PHYSICAL REVIEW VOLUME 164, NUMBER 3 15 DECEMBER 1967

Charge Density of Diamond

IZA GOROFF[*][†]
Physics Department, Case Western Reserve University, Cleveland, Ohio
and
Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania

AND

LEONARD KLEINMAN[‡]
Physics Department, University of Southern California, Los Angeles, California

(Received 26 May 1967)

Fourier transforms of the charge density of diamond are calculated using the orthogonalized-plane-wave OPW method. The full OPW wave function is used in calculating the charge density in contrast to previous calculations using only plane waves. The results are in excellent agreement with experiment.

I. INTRODUCTION

CALCULATIONS of x-ray scattering form factors in diamond have evolved from primitive calculations using superpositions of atomic charges to more refined calculations based on a variety of differing ways of treating the electronic structure of diamond.[1–3] Two of the more refined calculations, that of Kleinman and Phillips[1] and that of Bennemann[2] are more closely related to the present calculation than the others. Kleinman and Phillips constructed a local pseudopotential as an approximation to the nonlocal orthogonalized-plane-wave (OPW)[4,5] method previously used in calculating the electronic band structure in diamond.[6] Kleinman and Phillips also used pseudowave functions based on only the plane-wave parts of orthogonalized plane waves (OPW's). Bennemann[2] used the Kleinman-Phillips local pseudopotential, and he too considered only pseudowave functions. However, Bennemann's actual calculation differs vastly from that of Kleinman and Phillips, and his methods, though sharing a number of drawbacks with those of Kleinman and Phillips, may be used to attack a wide range of problems which are outside the realm of more conventional band theory.[7] Bennemann's results for this problem are presumably more self-consistent than those of Kleinman and Phillips and do not contain the same sampling errors (See Sec. V); however, they do contain a spherical average over the Brillouin zone.

The present work differs in several respects from these two previous calculations. Firstly, we do not use a local pseudopotential; rather the full nonlocal OPW method is adopted. Secondly, the full OPW wave function, including the orthogonalization terms, is used to calculate the charge density. Other improvements over the Kleinman-Phillips calculation are a fourfold finer sampling of the Brillouin zone and an expansion of the wave function in a larger portion of the complete basis set; both of these improvements are allowed by major advances in the speed of computation which have taken place in the last six years.

II. SOLUTION OF THE OPW EQUATIONS

The orthogonalized plane wave method of Herring[4] has received much attention in the literature.[5] The derivation of the OPW equations is well known, but the method of solving these equations, to give both eigenfunctions and eigenvalues, is not common in the OPW literature, although it well enough known in molecular and atomic physics.

We write our wave functions as a linear combination of OPW's

$$\psi^n(\mathbf{r})=\sum b_j^n\chi_{\mathbf{k}_j}(\mathbf{r})\,, \tag{2.1}$$

where the superscript refers to a particular eigenstate of the equations haivng the energy E_n, and the b's are chosen real. The χ's are defined by (4.1).

The OPW equations may be written for diamond as follows:

$$\sum_{i,j} b_i^n b_j^n\{H_{(\mathbf{k}_j-\mathbf{k}_i)}-E_cA(k_i)A(k_j)\cos[\boldsymbol{\tau}\cdot(\mathbf{k}_j-\mathbf{k}_i)]\}$$

$$=\sum_{i,j} b_i^n b_j^n E_n\{\delta_{ij}-A(k_i)A(k_j)\cos[\boldsymbol{\tau}\cdot(\mathbf{k}_j-\mathbf{k}_i)]\}, \tag{2.2a}$$

where $H_{(\mathbf{k}_j-\mathbf{k}_i)}$ is the $(\mathbf{k}_j-\mathbf{k}_i)$ Fourier transform of the Hamiltonian seen by the valence electron, E_c is the energy of the corelike eigenstate of the valence Hamiltonian, $A(k)$ is given by (4.3), and the two atoms in a unit cell are located at $\pm\boldsymbol{\tau}$ from the lattice point, with $\boldsymbol{\tau}=a(\frac{1}{8},\frac{1}{8},\frac{1}{8})$.

We now wish to write (2.2a) as a matrix equation. That which is in the curly brackets on the left-hand side of (2.2a) we call H_{ij}'. That which is in the curly brackets

---

[*] That portion of the work done at the Case Western Reserve University was supported by the Atomic Energy Commission. That portion of the work done at the University of Pennsylvania was supported by the Advanced Research Projects Agency.

[†] Present address: Argonne National Laboratory, Argonne, Illinois.

[‡] Supported by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under grant No. AFOSR 1115-66.

[1] L. Kleinman and J. C. Phillips, Phys. Rev. **125**, 819 (1962).
[2] K. H. Bennemann, Phys. Rev. **133**, A1045 (1964).
[3] H. Clark, Phys. Letters **11**, 41 (1964).
[4] C. Herring, Phys. Rev. **57**, 1169 (1940).
[5] T. O. Woodruff, Solid State Phys. 4, 367 (1957).
[6] F. Herman, Phys. Rev. **93**, 1214 (1954).
[7] K. H. Bennemann, Phys. Rev. **130**, 1763 (1963).

on the right-hand side of (2.2a) we call G_{ij}. We combine the column vector eigenfunctions into matrices, $X_{in}\equiv b_i^n$, and write the eigenvalues as a diagonal matrix, $E_{ij}=E_i\delta_{ij}$. Eq. (2.2a) is now written as

$$X^TH'X=X^TGXE. \qquad (2.2\text{b})$$

The first step in the solution is to transform G into the unit matrix using a nonunitary transformation; (2.2b) is transformed into

$$X^TW^{-1}WH'W^T(W^T)^{-1}X=X^TW^{-1}(W^T)^{-1}XE, \qquad (2.2\text{c})$$

where $WGW^T=1$. Then a unitary transformation is made to diagonalize $WH'W^T$.

$$\begin{aligned}(X^TW^{-1}U^T)&(UWH'W^TU^T)(U(W^T)^{-1}X)\\ &=(X^TW^{-1}U^T)(U(W^T)^{-1}X)E. \qquad (2.2\text{d})\end{aligned}$$

Since $(UWH'W^TU^T)$ is diagonal, $(U(W^T)^{-1}X)$ is also diagonal, and, by normalization is the unit matrix. Therefore

$$X=W^TU^T. \qquad (2.3)$$

The eigenvectors given by (2.3) are appropriately normalized,

$$\sum_{i,j} b_i^m b_j^n(\chi_i,\chi_j)=\delta_{mn}.$$

The matrix of eigenvalues is

$$E=UWH'W^TU^T. \qquad (2.4)$$

Equation (2.4) is not relevant to the results of this paper, which depend only on the eigenfunctions.

III. THE CRYSTAL POTENTIAL

The potential seen by the valence electrons is composed of a Coulomb part and an exchange part. The Coulomb contribution is calculated from Poisson's equation, written in atomic units as

$$V^{\text{Coul}}(\boldsymbol{\kappa})=8\pi\rho(\boldsymbol{\kappa})/\kappa^2, \qquad (3.1)$$

where $\boldsymbol{\kappa}$ is a reciprocal lattice vector, and $V^{\text{Coul}}(\boldsymbol{\kappa})$ and $\rho(\boldsymbol{\kappa})$ are the $\boldsymbol{\kappa}$th Fourier transforms of the Coulomb potential and charge density, respectively. The charge density ρ is composed of three terms, nuclear, core, and valence charge densities. The nuclear charge density is just a 6^+ charge at each nuclear site. The core charge density is taken to the same as that of an atom centered at each nuclear site. Calculations of Herman have shown that this is an excellent approximation in diamond[8]; $1s$ wave functions calculated by Herman in the diamond crystal are essentially the same as those calculated by Herman and Skillman[9] for the free neutral carbon atom. The valence charge density is calculated self-consistently. After a few iterations the calculated valence charge density becomes independent of the assumed initial charge density.

The exchange contribution to the potential is obtained from the Slater model.[10] The Slater formula gives

$$V^{\text{exch}}(\mathbf{r})=-6[(3/8\pi)\rho(\mathbf{r})]^{1/3}, \qquad (3.2\text{a})$$

where $\rho(\mathbf{r})$ is the total electronic charge density at $\mathbf{r}$. It is almost impossible to know the valence part of $\rho(\mathbf{r})$ at enough points in the crystal to calculate $V^{\text{exch}}(\mathbf{r})$ accurately; however, it is still possible to calculate $V^{\text{exch}}(\mathbf{r})$ in a rather different way.

We write $\rho(\mathbf{r})$ as a sum of three terms

$$\rho(\mathbf{r})=\rho_{\text{val sm}}(\mathbf{r})+\rho_{\text{val ortho}}(\mathbf{r})+\rho_{\text{core}}(\mathbf{r}). \qquad (3.3)$$

As we shall discuss in Sec. IV, the valence charge density is composed of two different types of terms. $\rho_{\text{val sm}}(\mathbf{r})$ [$\equiv\mathcal{A}(\mathbf{r})$ in Sec. IV] is that part of the valence charge density due to plane-wave plane-wave terms. There are terms in $\rho_{\text{val sm}}$ which can not be represented by spherical charge densities centered at nuclear sites. $\rho_{\text{val ortho}}$ is that part of the valence charge density (called $\mathcal{B}+\mathcal{C}$ in Sec. IV) due to plane wave-orthogonalization and orthogonalization-orthogonalization terms. $\rho_{\text{val ortho}}$ may be represented as a superposition of spherical charge densities, each centered at a nuclear site, a characteristic it shares with ρ_{core}.[11] We rewrite (3.2a) to take advantage of this

$$\begin{aligned}V^{\text{exch}}(\mathbf{r})=&-6(3/8\pi)^{1/3}\\ &\times\{\rho_{\text{val sm}}{}^{1/3}(\mathbf{r})+[\rho^{1/3}(\mathbf{r})-\rho_{\text{val sm}}{}^{1/3}(\mathbf{r})]\}. \qquad (3.2\text{b})\end{aligned}$$

We do not need to know $\rho_{\text{val sm}}(\mathbf{r})$ in order to calculate its contribution to $V^{\text{exch}}(\boldsymbol{\kappa})$. The term proportional to $\rho_{\text{val sm}}{}^{1/3}(\mathbf{r})$ calculated using a power series expansion takes one term further than is customary to gain higher accuracy. In order to simplify the following expressions we write $\mathcal{A}(\mathbf{r})$ in place of $\rho_{\text{val sm}}(\mathbf{r})$ and $\mathcal{A}(\boldsymbol{\kappa})$ in place of $\rho_{\text{val sm}}(\boldsymbol{\kappa})$. If we write

$$\mathcal{A}(\mathbf{r})=\mathcal{A}_0+\sum_{\kappa\neq0}\mathcal{A}(\boldsymbol{\kappa})e^{i\kappa\cdot r} \qquad (3.4)$$

then

$$\begin{aligned}\mathcal{A}^{1/3}(\mathbf{r})=\mathcal{A}_0{}^{1/3}+&\frac{\mathcal{A}_0{}^{-2/3}}{3}\sum_{\kappa\neq0}\mathcal{A}(\boldsymbol{\kappa})e^{i\kappa\cdot r}\\ &-\frac{2}{9}\mathcal{A}_0{}^{-5/3}\sum_{\kappa,\kappa'\neq0}\mathcal{A}(\boldsymbol{\kappa})\mathcal{A}(\boldsymbol{\kappa}')e^{i(\kappa+\kappa')\cdot r}. \qquad (3.5)\end{aligned}$$

Kleinman and Phillips and others have used the first two terms of this expansion. Quelle questioned its validity,[12] and Herman estimated that the two term power series might be in error by as much as 20%.[13] We

---

[8] F. Herman (private communication).

[9] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[10] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[11] F. Herman, *Proceedings of the International Conference on the Physics of Semiconductors, Paris* (Dunod, Cie., Paris, 1964), p. 3.

[12] F. Quelle, *Energy Band Calculations*, Tech. Rept. No. 295, Lincoln Laboratory, January 1963 (unpublished).

[13] F. Herman (private communication).

would expect that the three-term expansion is considerably more accurate than that with an error of about 4%. The exchange potential due to the smooth part of the valence charge density is written as follows:

$$V_{\mathrm{val\,sm}}(\boldsymbol{\kappa})^{\mathrm{exch}}=-6(3/8\pi)^{1/3}\mathcal{A}_0^{-2/3}\left\{\frac{1}{3}\mathcal{A}(\boldsymbol{\kappa})\right.$$

$$\left.-\frac{2}{9\mathcal{A}_0}\sum_{\kappa',\kappa''\neq 0}\mathcal{A}(\boldsymbol{\kappa}')\mathcal{A}(\boldsymbol{\kappa}'')\delta(\boldsymbol{\kappa}'+\boldsymbol{\kappa}''-\boldsymbol{\kappa})\right\}. \quad (3.2\mathrm{c})$$

We consider the rest of the exchange potential, that part proportional to $[\rho^{1/3}(\mathbf{r})-\mathcal{A}^{1/3}(\mathbf{r})]$ next. Of the three terms which sum to give $\rho(\mathbf{r})$ in (3.3) only $\rho_{\mathrm{val\,sm}}(\mathbf{r})$ $\times(\equiv\mathcal{A}(\mathbf{r}))$ is not easily obtained as a function of $\mathbf{r}$. However, a small error in $\mathcal{A}(\mathbf{r})$ gives rise to a much smaller error in $[\rho^{1/3}(\mathbf{r})-\mathcal{A}^{1/3}(\mathbf{r})]$. We are therefore justified in using a spherical average of $\mathcal{A}(\mathbf{r})$ about each atomic site in *this term alone*, which we do. With the spherical average of $\mathcal{A}(\mathbf{r})$, the rest of the exchange potential is easily evaluated.

IV. THE CHARGE DENSITY OF AN ELECTRON

For the particularly simple case of diamond we may write an OPW as

$$\chi_k(\mathbf{r})=(4/Na^3)^{1/2}\exp i\mathbf{k}\cdot\mathbf{r}-A(k)\psi_c^k(\mathbf{r}), \quad (4.1)$$

where N is the number of unit cells in the crystal, two atoms per unit cell,

$$\psi_c^k(\mathbf{r})=(1/\sqrt{2N})\sum_{\nu=1}^{2N}\psi_{1s}(|\mathbf{r}-\mathbf{R}_\nu|)\exp i\mathbf{k}\cdot\mathbf{R}_\nu, \quad (4.2)$$

where $\mathbf{R}_\nu$ is the location of the νth atomic site and $\psi_{1s}(|\mathbf{r}-\mathbf{R}_\nu|)$ is an atomiclike $1s$ wave function centered on the νth site,

$$A(k)=(8/a^3)^{1/2}\int\psi_{1s}(r)\exp i\mathbf{k}\cdot\mathbf{r}\,d^3r$$

$$=(8/a^3)^{1/2}(4\pi/k)\int_0^\infty\psi_{1s}(r)\sin kr\,rdr. \quad (4.3)$$

These A's are real numbers in diamond.

A wave function of an electron is composed of a linear combination of OPW's

$$\psi=\sum_i b_i\chi_{\mathbf{k}_i}, \quad (4.4)$$

where the b's are real. The normalization condition is that (ψ,ψ) is one. Since the ψ's are not an orthonormal set, $\sum b_i^2$ is not necessarily equal to one.

We now write the charge density due to one electron.

$$\rho(\mathbf{r})\equiv\psi^*\psi=\mathcal{A}(\mathbf{r})+\mathcal{B}(\mathbf{r})+\mathcal{C}(\mathbf{r}), \quad (4.5)$$

where $\mathcal{A}(\mathbf{r})$ is due to plane-wave plane-wave terms.

$$\mathcal{A}(\mathbf{r})=\frac{4}{Na^3}\sum_{i,j}b_ib_j\exp i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{r} \quad (4.6)$$

$\mathcal{B}(\mathbf{r})$ is due to cross terms,

$$\mathcal{B}(\mathbf{r})=-2\,\mathrm{Re}\frac{1}{2N}\left(\frac{8}{a^3}\right)^{1/2}\sum_{\nu=1}^{2N}\sum_{i,j}\{b_ib_j\exp[i(\mathbf{k}_j-\mathbf{k}_i)\cdot R_\nu]$$

$$\times\exp[i\mathbf{k}_j\cdot(r-\mathbf{R}_\nu)]\psi_{1s}(|\mathbf{r}-\mathbf{R}_\nu|)A(\mathbf{k}_i)\}, \quad (4.7\mathrm{a})$$

and $\mathcal{C}(\mathbf{r})$ is due to the atom-atom like terms,

$$\mathcal{C}(\mathbf{r})=(1/2N)\sum_{i,j}b_ib_jA(k_i)A(k_j)$$

$$\times\sum_\nu\exp[i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{R}_\nu]\times|\psi_{1s}^2(|\mathbf{r}-\mathbf{R}_\nu|)|, \quad (4.8)$$

where we assume no overlap of ψ_{1s} wave functions of neighboring atoms.

We take the Fourier transform of $\mathcal{A}(\mathbf{r})$

$$\mathcal{A}(\boldsymbol{\kappa})=(8/a^3)\sum_{i,j}b_ib_j\delta(\mathbf{k}_j-\mathbf{k}_i-\boldsymbol{\kappa}). \quad (4.9)$$

This term is readily evaluated from information used previously in the calculation. The Fourier transform of $\mathcal{C}(\mathbf{r})$ is also readily obtained

$$\mathcal{C}(\boldsymbol{\kappa})=\{\sum_{i,j}b_ib_jA(k_i)A(k_j)\cos[(\mathbf{k}_j-\mathbf{k}_i)\cdot\boldsymbol{\tau}]\}$$

$$\times\cos\boldsymbol{\kappa}\cdot\boldsymbol{\tau}\int_\infty|\psi_{1s}(\mathbf{r})|^2\exp i\boldsymbol{\kappa}\cdot\mathbf{r}d^3r, \quad (4.10)$$

where the bracketed sum as well as the integral are easily calculated with information used in other parts of the calculation.

The Fourier transform of $\mathcal{B}(\mathbf{r})$ is easily written down

$$\mathcal{B}(\boldsymbol{\kappa})=\sum_{i,j}\{b_i^*b_j[A(k_i)A(|\mathbf{k}_j-\boldsymbol{\kappa}|)$$

$$+A(k_j)A(|\mathbf{k}_i+\boldsymbol{\kappa}|)]\cos[(\mathbf{k}_j-\mathbf{k}_i-\boldsymbol{\kappa})\cdot\tau]\}. \quad (4.11)$$

Unfortunately, although (4.11) is easy to write down it is very difficult to compute numerically, requiring exorbitant amounts of computer time. This is because each term in the sum must be calculated separately for each different value of κ. Instead of calculating the sum directly, we make an approximation which we feel is well justified. Let us look once more at Eq. (4.7). We now restrict our attention to one atomic cell, the μth, and we ignore the overlap of $1s$ functions centered on different atoms. We transform coordinates so $\mathbf{a}=\mathbf{r}-\mathbf{R}\mu$.

$$\mathcal{B}(\mathbf{a})=2\,\mathrm{Re}\left(\frac{8}{a^3}\right)^{1/2}\{\sum_{i,j}b_ib_j\exp[\pm i(\mathbf{k}_j-\mathbf{k}_i)\cdot\tau]$$

$$\times A(k_i)\exp i\mathbf{k}_j\cdot\mathbf{a}\}\psi_{1s}(a), \quad (4.7\mathrm{b})$$

when **a** is within the μth atomic cell. Until this point we have made no approximations. Now, however, we take the spherical average of $\mathcal{B}(\mathbf{a})$; i.e., we replace $\mathcal{B}(\mathbf{a})$ by $\mathcal{B}(a)$ where $\mathcal{B}(a)=(1/4\pi)\int\mathcal{B}(\mathbf{a})d\Omega_a$. Everything but the $\exp i\mathbf{k}_j\cdot\mathbf{a}$ term is independent of angle.

$$\mathcal{B}(a)=2(8/a^3)^{1/2}\psi_{1s}(a)\sum_{i,j}b_ib_jA(k_i)\times\cos[(\mathbf{k}_j-\mathbf{k}_i)\cdot\boldsymbol{\tau}]\frac{\sin k_ja}{k_ja}. \quad (4.12)$$

Equation (4.12) may not look computationally more convenient than (4.11), but it is very much so. Furthermore, it is a simple matter, once possessing $\mathcal{B}(a)$, to calculate $\mathcal{B}(\boldsymbol{\kappa})$ for any number of $\boldsymbol{\kappa}$'s, whereas (4.11) requires a fresh start for each $\boldsymbol{\kappa}$,

$$\mathcal{B}(\boldsymbol{\kappa})=(4\pi/\kappa)(\cos\boldsymbol{\kappa}\cdot\boldsymbol{\tau})\int_0^\infty\mathcal{B}(a)(\sin\kappa a)ada. \quad (4.13)$$

V. SAMPLING THE BRILLOUIN ZONE

In this calculation it is necessary to replace an average over all states in the Brillouin zone by a discrete sum over a finite number of states. We use a sampling procedure based upon one used by Kleinman and Phillips.[14]

The method used has a procedure for successive approximations. In the first-approximation reciprocal space is divided into its unit cells. The average over all states is replaced by a sum over the reciprocal lattice points located at the centers of its unit cells. In diamond we may most easily represent the electronic states by "folding them back" into the first Brillouin zone. Therefore, the average of a function is replaced by a weighted sum over the occupied states at Γ, the weight corresponding to the degeneracy of the state.

$$\bar{f}\cong\tfrac{1}{4}(1f(\Gamma_1)+3f(\Gamma_{25'})). \quad (5.1)$$

In the second approximation we introduce new points midway between each pair of points sampled in the first approximation, in this case between each pair of points of the reciprocal lattice. Upon some reflection one can see that resulting set of points forms another body-centered cubic lattice with a lattice constant half as large as the reciprocal lattice and with a unit cell volume one-eighth the volume of the reciprocal unit cell. If we once again consider the first Brillouin zone, we see that this procedure has introduced points at the X and L points on the boundary of the first Brillouin zone. Recognizing that only half of each of the volumes these points represent lie in the first Brillouin zone, we write the result of this approximation as

$$\bar{f}\cong\frac{\{1[1f(\Gamma_1)+3f(\Gamma_{25'})]+3[2f(X_1)+2f(X_4)]+4[1f(L_1)+1f(L_{2'})+2f(L_{3'})]\}}{1+3+3(2+2)+4(1+1+2)}, \quad (5.2)$$

where the 3 is for the six X points and the 4 is for the eight L points.

In the third approximation we introduce new points midway between each pair of points sampled in the second approximation. The new sample points represent volumes one sixty-fourth the size of the volume used in the first approximation. In the first approximation we sampled only at all points which were located in the first Brillouin zone only at all even or all odd integer values of h_1, h_2, and h_3 where $\mathbf{k}$ is $(2\pi/a)(h_1,h_2,h_3)$. In the second approximation we sample at all points in the first Brillouin zone for which h_1, h_2, and h_3 are either all even or all odd integer multiples of one half. In the third approximation we sample at all points in the first Brillouin zone for which h_1, h_2, and h_3 are either all even or all odd integer multiples of on quarter. In addition to Γ, X, and L we get $(|h_1|,|h_2|,|h_3|)$ of $(\frac{1}{2},\frac{1}{2},0)$ or Σ, $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ or Λ, $(1,\frac{1}{2},0)$ or W, and $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$. There are twelve Σ points, six W points, and twenty-four $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$ points lying within the first Brillouin zone. The third approximation gives

$$\bar{f}=\frac{1f(\Gamma)+3f(X)+4f(L)+6f(\Delta)+8f(\Lambda)+12f(\Sigma)+24f(\frac{3}{4},\frac{1}{4},\frac{1}{4})+6f(W)}{1+3+4+6+8+12+24+6}, \quad (5.3)$$

where $f(\Gamma)=\frac{1}{4}(f(\Gamma_1)+3f(\Gamma_{25'}))$, etc.

Because of insufficient computer time we have been unable to carry through this third approximation as is. Herman has used a variation of this third approximation, which we also adopt.[11] Instead of considering all sixty-four bcc sublattice sites, we consider only those on a cubic lattice, i.e., only half of these sixty-four points. In this way we avoid calculating the band structure at the very low symmetry $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$ points in the Brillouin zone. The calculation of the band structure at these points would involve diagonalizing matrices larger than 80×80, a very time consuming feat, since the computer time for matrix diagonalization goes as the cube of linear size of the matrix (i.e., $\propto 80^3$). As a

---

[14] L. Kleinman and J. C. Phillips, Phys. Rev. **116**, 880 (1959).

result we use the following

$$\bar{f}=\frac{1f(\Gamma)+3f(X)+4f(L)+6f(\Delta=\frac{1}{2},\frac{1}{2},0)+6f(W)+12f(\Sigma=\frac{1}{2},\frac{1}{2},0)}{32}, \tag{5.4}$$

where $f(\Gamma)=(f(\Gamma_1)+3f(\Gamma_{25'})/4)$, etc.

VI. RESULTS AND CONCLUSIONS

The results of the present calculation are listed in Table I. Although we calculated the Fourier transforms of the charge density for the forty lowest reciprocal lattice vectors, we list here results for only the lowest ten reciprocal lattice vectors as the reliability of the results probably decreases with $|\boldsymbol{\kappa}|$ for a variety of reasons concerning the results in Table I.

Several comments should be made at this point. The contribution of the orthogonalization terms $\mathcal{B}(\boldsymbol{\kappa})+\mathcal{C}(\boldsymbol{\kappa})$ varies from eight per cent for $\boldsymbol{\kappa}=(2\pi/a)(1,1,1)$ to much higher values when $|\boldsymbol{\kappa}|$ is larger than those considered in Table I. The calculations of Kleinman and Phillips[1] and of Bennemann,[2] which ignored these orthogonalization terms which tend to reduce the magnitudes of the low Fourier transforms of the charge density, usually obtained smaller magnitudes than this calculation or experiment.[15,16] (See Table II.) This may be understood from the fact that the plane-wave pseudo-wave functions of Kleinman and Phillips and of Bennemann are normalized to one, i.e., $\sum b_i^2=1$, whereas, in the present calculation, the plane-wave part for the OPW wave function is not normalized to one. In particular, for $\Gamma_1 \sum b_i^2=1.09$. Therefore, the plane-wave contribution in this calculation is somewhat larger than in the others. The assumptions of pseudowave functions and pseudopotentials also may have other more subtle effects on the b_i's and, therefore, on the calculated charge density.

There are no adjustable parameters in this calculation; all parameters are determined from first principles (or reasonable approximations to first principles such as the exchange potential presented in Sec. III) and self-consistency. However, we did experiment with varying some parameters in order to see how sensitive the calculation was to a small error or uncertainty in these parameters. The parameters varied were the valence potential and the core energy. The variation of the valence potential over a range wide compared with its uncertainty had almost no effect on the listed charge densities. A 10% decrease in the magnitude of the core energy changed $\mathcal{A}(\boldsymbol{\kappa})$, $\mathcal{B}(\boldsymbol{\kappa})$, and $\mathcal{C}(\boldsymbol{\kappa})$, each appreciably, $\mathcal{B}$ and $\mathcal{C}$ more than doubling, yet the total $\mathcal{A}+\mathcal{B}+\mathcal{C}$ changed by less than 10%. The results quoted here are based on a calculation involving from 132 to 140 OPW's at each point in the Brillouin zone. Although we have not tested the convergence of the charge density with a variation in the size of the OPW basis set, the results of other calculations[14,17] indicate that this number of OPW's is more than adequate, especially for those Fourier transforms we calculate. In addition to the question of convergence there is also the question of self-consistency and the associated question of the stability of the solution with respect to further iteration. Our results are based on four iterations; however, our starting potential was taken from a previous calculation of ours which differed in only a few minor details from the final calculation, and so the effective number of

TABLE I. The calculated Fourier coefficients of the valence charge density. The units are electrons/atom. $\boldsymbol{\kappa}=(2\pi/a)\mathbf{h}$. $\rho=\text{I}+\text{II}+\text{III}$.

h	I	II	III	ρ
⟨000⟩	−4.160	0.320	−0.160	−4.000
⟨111⟩	1.098	−0.196	0.109	1.011
⟨022⟩	0.298	−0.221	0.144	0.221
⟨311⟩	0.013	−0.138	0.098	−0.037
⟨222⟩	−0.105	0.000	0.000	−0.105
⟨400⟩	−0.074	−0.130	0.130	−0.105
⟨133⟩	0.016	0.102	−0.089	0.029
⟨422⟩	0.080	0.122	−0.118	0.084
⟨333⟩	0.087	0.079	−0.081	0.085
⟨511⟩	0.056	0.079	−0.081	0.054

TABLE II. A comparison of the various calculated Fourier coefficients of the valence charge density with experiment. Column 2 lists the experimental values of Götlicher and Wölfel. Column 3 lists the calculated results of Kleinman and Phillips, Column 4 those of Bennemann, Column 5, those of Clark and Column 6 those of the present calculation. $\boldsymbol{\kappa}=(2\pi/a)\mathbf{h}$. The units are electrons/atom. The 1*s* contribution to the total scattering has been recalculated using the Herman-Skillman wave functions as opposed to the Jucys functions used by Kleinman and Phillips. This affects the experimental results in Column 2 which differ slightly from those listed in Kleinman and Phillips's Table II.

h	GW	KP	B	C	GK
⟨111⟩	0.991±0.005	0.88	0.91	0.984	1.011
⟨022⟩	0.185±0.009	0.01	0.12	0.146	0.221
⟨311⟩	−0.045±0.005	−0.14	−0.10	−0.022	−0.037
⟨222⟩	±0.15[a]	−0.15	−0.13	−0.064	−0.105
⟨400⟩	−0.139±0.009	−0.13	−0.11	−0.046	−0.105
⟨133⟩	0.012±0.004	···	···	···	0.029
⟨422⟩	0.026±0.002	···	···	···	0.084
⟨333⟩	0.001±0.004[b]	···	···	···	0.085
⟨511⟩	0.001±0.004[b]	···	···	···	0.054

[a] Measured by Renninger, Ref. 16, with the same results as Götlicher and Wölfel.

[b] The powder method used by Götlicher and Wölfel cannot distinguish between ⟨333⟩ and ⟨511⟩ reflections.

---

[15] S. Götlicher and E. Wölfel, Z. Elektrochem. **63**, 891 (1959).

[16] M. Renninger, Acta Cryst. **8**, 606 (1955).

[17] F. Herman, R. L. Kortum, and C. D. Kuglin, International J. Quant. Chem. (to be published).

iterations is somewhat larger than four. Between the third and fourth iterations only two of the independent numbers of Table I changed sufficiently to alter the appearance of the table, and these numbers changed only in the last decimal digit quoted. There is nothing new or startling in that part of the band structure we have calculated.[18] This calculation is the offshoot of another, a highly successful first-principles calculation of the bulk modulus, cohesive energy, and lattice constant, of diamond,[19] and since the total crystal energy (as well as the charge density) does not depend on the energies or wave functions of the conduction electrons, the only states in the conduction band considered were those whose location and symmetry coincided with calculated valence band states.

In a calculation such as the present one, there is always the question of the exchange potential. The recent paper of Kohn and Sham,[20] in which the authors suggest that the Slater exchange should be multiplied by a factor of $\frac{2}{3}$, has inspired a certain amount of controversy.[21] The Kohn-Sham suggestion encouraged Herman *et al.*[22] to try various multiplicative factors to try to fit their calculated band structures to the more certain of the experimental data. In their most recent work Herman *et al.*[17] came to the conclusion that the multiplicative factor which best fit the band structure to the optical data of diamond was 7/4,[23] almost twice the Slater value (of 1) and almost three times the Kohn-Sham value. In a study of exchange and correlation in silicon Phillips and Kleinman[24] found that the Slater exchange was in excellent agreement with their estimated screened Hartree-Fock exchange. Rather than try a variety of different multiplicative factors, we have decided to use the original Slater exchange. This also facilitates comparison with the earlier calculations[1,2]; the use of a different exchange potential would obscure the effects of the other novel features of this calculation.

These rather large changes in the exchange potential would have an effect on the calculated charge densities but these effects are smaller than one might at first expect. This is because the Slater exchange potential is less than one fifth of the total crystal potential [for the (1,1,1) Fourier transform] and because there are a variety of "restoring forces" in the calculation, e.g., the energy-dependent "repulsive potential" of the orthogonalization terms.

Until the question of exchange is settled, we feel the only improvement of any consequence to the calculation is a finer sampling of the Brillouin zone which awaits yet larger and faster computers.

ACKNOWLEDGMENTS

The authors take pleasure in thanking Professor E. Burstein, Professor C. S. Smith, Professor F. Reines, and Professor M. J. Klein, for their support and encouragement. One author (I.G.) wishes to acknowledge very helpful conversations with David Neumann, Dr. F. Herman, Professor P. L. Taylor, and Professor V. Heine. Finally we wish to thank the staff of the A.E.C. computing center at the Courant Institute of Mathematical Science for their expert help. These calculations were performed on their CDC-6600 computer.

---

[18] These numbers are available from one of the authors (I.G.).

[19] I. Goroff and L. Kleinman (to be published).

[20] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[21] Slater has replied to Kohn and Sham [J. C. Slater, Quarterly Progress Report No. 58, Solid State and Molecular Theory Group, M.I.T. (1965)].

[22] F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, *Quantum Theory of Atoms, Molecules and the Solid State: A Tribute to J. C. Slater* (Academic Press Inc., New York, 1966).

[23] This is not to imply that Herman *et al.*, believe that the exchange and correlation in diamond is actually 7/4 as large as the Slater exchange.

[24] J. C. Phillips and L. Kleinman, Phys. Rev. **128**, 2098 (1962).