good agreement with experiment, with values of 5.6 and 7.6 eV for indirect and direct band gap. Another bulk property, the cohesive energy, is interesting because it is sensitive not only to the shape of the bands, but also to their energy with respect to the vacuum. We have calculated the HF eigenvalues assuming that the 2*s* atomic orbital was given by Eq. (2.1), and assuming that the 2*s* orbital was given by Eq. (2.3) with $\lambda\neq 0$. The method to orthogonalize the 2*s* Slater-type orbital to 1*s* by choosing a suitable value of $\lambda$ has been used, for example, in the calculation of the binding energy in diamond.[29] This parameter $\lambda$ does not affect the shape of the bands, but shifts them, and has a drastic effect on the cohesive energy. The reason is that the 1*s* part of the valence states, when $\lambda\neq 0$, gives a rather large contribution to the kinetic energy, determined by Eq. (4.5). In effect, although the coefficient $\lambda$ is small (about 0.2), $E_{\text{kin}}^0$ and $E_{\text{kin}}^1$ are larger than 10 eV, because the kinetic energy of the 1*s* state is 30 Ry! In fact, the atomic orbitals in Eq. (2.1) and the values of the parameters given in Eq. (2.2) determined by Slater,[30] are very similar to those determined by Zener.[31] They result from a variational calculation of the wave functions of the carbon atom in which the parameters $\alpha$ and $\beta$ were already variational parameters. It is only because the ionization energy of the carbon element is well accounted by the values of $\alpha$ and $\beta$ in Eq. (2.2) that these functions can be chosen in a first approximation. In particular, a method to have a 2*s* function orthogonal to the 1*s* one would be to choose $2s\propto(\gamma-r)e^{-\beta r}$, with a suitable value of $\gamma$, as in the hydrogen atom. Nevertheless, Zener has shown that a variational treatment of $\gamma$ led to $\gamma=0$ for the carbon atom, which compels us to choose the 2*s* orbital of Slater, [in Eq. (2.1)] without any node. In the same way we are justified in choosing an orbital given by Eq. (2.3) only if $\lambda$ is considered as a variational parameter. We thus find that, for the atomic orbital as well as in the diamond crystal, the value of $\lambda$ must be $\lambda = 0$. So any attempt to orthogonalize valence states to the core functions courts a failure in the LCAO approximation, with so simplified atomic orbitals. Taking $\lambda = 0$, we find an eigenvalue for the top of the valence band as it comes from our Hartree-Fock self-consistent field: $E(\Gamma_{25'}) \simeq -4$ eV $\simeq -0.30$ Ry. This is also in good agreement with the results in Ref. 13. This allows us to conclude that the value of the cohesive energy $E_{co}$ will be the same as in Ref. 13, for the set of Gaussian lobes giving $E(\Gamma_{25'}) = -0.30$ Ry (column 11 in Table IV of this reference) which is 4 eV/atom. The difference with respect to the experimental value of 7.6 eV/atom is ascribed to correlation effects.

Now that the energy bands have been investigated, let us discuss the accuracy of our HF wave functions. This can be achieved by comparing the Fourier components of the charge density with the x-ray scattering factors. In fact, almost all calculations, whether the OPW or the pseudopotential approximation, as well as the LCAO method, give $F_{111}$, $F_{220}$, and $F_{311}$ factors in good agreement with experiment. Such is not the case for the "forbidden" reflection $F_{222}$. This reflection would be absent if the electronic cloud consisted of spherically symmetrical regions around each atom. The strength of this (222) reflexion is thus due to asphericities in the charge density arising from the crystal hybridization responsible for covalent effects. Although a naive interpretation of a chemical bond suggests that it is a quite reasonable figure, many calculations have yielded a considerable lower value: $F_{222} = 0.03$,[32] 0.09,[24] 0.02.[33] The experimental value is $F_{222} = 0.14$.[34] All these numbers are in electrons per atom. More recently, an OPW calculation gave $F_{222} = 0.15$.[35] A calculation of this scattering factor in the tight-binding method[36] led to the same results, but the eigenstates chosen implied a wrong band structure, especially for the conduction band.

In the OPW formalism, the scattering factors are easily obtained because almost all the charge density is automatically obtained in the Fourier form. This is not the case in the tight-binding method, and some approximation will be useful to determine $F_{222}$. We can write in first approximation (see Ref. 37):

$$F_{222} = \frac{4}{1+S} \int \chi_0(\vec{r} - \vec{\tau}_0)\, \chi_0(-\vec{r} + \vec{\tau}_0)\, e^{i\vec{K}\cdot\vec{r}}\, d^3r \tag{5.1}$$

with $\vec{K} = (2,2,2)$. To calculate this quantity, we have replaced the product $\chi_0(\vec{r} - \vec{\tau}_0)\,\chi_0(-\vec{r} + \vec{\tau}_0)$ by a Gaussian lobe: $Ae^{-\nu r^2}$, the parameters $A$ and $\nu$ being chosen such that

$$\int Ae^{-\nu r^2} d^3r = S,$$

$$\langle r^2 \rangle = \int r^2 A e^{-\nu r^2} d^3r = \int r^2 \chi_0(r - \tau_0)\, \chi_0(r + \tau_0)\, d^3r. \tag{5.2}$$

Both $S$ and $\langle r^2 \rangle$ have been calculated exactly by using a degenerate form of the ellipsoidal coordinated called spheroidal coordinates.[37] We can then write

$$F_{222} = [4S/(1+S)]\, e^{-K^2 \langle r^2 \rangle / 6S}. \tag{5.3}$$

When we choose free-atom orbitals, in Eqs. (2.1) and (2.2), we find $F_{222} \simeq 0.07$. But if we choose the crystal orbitals with $\beta_s = \beta_p = 2.1$, we find $F_{222} \simeq 0.12$, which is in good agreement with the experimental value. It is noticeable that our theoretical value fully agrees with the value of 0.11 found in Ref. 13 for the set of Gaussian lobes mentioned above. Our results, at least those concerning valence states and bands, thus coincide with those plotted in column 11 of Table IV in Ref. 13. It then appears that these Gaussian lobes, with which the valence states are built, add up to reconstitute $sp^3$ covalent bonds. Remembering the reason for which the 222 x ray is not forbidden, it is not surprising that this set of Gaussian lobes is the only one which gives a $F_{222}$ value in good agreement with experiment. The other ones give a smaller value $F_{222} \leq 0.09$. Though the maximum cohesive energy is then not reached, we are led to consider the basis corresponding to column 11 of Table IV in Ref. 13 as the best one. The results are summarized in Table I.

The good agreement between the HF scattering factors and the experiment shows that correlations do not affect significantly the charge density. At first sight, this can seem surprising because the energy gap is reduced by a factor of 2 by correlations.[13,28] But this strong effect is due to the addition of two correlation effects, the moving up of the valence band, and the moving down of the conduction band.[38] Nevertheless, the shift of either the $\Gamma_{25'}$ level (2.45 eV) or the $\Gamma_{15}$ level (3.6 eV),[28] are very small compared with the kinetic energy or Coulomb plus exchange energies which both are at least ten times larger. So, the correlation effect in the charge density is expected to be smaller than 10%.

We must also emphasize that the HF energy bands, without correlations, are in less good agreement with experiment than other results. This is not surprising in pseudopotential calculations. In effect, generally, the results are ob-

TABLE I. Diamond HF calculational results. The energies are given in Ry. The self-consistent field row gives the energy for the top of the valence band as it comes from the self-consistent field. All other band eigenvalues are given relative to this level. Column 1 gives experimental results on diamond. Column 2 gives the results of Euwema *et al.* (Ref. 13) for the set of Gaussian lobes giving the closest agreement with our calculations reported in column 3. The x-ray scattering factor $F_{222}$ is in electrons per atom.

| Term | Expt. | LBF | LCAO |
|---|---|---|---|
| SCF $\Gamma_{25'v}$ | | $-0.30$ | $-0.30$ |
| $1s$ | | $-21.96$ | $-22$ |
| $\Gamma_{1v}$ | $-1.5$ | $-2.15$ | $-2.13$ |
| $\Gamma_{25'v}$ | | 0 | 0 |
| $X_{1v}$ | $-0.7$ | $-1.36$ | $-1.25$ |
| $X_{4v}$ | | $-0.65$ | $-0.66$ |
| $\Gamma_{15c}$ | 0.54 | 1.06 | 1.10 |
| $\Delta_{(0.25)c}$ | | 1.05 | 1.07 |
| $\Delta_{(0.5)c}$ | | 1.06 | 0.99 |
| $\Delta_{(0.75)c}$ | 0.4 | 1.16 | 0.96 |
| $X_{1c}$ | | 1.42 | 1.10 |
| $\Gamma_{2'c}$ | | 1.91 | 1.91, 1.62[a] |
| $F_{222}$ | 0.15 | 0.11 | 0.12 |

[a] This value is obtained by OPW. All the other quantities are the results of the LCAO calculations.

tained by considering an empirical pseudopotential accounting for correlation and some exchange effects chosen to fit experimental results.[22] When pseudopotential form factors do not contain any empirical correction, they are chosen so as to fit spectroscopic term values.[39] The spectroscopic data of the single, isolated, and triply ionized ion, already implicitly contain both correlation and exchange effects, which explains the good results obtained by this method. For OPW calculations, the correlations are usually not considered and the exchange is accounted for in the Slater approximation. Not only does such an approximation lead to approximate eigenvalues, but also the Koopman's theorem is not satisfied so that the eigenvalues do not have exactly the same signification as the true HF eigenvalues. These two causes for inaccuracy add up to give an energy gap different from that found in exact HF calculations and which is in agreement with experimental results only by a mere chance. Besides, if correlation effects were added, this agreement would disappear.

## VI. CONCLUSION

We have computed the noncorrelated Hartree-Fock energy bands in diamond. Our results corroborate the previous calculation based on the local basis function (LBF) method. The method we have used is, however, different. We have calculated the valence bands using a LCAO basis method. The conduction bands have been calculated both by a LCAO method and by an OPW method. It turns out that the Gaussian lobes used to describe wave functions in the LBF method interfere so as to reconstitute $sp^3$ orbitals. The LBF and LCAO methods are thus quite similar. Usually, in the LCAO approximation, free-atom approximations to the diamond charge density replace the $sp^3$ crystal wave functions by free-atom $sp^3$ charge densities. This is insufficient not only to describe the detailed features of the band structure but also the covalent bonding effects such as the forbidden reflection $F_{222}$. One of the most important features of our model is that the atomic orbitals we have chosen are allowed to be distinct from the free-atom orbitals. It is implied by the fact that the electrons in an atomic orbital of the diamond interact with all other electrons and nucleus of the crystal and cannot be in the same state as in a free carbon atom. This results in a departure of the crystal charge density from the superpositions of free-atom $sp^3$ charge densities. In turn, any change in the charge density implies a change of the crystal field. The variational procedure we have used to determine crystal orbitals is a self-consistent treatment of the valence contribution to the crystal potential. The fundamental difference with previous LCAO calculations is that the crystal potential was determined assuming that the atomic orbitals were those of the free atom. We have found that the crystal $sp^3$ orbitals are contracted by 30% with respect to the free-atom orbitals. The resulting scattering factor $F_{222}$ is then in quite good agreement with experiment. For the first time, we have calculated the wave functions and eigenstates directly in the reciprocal space. This method allows a full account of the translational periodicity. In particular, the interactions of an electron and these centered on all other sites are all automatically included. This is a great improvement on the usual LCAO methods in which such interactions were truncated to the second- or third-neighboring atoms. It is one reason for which not only the valence but also the conduction bands were so well described. In effect, the broadening of levels into energy bands are closely related to the periodic boundary condition of the wave function and the spacial periodicity of the crystal potential. The calculation in the reciprocal space is a reason for which our model is by far less complicated than the previous LBF calculations. The many two-, three-, and more-center integrals appearing in the calculation in the real space do not appear in the reciprocal space. Moreover the calculation of such integrals is tedious for a $sp^3$ basis function and is easily worked out only in LBF basis (which explains its extensive use). The other simplification is that in our model, the absence of these integrals allows us to choose a basis of four $sp^3$ orbitals on each atom. On the contrary many Gaussian lobes are needed to rebuild $sp^3$ lobes, so that the number of basis functions in the LBF formalism must be much larger.

It is of a great practical interest to simplify as much as possible the HF band calculations. In effect, important defects such as vacancies or surfaces, give a further perturbation potential to the pure crystal Hamiltonian. Till now the calculation of HF eigenstates of the unperturbed Hamiltonian was already so complicated that it became impossible to solve the problem of a perturbed Hamiltonian. On the other hand, usual simplified tight-binding methods did not describe correctly the excited states, and were thus irrelevant to treat the problem of strong perturbations. Our OPW calculation of the HF conduction band has shown that the conduction band is very well described by our LCAO formalism up to energies equal to the experimental energy gap (5–7 eV). Our LCAO basis then accounts not only for the valence bands and the crystal charge densities, but also the bottom of the conduction band. This basis can thus be used to treat even perturbations giving eigenvalues in the middle of the energy gap. Since the tight-binding methods are particularly suited to the treatment of vacancies and surface states, our model should be the starting point for the accurate studies of these effects. Previously, the inclusion of correlation effects on the band structure should be achieved since they are particularly important in covalent systems. A simplified calculation of these effects are under study at present time.

## ACKNOWLEDGMENTS

The authors are pleased to acknowledge a number of helpful and stimulating discussions with J. Friedel. They are indebted to F. Debaecker for the computations performed at Laue Langevin Institute at Grenoble (France). The authors are also grateful to D. Lohez for supplying us with an overlap integrals computer routine.

## APPENDIX A

Let us calculate the Fourier transform $f(q)$ for $s$ and $p$ Slater-type orbitals with quantum number $n$:

$$\varphi^{s}(\vec{r}) = c_s r^{n-1} e^{-\theta r}, \qquad \varphi^{p\eta}(\vec{r}) = c_p \eta r^{n-2} e^{-\theta r}, \tag{A1}$$

where $\eta$ stands for $x$, $y$, $z$, $c_s$ and $c_p$ being normalization constants. Owing to the spherical symmetry of $\varphi_s$, the Fourier transform is

$$f^s(q) = 4\pi \int_0^\infty \varphi^s(r) \frac{\sin qr}{qr} r^2\, dr, \tag{A2}$$

which leads to:

$$f^s(q) = c_s \frac{4\pi(n+1)!}{(\theta^2 + k^2)^{n+1}} \theta^n \sum_{P=0}^{I[n/2]} C_n^{2P} (-1)^P \frac{(q/\theta)^{2P}}{2P+1}. \tag{A3}$$

$I[n/2]$ means the integer part of $\frac{1}{2}n$.

To calculate the Fourier transform $f^{p\eta}(\vec{q})$ of $\varphi^{p\eta}(\vec{r})$, it is convenient to choose the $z$ axis along the $\vec{q}$ vector. Only the projection of the $p_\eta$ function along this axis will give a nonvanishing contribution as can be seen by considerations of symmetry. Using polar coordinates, we can write

$$f^{p\eta}(\vec{q}) = -4\pi \frac{\vec{\eta}\cdot\vec{q}}{q} c_p \int r^{n+1} \left[\frac{\cos qr}{iqr} - \frac{i \sin qr}{(iqr)^2}\right] dr, \tag{A4}$$

where $\vec{\eta}$ is the unit vector along the $\eta$ axis. After integration, we obtain

$$f^{p\eta}(\vec{q}) = ic_p \frac{4\pi(n-1)!}{\theta^{n+2}(1+x^2)^{n+1}} \times \left(n \sum_{P=0}^{I[(n+1)/2]} C_{n+1}^{2P} (-1)^P x^{2P-1} - (1+x^2) \sum_{P=0}^{I[(n-1)/2]} C_n^{2P+1} (-1)^P x^{2P-1}\right) \frac{\vec{\eta}\cdot\vec{q}}{q}, \tag{A5}$$

where $x$ stands for $q/\theta$. For $n=2$, these relations become:

$$f^{2s}(q) = \left(\frac{\pi\beta_s}{3}\right)^{1/2} 8\beta_s^2 \frac{3\beta_s^2 - q^2}{(\beta_s^2 + q^2)^3}, \qquad f^{2p_z}(q) = -i(\pi\beta_p)^{1/2} \frac{32k\beta_p^3}{(k^2 + \beta_p^2)^3}. \tag{A6}$$

$\beta_s$ and $\beta_p$ are the Slater coefficients defined in Eq. (2.1). For $n=1$, we can write

$$f^{1s}(q) = (\pi\alpha)^{1/2} \frac{8\pi\alpha^2}{(\alpha^2 + q^2)^2}. \tag{A7}$$

Note that the functions $f(q)$ are distinct of the quantities $g^\alpha(q)$ in Eq. (1.3), since there are two atoms per unit cell. $f(q)$ is the Fourier transform of atomic orbitals centered on one atom.

## APPENDIX B

To calculate S, $\beta^1$, and $\gamma$, it is most convenient to express $p$-type orbitals in terms of $\pi$ and $\sigma$ orbitals. The expression of the integrals is then

$$
\begin{aligned}
S &= \tfrac{1}{4}(\langle s_A | s_B\rangle - 2\sqrt{3}\,\langle s_A|\sigma_B\rangle - 3\langle\sigma_A|\sigma_B\rangle),\\
\beta' &= \tfrac{1}{4}(\langle s_A | s_B\rangle - (2/\sqrt{3})\langle s_A|\sigma_B\rangle + \langle\sigma_A|\sigma_B\rangle), \qquad \text{(B1)}\\
\gamma &= \tfrac{1}{4}(\langle s_A | s_B\rangle - 2\sqrt{2}\,\langle s_A|\sigma_B\rangle\\
&\qquad -2\langle\sigma_A|\sigma_B\rangle + \langle\pi_A|\pi_B\rangle).
\end{aligned}
$$

The indices $A$ and $B$ indicate the sites on which the orbitals are localized. We have chosen the convention

$$
\begin{aligned}
\sigma_A &= c_p r_A^{n-2}\cos\alpha_A e^{-\theta r_A},\\
\sigma_B &= -c_p r_B^{n-2}\cos\alpha_B e^{-\theta r_B},\\
\pi_A &= c_p r_A^{n-2}\sin\alpha_A e^{-\theta r_A}, \qquad \text{(B2)}\\
\pi_B &= c_p r_B^{n-2}\sin\alpha_B e^{-\theta r_B}.
\end{aligned}
$$

The notations are those used in Appendix A; $\alpha_A$ and $\alpha_B$ are polar angles. The integrals are then easily calculated in spheroidal coordinates.[38] Let $R$ be the distance between $A$ and $B$. The new variables $\lambda'$ and $\mu'$ being defined by

$$\lambda' = (1/R)(r_A + r_B), \quad \mu' = (1/R)(r_A - r_B), \qquad \text{(B3)}$$

each scalar product can be expressed in a finite sum of terms $A_i(\xi)$ and $B_i(\xi)$, with

$$
\begin{aligned}
A_i(\xi) &= \int_1^{\infty} e^{-\xi\lambda'}(\lambda')^i d\lambda',\\
B_i(\xi) &= \int_{-1}^{+1} e^{-\xi\mu'}(\mu')^i d\lambda'.
\end{aligned}
$$

These integrals are calculated by recurrence.

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*This work has been supported by the Direction de Recherches et de Moyens d'Essai.

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