

First-Principles Calculation of the Bulk Modulus of Diamond*

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A Hartree-Fock-Slater calculation of the total crystal energy of diamond is performed using the orthogonalized-plane-wave (OPW) method. Half of the electron-electron interaction energy is subtracted from the one-electron value so that these terms are counted once. The full OPW wave function is used to calculate the electron-electron interaction. The results for the equilibrium lattice constant, bulk modulus, and cohesive energy are in excellent agreement with experiment.

I. INTRODUCTION

FOR a long time cellular methods have yielded binding energies of alkali metals.¹ More recently Brooks² has extended the method to polyvalent metals and semiconductors. He obtained very good agreement with experimental cohesive energies for most all metals with no loosely bound *d* electrons. His results were much poorer for the semiconductors. There are two reasons for this failure: (a) The Wigner-Seitz method does not take covalent bonding into account; (b) the diamond atomic cell is highly nonspherical and so any cellular spherical average is bound to be poor. For this latter reason not only cellular methods, but also expansion methods [like the augmented-plane-wave (APW)] which require muffin-tin potentials, must give incorrect results.

Herring's orthogonalized-plane-wave (OPW) method³ was first applied to the band structure of diamond by Herman in 1952.⁴ This and subsequent OPW studies of diamond have been successful in explaining the band structure⁵ and electronic charge distribution⁶ of diamond.

At the time this work was begun it was believed that the OPW method was not suitable for studies of binding energies. This study, together with the first successful OPW calculation of the binding energy of a metal,⁷ shows that the OPW method may be quite successful, if the calculation is sufficiently careful and exhaustively detailed.

Much of the calculation repeats that of GKI. We have attempted to limit the overlap of GKI with that

of the present paper. A discussion of the OPW method and of the sampling technique used are to be found in GKI. In Sec. II we discuss the total crystal Hamiltonian and the total crystal energy (TCE). In Sec. III we discuss the one-electron crystal potential, in Sec. IV the energy of the 1s eigenvalues of the valence Hamiltonian, and in Sec. V we obtain our results. The results for the equilibrium lattice constant, cohesive energy, and bulk modulus are in excellent agreement with experiment.

II. TOTAL CRYSTAL ENERGY

The total crystal Hamiltonian is

$$H_{\text{crystal}} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}e^2 \sum'_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_n \frac{\mathbf{p}_n^2}{2M} + e^2 \frac{1}{2} Z^2 \sum'_{n,m} \frac{1}{|\mathbf{R}_n - \mathbf{R}_m|} - e^2 Z \sum_{i,n} \frac{1}{|\mathbf{R}_n - \mathbf{r}_i|}, \quad (2.1a)$$

where p_i and r_i are the momentum and position of the *i*th electron, m is the electron mass, P_n , R_n , and M are the corresponding quantities of the nuclear core, and Z is the atomic number. In calculating the TCE one usually divides the crystal Hamiltonian into three parts.

$$H_{\text{crystal}} = H_{\text{el}} + H_{\text{el-ion}} + H_{\text{ion}}, \quad (2.1b)$$

where

$$H_{\text{ion}} = \sum_n \frac{\mathbf{p}_n^2}{2M} + \frac{1}{2}e^2 Z^2 \sum'_{n,m} \frac{1}{|\mathbf{R}_n - \mathbf{R}_m|} \quad (2.2)$$

and

$$H_{\text{el}} + H_{\text{el-ion}} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}e^2 \sum'_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - Ze^2 \sum_{i,m} \frac{1}{|\mathbf{R}_m - \mathbf{r}_i|}. \quad (2.3)$$

In the one-electron theory of crystals an electron "sees" a Hamiltonian H_{el}^i of

$$H_{\text{el}}^i = \frac{\mathbf{p}_i^2}{2m} + V(\mathbf{r}_i), \quad (2.4)$$

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¹ E. Wigner and F. Seitz, *Phys. Rev.* **46**, 509 (1934).

² H. Brooks, *Trans. AIME* **227**, 546 (1963).

³ C. Herring, *Phys. Rev.* **57**, 1169 (1940).

⁴ F. Herman, *Phys. Rev.* **88**, 1210 (1952).

⁵ F. Herman, *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1963), p. 3.

⁶ I. Goroff and L. Kleinman, *Phys. Rev.* **164**, 1100 (1967), hereafter referred to as GKI.

⁷ L. Kleinman, *Phys. Rev.* **146**, 479 (1966).

where, in the Hartree-Fock approximation,

$$V(r_i) = e^2 \sum_{j \neq i} \frac{\rho(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} - Ze^2 \sum_n \frac{1}{|\mathbf{R}_n - \mathbf{r}_i|} + V_{\text{ex}}(\mathbf{r}_i), \quad (2.5)$$

where $V_{\text{ex}}(\mathbf{r}_i)$ is the exchange contribution to the i th electron potential and $\rho(\mathbf{r}_j)$ is the probability density of the j th electron. For zero temperature one usually neglects the contribution of lattice vibrations (in particular the zero-point vibrations) to the crystal energy. This means that one assumes that the $P_n^2/2M$ term is negligible and that the positions of the ions, the \mathbf{R}_n 's, are fixed. The problem of finding the total crystal energy is then reduced to the problems of finding the electronic (i.e., electron+electron-ion) contribution to the crystal energy and of determining the electrostatic energy of the ions in the neutral crystal. The electronic contribution TCE_e is

$$\begin{aligned} \text{TCE}_e &= \langle H_{\text{el}} + H_{\text{el-ion}} \rangle \\ &= \sum_i \{ E_i - 1/2 \langle \psi_i | V_{\text{val-val}} | \psi_i \rangle \}, \quad (2.6) \end{aligned}$$

where the sum is over the valence electrons, E_i are their one-electron energies, ψ_i their wave functions, and $V_{\text{val-val}}$ is the valence-valence potential. The contributions to this term are listed in Sec. V.

In the present work, the wave function of the core electron is assumed to be independent of the lattice constant. Still there are two changes in the TCE due to the 1s core electrons. The first, due to core-valence interactions, is already included in TCE_e . The second TCE_i , the electrostatic interaction of the ion cores, is described in Sec. IV. The Coulomb field of the $\kappa=0$ Fourier transform of the valence charge density is taken together with that of the $\kappa=0$ Fourier transform of the ions as part of TCE_i so that TCE_e and TCE_i are finite.

III. CRYSTAL POTENTIAL

The potential comes from two types of interactions, the direct Coulomb and the exchange.

We first consider the Coulomb interaction. In atomic units Poisson's equation is written as

$$\nabla^2 V(\mathbf{r}) = 8\pi\rho(\mathbf{r}) \quad (3.1a)$$

and the Fourier transform of Poisson's equation is

$$-k^2 V^{\text{Coul}}(\mathbf{k}) = 8\pi\rho(\mathbf{k}). \quad (3.1b)$$

Since the matrix elements of the potential are taken between plane waves, the Fourier transform of the smooth part of the valence charge density is calculated without ever calculating the smooth part in real space.

The Coulomb potential may be divided into three parts, corresponding to three charge densities:

$$V^{\text{Coul}}(\mathbf{k}) = V_{\text{nuc}}^{\text{Coul}}(\mathbf{k}) + V_{\text{core}}^{\text{Coul}}(\mathbf{k}) + V_{\text{val}}^{\text{Coul}}(\mathbf{k}), \quad (3.2)$$

where $V_{\text{nuc}}^{\text{Coul}}(\mathbf{k})$ is due to the nuclei at their equilibrium positions in either the strained or unstrained lattice, $V_{\text{core}}^{\text{Coul}}(\mathbf{k})$ is due to the 1s core electrons localized about the nuclei, and $V_{\text{val}}^{\text{Coul}}(\mathbf{k})$ is due to the valence charge density distributed throughout the crystal:

$$\begin{aligned} \rho_{\text{nuc}}(\mathbf{r}) &= Z \sum_{i=1}^N \sum_{\nu=1}^2 \delta(\mathbf{r} - \mathbf{R}_i - \boldsymbol{\tau}_\nu) \\ &= 6 \sum_{i=1}^N \sum_{\nu=1}^2 \delta(\mathbf{r} - \mathbf{R}_i - \boldsymbol{\tau}_\nu), \quad (3.3a) \end{aligned}$$

where Z is the nuclear charge, \mathbf{R}_i is the position vector of the i th lattice point, $\boldsymbol{\tau} = -\boldsymbol{\tau}_2 = \frac{1}{8}a(1,1,1)$ where $\boldsymbol{\tau}_1$ and $\boldsymbol{\tau}_2$ are the positions of the two atoms in the unit cell relative to the lattice point, and N is the number of unit cells in the crystal. N is taken to be a very large number; in this limit none of the quantities sought depend on N .

We write the Fourier transform of (3.3a) as follows:

$$\begin{aligned} \rho_{\text{nuc}}(\mathbf{k}) &= \frac{4}{a^3} \frac{1}{N} \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{R}_i) \left[\sum_{\nu=1}^2 \exp(i\mathbf{k} \cdot \boldsymbol{\tau}_\nu) \right], \quad (3.3b) \end{aligned}$$

where a is the lattice constant, $\frac{1}{4}a^3$ is the volume of a unit cell, and $\frac{1}{4}Na^3$ is the volume of the crystal. The normalization of the Fourier transform of a function is chosen such that the Fourier transform is just the matrix element of the function between normalized plane waves. The plane waves are normalized to unity over the volume of the crystal. The first sum in (3.3b) in the limit of large N becomes zero when \mathbf{k} is not a reciprocal-lattice vector and is equal to N when $\mathbf{k} = \boldsymbol{\kappa}$ where $\boldsymbol{\kappa}$ is a reciprocal-lattice vector. The second sum is just $2 \cos \boldsymbol{\kappa} \cdot \boldsymbol{\tau}$ where $\boldsymbol{\tau} = (\frac{1}{8}a)(1,1,1)$.

Therefore,

$$\begin{aligned} V_{\text{nuc}}^{\text{Coul}}(\boldsymbol{\kappa}) &= 8\pi\rho_{\text{nuc}}(\boldsymbol{\kappa})/\kappa^2 \\ &= 8\pi \times \frac{48}{\kappa^2 a^3} \cos(\boldsymbol{\kappa} \cdot \boldsymbol{\tau}). \quad (3.4) \end{aligned}$$

The charge density due to the 1s core electrons is

$$\rho_{\text{core}}(\mathbf{r}) = 2 \sum_{i=1}^N \sum_{\nu=1}^2 \psi_c^2(\mathbf{r} - \mathbf{R}_i - \boldsymbol{\tau}_\nu). \quad (3.5a)$$

We write the Fourier transform of (3.5a) as follows:

$$\begin{aligned} \rho_{\text{core}}(\boldsymbol{\kappa}) &= \frac{4}{a^3} \frac{1}{N} 2 \sum_{i=1}^N \sum_{\nu=1}^2 \int \psi_c^2(\mathbf{r} - \mathbf{R}_i - \boldsymbol{\tau}_\nu) e^{i\boldsymbol{\kappa} \cdot \mathbf{r}} d^3r \\ &= \frac{64\pi}{Ka^3} \cos \boldsymbol{\kappa} \cdot \boldsymbol{\tau} \int_0^\infty r \psi_c^2(r) \sin kr \, dr \quad (3.5b) \end{aligned}$$

and

$$V_{\text{core}}^{\text{Coul}}(\mathbf{k}) = 8\pi\rho_{\text{core}}(\mathbf{k})/\kappa^2 \\ = \frac{512\pi^2}{a^3\kappa^3} \cos\mathbf{k}\cdot\boldsymbol{\tau} \int_0^\infty r\psi_c^2(r) \sin\kappa r dr. \quad (3.6)$$

ψ_c is taken directly from the Herman-Skillman⁸ calculation of the carbon atom. An improvement in this calculation would be to calculate $\psi_c(r)$ self-consistently by solving the Schrödinger equation in the crystal potential; this is not done in the present calculation.

The third contribution to the direct Coulomb potential is from the valence electrons. In this calculation the valence charge density is evaluated self-consistently. The starting potential is actually taken from the result of many iterations of an earlier version of the present calculation.

We write a valence-electron wave function as

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) - (\phi, \psi_s)\psi_s(\mathbf{r}), \quad (3.7)$$

where ψ_s is the Bloch function made from the atomic ψ_c [see (4.2)]. The average charge density due to such an electron is

$$\rho(\mathbf{r}) = \phi^*(\mathbf{r})\phi(\mathbf{r}) - 2 \operatorname{Re}[(\phi, \psi_s)\phi^*(\mathbf{r})\psi_s(\mathbf{r})] \\ + |(\phi, \psi_s)|^2 \psi_s^*(\mathbf{r})\psi_s(\mathbf{r}). \quad (3.8)$$

The procedure for calculating the valence charge density has been treated in detail in GKI. Each of the three contributions to the valence charge density, plane-wave-plane-wave (A), plane-wave-core (B), and core-core (C), is treated somewhat differently. *A* is never evaluated in real space, whereas *B* and *C* are evaluated in both real and reciprocal space:

$$V_{\text{val}}^{\text{Coul}}(\mathbf{k}) = 8\pi[A(\mathbf{k}) + B(\mathbf{k}) + C(\mathbf{k})]/\kappa^2. \quad (3.9)$$

The exchange potential is handled in the Slater free-electron approximation.⁹ This assumes that the effect of exchange on an electron is to exclude a spherical charge equal to that of the electron and centered at the electron from the charge density due to all the other electrons; that is, the electron "digs a hole" in the electron charge density, such that the "hole" contains one positive charge. The Slater approximation gives an exchange potential

$$V^{\text{exch}}(\mathbf{k}) = -3[3\rho(\mathbf{k})/\pi]^{1/3}. \quad (3.10)$$

There has been a recent spate of research on the question of an exchange potential appropriate to both band-structure and cohesive-energy calculations. Herman *et al.*¹⁰ have argued from a variational principle that the best one-electron wave functions are obtained

⁸ F. Herman and S. Skillman, *Atomic Structure Calculations*, (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

⁹ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

¹⁰ F. Herman, I. B. Ortenburger, and J. P. Van Dyke, *Int. J. Quantum Chem.* (to be published).

from the Gaspar-Kohn-Sham^{11,12} potential ($\frac{2}{3}$ of the Slater exchange potential), but that the one-electron binding energies should be calculated by taking expectation values of the Slater potential between the Gaspar-Kohn-Sham eigenfunctions. Our use of the Slater exchange (made before Herman's proposal) was based on the work of Phillips and Kleinman¹³ who calculated the off-diagonal matrix elements of a screened Hartree-Fock exchange Hamiltonian in Si and found them to be almost identical with matrix elements calculated from the Slater exchange.

These considerations, combined with the fact that the most suitable core functions available, those of Herman and Skillman, were derived using the Slater exchange, led us to use this approximation. However, although this choice simplifies the calculation in many respects, it gives rise to a problem peculiar to this type of study. In determining the valence contribution to the crystal potential it is necessary to subtract half the valence-valence interactions from the one-electron energies. Since the Slater exchange potential is proportional to the total (i.e., core plus valence) electron charge density to the one-third power, and since the core and valence charge densities overlap slightly, it is not possible to divide $V^{\text{exch}}(\mathbf{r})$ into $V_{\text{val}}^{\text{exch}}(\mathbf{r})$ and $V_{\text{core}}^{\text{exch}}(\mathbf{r})$ without approximation. A first approximation one might try would be to assume that

$$\rho_{\text{total}}^{1/3}(\mathbf{r}) \equiv [\rho_{\text{core}}(\mathbf{r}) + \rho_{\text{val}}(\mathbf{r})]^{1/3} = \rho_{\text{core}}^{1/3}(\mathbf{r}) + \rho_{\text{val}}^{1/3}(\mathbf{r}).$$

This approximation would be true if there were no core-valence overlap. Unfortunately there is a small though finite tail of the core charge density which persists to the edge of the next atomic cell and which, when taken to the one-third power, gives a disproportionately large contribution to the core-valence exchange. We estimate that this approximation gives more than twice the core-valence exchange that it should.

This and other considerations led us to another approximate separation:

$$\rho_{\text{total}}^{1/3}(\mathbf{r}) = \{[\rho_{\text{val}}(\mathbf{r}) + \rho_{\text{core}}(\mathbf{r})]^{1/3} - \rho_{\text{val}}^{1/3}(\mathbf{r})\} \\ + \rho_{\text{val}}^{1/3}(\mathbf{r}). \quad (3.11)$$

Herman¹³ and Heine¹⁴ have suggested that this is the separation most in the spirit of Slater's original proposal. The core-valence exchange is taken to be proportional to the term in the curly brackets in Eq. (3.11) while the valence-valence exchange is proportional to the cube root of the valence charge density:

$$V_{\text{core}}^{\text{exch}}(\mathbf{r}) = -3(3/\pi)^{1/3}\{[\rho_{\text{val}}(\mathbf{r}) + \rho_{\text{core}}(\mathbf{r})]^{1/3} \\ - \rho_{\text{val}}^{1/3}(\mathbf{r})\}. \quad (3.12)$$

Writing this expression for the core-valence exchange

¹¹ R. Gaspar, *Acta Phys. Acad. Sci. Hung.* **3**, 263 (1954).

¹² W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

¹³ J. C. Phillips and L. Kleinman, *Phys. Rev.* **129**, 2098 (1962).

¹⁴ F. Quelle, Lincoln Laboratory Technical Report No. 295, 1963 (unpublished).

does not quite end the problem. $\rho_{\text{core}}(\mathbf{r})$ is easily obtained from (3.5a). It is just the sum of spherical charge densities, approximately nonoverlapping, centered on each atomic site. This is certainly not true for the valence charge density for a number of reasons. First, if the valence charge density were spherical, all Fourier transforms of the charge density, having a $\mathbf{\kappa}$ for which $\cos \mathbf{\kappa} \cdot \boldsymbol{\tau}$ is zero, would vanish. This is not the case; $\rho_{\text{val}}[(2\pi/a)(2,2,2)]$ is quite large. Second, the valence charge is finite over an atomic cell which is definitely nonspherical in shape. The distance from an atomic site to the atomic cell wall varies with direction by a factor of 2. These objections, however, are not severe when we wish to use $\rho_{\text{val}}(\mathbf{r})$ in Eq. (3.12); that is, a spherical average of the valence charge density does not materially affect the results of (3.12). There are three reasons for this. First, the valence charge density is approximately spherical in the neighborhood of the nucleus. Second, small mistakes in calculating $\rho_{\text{val}}(\mathbf{r})$ do not much affect the quantity in brackets; the cube root is a great leveler. Third, since the quantity in the curly brackets is near zero at even the closest atomic cell wall, the nonsphericity of the atomic cell has negligible effect.

The valence-valence exchange potential as a function of position is

$$V_{\text{val}}^{\text{exch}}(\mathbf{r}) = -3[3\rho_{\text{val}}(\mathbf{r})/\pi]^{1/3}. \quad (3.13)$$

This seemingly simple expression provides some of the most difficult work in this calculation. We have written the valence charge density as a sum of three terms, namely, $A(\mathbf{r})$, $B(\mathbf{r})$, and $C(\mathbf{r})$. $A(\mathbf{r})$, the result of plane-wave-plane-wave interference, is a relatively smooth and spread out function of \mathbf{r} . $B(\mathbf{r})$ and $C(\mathbf{r})$ are relatively spherical and localized functions of \mathbf{r} , i.e., they may be treated in the same manner as $\rho_{\text{core}}(\mathbf{r})$. Therefore, we have made another separation to more readily facilitate taking the cube root, our final goal being the Fourier transform of this cube root. This separation is

$$= \{[A(\mathbf{r})+B(\mathbf{r})+C(\mathbf{r})]^{1/3} - A^{1/3}(\mathbf{r})\} + A^{1/3}(\mathbf{r}). \quad (3.14)$$

The term in curly brackets is treated in the same way as the curly-bracketed term in (3.11), i.e., the smooth part of the valence charge is approximated by its spherical average. The charge density of $B(\mathbf{r})+C(\mathbf{r})$ we call the valence "wobble." The exchange potential due to this wobble is

$$V_{\text{val}}^{\text{wobble}}{}^{\text{exch}}(\mathbf{r}) = -3(3/\pi)^{1/3} \times \{[A(\mathbf{r})+B(\mathbf{r})+C(\mathbf{r})]^{1/3} - A^{1/3}(\mathbf{r})\}. \quad (3.13')$$

The Fourier transform of this spherical potential is readily taken.

The remaining part of the valence exchange potential is treated quite differently. The Fourier transform of $A^{1/3}(\mathbf{r})$ is calculated. Two different methods have been used to calculate this quantity. Kleinman and Phillips¹¹ used the first two terms of a Taylor series expansion of

the cube root of the charge density as follows:

$$\begin{aligned} A^{1/3}(\mathbf{r}) &= [A(\mathbf{\kappa}=0) + \sum_{\mathbf{\kappa} \neq 0} A(\mathbf{\kappa})e^{i\mathbf{\kappa} \cdot \boldsymbol{\tau}}]^{1/3} \\ &= A^{1/3}(\mathbf{\kappa}=0) \left(1 + \frac{1}{3} \sum_{\mathbf{\kappa} \neq 0} \frac{A(\mathbf{\kappa})}{A(\mathbf{\kappa}=0)} e^{i\mathbf{\kappa} \cdot \boldsymbol{\tau}} \right). \end{aligned}$$

Quelle,¹⁴ who also used this procedure in his Si calculation, questioned its validity. Herman⁵ has claimed that the power series method, as used by Kleinman and Phillips and by Quelle, is inadequate. Herman instead evaluated the valence charge density at a large number of points in the unit cell and used a least-squares fit to determine the exchange potential. Herman's procedure is rather time consuming. We decided to improve the power-series-expansion method by taking one more term in the expansion. Our expansion is

$$\begin{aligned} A^{1/3}(\mathbf{r}) &= A^{1/3}(\mathbf{\kappa}=0) \left(1 + \frac{1}{3} \sum_{\mathbf{\kappa} \neq 0} \frac{A(\mathbf{\kappa})}{A(\mathbf{\kappa}=0)} e^{i\mathbf{\kappa} \cdot \boldsymbol{\tau}} \right. \\ &\quad \left. - \frac{2}{9A^2(\mathbf{\kappa}=0)} \sum_{\mathbf{\kappa}_i, \mathbf{\kappa}_j \neq 0} A(\mathbf{\kappa}_i)A(\mathbf{\kappa}_j) e^{i(\mathbf{\kappa}_i + \mathbf{\kappa}_j) \cdot \boldsymbol{\tau}} \right). \quad (3.15) \end{aligned}$$

Herman estimated that the two-term power-series expansion might be in error by as much as 20%.¹⁵ We would expect that the three-term expansion we use is considerably better than that with an error of about 4%. We write the Fourier transform of the exchange potential due to the smooth charge density A in this approximation as

$$\begin{aligned} V_{\text{val}}^{\text{sm}}{}^{\text{exch}}(\mathbf{\kappa}) &= -3[3/A^2(0)\pi]^{1/3} \left(\frac{1}{3}A(\mathbf{\kappa}) - \frac{2}{9A(\mathbf{\kappa}=0)} \right. \\ &\quad \left. \times A(\mathbf{\kappa}_i)A(\mathbf{\kappa}_j) \sum_{\mathbf{\kappa}_i, \mathbf{\kappa}_j \neq 0} \delta(\mathbf{\kappa}_i + \mathbf{\kappa}_j - \mathbf{\kappa}) \right). \quad (3.13'') \end{aligned}$$

We now write in reciprocal space the one-electron potential "seen" by a valence electron

$$V = (3.4) + (3.6) + (3.9) + (3.12'') + (3.13''), \quad (3.16)$$

where the numbers in parentheses refer to the right-hand sides of the corresponding equations.

The Fourier transform core and valence potential are listed in Tables I and II, respectively.

The variation with the (1,1,1) component of the crystal potential is listed in Table III.

IV. 1s ENERGY

The Schrödinger equation for the valence electron in the OPW representation is

$$H[\phi - (\phi, \psi_s)\psi_s] = E[\phi - (\phi, \psi_s)\psi_s], \quad (4.1a)$$

¹⁵ F. Herman (private communication).

TABLE I. The Fourier coefficients of the ionic potential. For $a = a_0 = 6.7238$ Bohr units. The structure factor is included.

| $\mathbf{h} = (a/2\pi)\boldsymbol{\kappa}$ | Nuclear Coulomb | Core Coulomb | Core exchange | Total ionic potential |
|--|-----------------|--------------|---------------|-----------------------|
| (1,1,1) | 1.071 | 0.343 | 0.027 | 0.755 |
| (2,2,0) | 0.568 | -0.170 | 0.033 | 0.431 |
| (1,1,3) | 0.292 | -0.084 | 0.022 | 0.230 |
| (2,2,2) | 0.0 | 0.0 | 0.0 | 0 |
| (0,0,4) | 0.284 | -0.077 | 0.027 | 0.234 |
| (3,3,1) | -0.69 | 0.044 | 0.018 | -0.142 |
| (2,2,4) | -0.189 | 0.046 | -0.022 | -0.165 |
| (3,3,3) | -0.119 | 0.028 | -0.014 | -0.105 |
| (1,1,5) | -0.119 | 0.028 | -0.014 | -0.105 |
| (4,4,0) | -0.142 | 0.032 | -0.018 | -0.128 |
| (5,3,1) | -0.091 | 0.020 | -0.012 | -0.083 |
| (4,4,2) | 0.0 | 0 | 0 | 0 |
| (6,2,0) | -0.114 | 0.023 | -0.015 | -0.105 |
| (3,3,5) | 0.075 | -0.015 | 0.010 | 0.070 |
| (2,2,6) | 0.0 | 0 | 0 | 0 |
| (4,4,4) | 0.095 | -0.018 | 0.012 | 0.089 |
| (5,5,1) | 0.063 | -0.012 | 0.008 | 0.059 |
| (1,1,7) | -0.063 | 0.012 | -0.008 | -0.059 |
| (6,4,2) | 0.081 | -0.014 | 0.010 | 0.077 |
| (5,5,3) | 0.054 | -0.009 | 0.006 | 0.051 |

where ψ_s is the $1s$ eigenstate of the valence Hamiltonian H . This enables us to rewrite (4.1a) as follows:

$$(H - E) = (E_s - E)(\phi, \psi_s)\psi_s, \quad (4.1b)$$

where E_s is the eigenvalue of H associated with ψ_s . Since (ϕ, ψ_s) is of the order of a few tenths, the importance of E_s to the determination of the valence eigenvalues is self-evident.

The $1s$ energy is important in another way. The electrostatic terms contributing to TCE, as well as those of TCE_e which are due to B and C of the valence charge density, are very similar to those entering into the calculation of the $1s$ energy. One must remember that the electron entering most of these calculations is not the actual $1s$ core electron, but, rather, the corelike part of

TABLE II. The Fourier coefficients of the self-consistent valence potential. For $a = a_0 = 6.7238$ Bohr units.

| $\mathbf{h} = a/2\pi$ | Valence exchange potential | Valence Coulomb potential | Total valence potential |
|-----------------------|----------------------------|---------------------------|-------------------------|
| (1,1,1) | 0.122 | -0.255 | -0.134 |
| (2,2,0) | 0.035 | -0.021 | 0.014 |
| (1,1,3) | 0.001 | 0.002 | 0.003 |
| (2,2,2) | -0.018 | 0.007 | -0.011 |
| (0,0,4) | -0.013 | 0.005 | -0.008 |
| (3,3,1) | 0.004 | -0.001 | 0.003 |
| (2,2,4) | 0.017 | -0.003 | 0.014 |
| (3,3,3) | 0.012 | -0.002 | 0.010 |
| (1,1,5) | 0.004 | -0.002 | 0.002 |
| (4,4,0) | 0.006 | -0.001 | 0.005 |
| (5,3,1) | 0.007 | -0.000 | 0.006 |
| (4,4,2) | -0.001 | -0.000 | -0.001 |
| (6,2,0) | 0.005 | -0.000 | 0.005 |
| (3,3,5) | 0.002 | -0.000 | 0.002 |
| (2,2,6) | 0.001 | 0.000 | 0.001 |
| (4,4,4) | -0.001 | -0.000 | -0.002 |
| (5,5,1) | 0.001 | -0.000 | 0.000 |
| (1,1,7) | 0.006 | 0.000 | 0.007 |
| (6,4,2) | 0.000 | -0.000 | -0.000 |
| (5,5,3) | 0.005 | -0.000 | 0.005 |

TABLE III. The variation with lattice constant of the (1,1,1) Fourier coefficient of the crystal potential.

| a/a_0 | 0.98 | 1.00 | 1.02 | 1.04 |
|------------------------|--------|--------|--------|--------|
| Nuclear Coulomb | 1.093 | 1.071 | 1.050 | 1.030 |
| Core Coulomb | -0.349 | -0.343 | -0.336 | -0.330 |
| Core exchange | 0.028 | 0.027 | 0.025 | 0.023 |
| Total core and nuclear | 0.772 | 0.755 | 0.739 | 0.723 |
| Valence Coulomb | -0.254 | -0.255 | -0.257 | -0.261 |
| Valence exchange | 0.120 | 0.122 | 0.123 | 0.126 |
| Total valence | -0.133 | -0.134 | -0.134 | -0.135 |
| Total crystal | 0.639 | 0.622 | 0.605 | 0.588 |

the OPW valence wave function. In practice the wave function of the $1s$ core electron and the wave function of the valence Hamiltonian are numerically almost identical.¹⁶

The problem which has caused the most confusion in the calculation of this energy is the determination of the Coulomb potential as a function of position. For the smooth part (i.e., the plane-wave part) of the valence-electrons wave function it is sufficient to determine the Fourier transforms of the Coulomb potential, since the high Fourier transforms (i.e., those for large $\boldsymbol{\kappa}$) contribute only slightly to the valence-electrons's energy. However, the high Fourier transforms of the potential contribute heavily to the energy of the more localized core functions as well as the corelike part of the valence wave function. The number of Fourier transforms of the core and nuclear potential required to make the core energy coverage is prohibitively large.

Since the core electrons on neighboring sites have practically no overlap, we assume that the Bloch core state of wave vector \mathbf{k} may be written in the tight-binding approximation as

$$\psi_s^{\mathbf{k}}(\mathbf{r}) = \frac{1}{(2N)^{1/2}} \sum_{n=1}^2 \sum_{\nu=1}^2 \psi_c(\mathbf{r} - \mathbf{R}_n - \boldsymbol{\tau}_\nu) e^{i\mathbf{k} \cdot (\mathbf{R}_n + \boldsymbol{\tau}_\nu)}, \quad (4.2)$$

where ψ_c is an atomic-type wave function. In the preceding section we divide the Coulomb potential into three parts, $V_{\text{nuc}}^{\text{Coul}}$, $V_{\text{core}}^{\text{Coul}}$, and $V_{\text{val}}^{\text{Coul}}$. This is the most useful division for evaluating $V^{\text{Coul}}(\mathbf{k})$. In order to obtain $V^{\text{Coul}}(\mathbf{r})$ it is necessary to divide the potential differently. It is very difficult to obtain $V_{\text{val}}^{\text{Coul}}(\mathbf{r})$; and since the Fourier series representing the valence potential converges much more quickly than that of the core and nuclear potentials, we evaluate the Coulomb contribution of the smooth part of the valence charge density to the core energy as

$$\langle \psi_s | V_{\text{val sm}}^{\text{Coul}} | \psi_s \rangle = \sum \rho_{1s}(\boldsymbol{\kappa}) V_{\text{val sm}}^{\text{Coul}}(\boldsymbol{\kappa}), \quad (4.3)$$

where $\rho_{1s}(\boldsymbol{\kappa})$ is as defined in (3.5b) and the sum in (4.3) is over the nonzero reciprocal-lattice vectors. Since the core electrons do not overlap, the energy of the Bloch state $\psi_s(\mathbf{r})$ in the crystal is the same as that of the atomic-type wave function $\psi_c(\mathbf{r} - \mathbf{R}_i - \boldsymbol{\tau}_\nu)$ in the i, ν

¹⁶ F. Herman (private communication).

atomic cell. It is, therefore, necessary to distinguish the core plus nuclear potential caused by charge within the i,ν atomic cell from that created by charge lying outside the i,ν atomic cell.

The potential due to the external core plus nuclear charge together with the $\kappa=0$ component of the valence charge (including the internal valence charge) we call the Madelung potential $M(\mathbf{r})$. The external core plus nuclear potential is the same as that due to $4+$ ions at each atomic site in a diamond lattice with a uniform compensating background of negative charge. E_m , the energy per unit charge of $4+$ ions in a diamond lattice, has been calculated by Kleinman¹⁷ using the formula given by Fuchs¹⁸ derived by the Ewald sum technique. We have recalculated this energy to higher accuracy:

$$E_m = -21.5472/a. \quad (4.4)$$

The Madelung potential at the i,ν atomic site is just twice E_m , and the potential seen by an electron at the lattice site is

$$\begin{aligned} M(\mathbf{R}_i + \boldsymbol{\tau}_\nu) &= -2E_m \\ &= 43.0944/a. \end{aligned} \quad (4.5)$$

The Madelung potential seen by an electron has a maximum at the atomic site. Since the core function is not completely concentrated at the atomic site, we must calculate the variation in the Madelung potential in the vicinity of the atomic site. Remembering that in the units we have adopted Poisson's equation is $\nabla^2 V = 8\pi\rho$, we may write the potential seen by an electron due to the zeroth Fourier component of valence charge, by definition the only charge in the vicinity of the atomic site which contributes to the Madelung potential, as

$$\Delta M(\mathbf{r}) = -\alpha r^2, \quad (4.6)$$

where

$$\alpha = \frac{4}{3}\pi\rho_{\text{val}}(\kappa=0) = \frac{4}{3}\pi \times 4 \times \frac{8}{a^3} = \frac{128\pi}{3a^3},$$

where r is again measured with respect to the i,ν nucleus. From potential theory we know that the spherical average of the potential due to point ions outside the sphere is equal to the potential at the center of the sphere. Thus $M(\mathbf{R}_i + \boldsymbol{\tau} + \mathbf{r}) = -2E_m - \alpha r^2$ is an exact formula for the spherical average (which is all we need for the expectation value of the $1s$ energy) of the Madelung potential about an atomic site.

The Coulomb potential due to the total ionic charge within the i,ν cell (nuclear plus core) is

$$\begin{aligned} V_{\text{ion}}^{\text{Coul}}(r) &= -\frac{12}{r} + \frac{2}{r} \int_0^r 4\pi r'^2 \rho_{\text{core}}(r') dr' \\ &\quad + 2 \int_r^\infty 4\pi r' \rho_{\text{core}}(r') dr', \end{aligned} \quad (4.7)$$

where $\rho_{\text{core}}(r)$ is $2\psi_c^2(r)$.

The remaining Coulomb contribution is due to the orthogonalization parts of the valence charge density. The procedure used in calculating the Coulomb contribution of the core energy of the smooth part of the valence charge density is too slowly convergent for use in calculating the corresponding contribution of the orthogonalization terms $B(\mathbf{r})$ and $C(\mathbf{r})$. In order to obtain satisfactory convergence we must consider orthogonalization terms as functions of \mathbf{r} rather than as functions of $\boldsymbol{\kappa}$. When we do this, we distinguish that part of the potential due to orthogonalization charge external to the i,ν cell from that due to the internal orthogonalization charge. Pick and Sarma¹⁹ have shown that one major effect of the orthogonalization terms is to extract a quantity of valence charge ϵ from the core region, where ϵ is just the zeroth Fourier transform of $B(\mathbf{r}) + C(\mathbf{r})$, which has the same absolute value as the zeroth Fourier Transform of $C(r)$ alone. When we discuss A , B , and C in this section, we implicitly assume that we have summed the contributions from all the electrons in the Brillouin Zone, four per ion (see GKI), in advance. The potential due to the external orthogonalization charge is just a Madelung-like term due to a positive charge ϵ situated on each atomic cell. The combined Madelung and external orthogonalization contribution to the core energy is just $\frac{1}{4}(4+\epsilon)$ times the Madelung energy alone. The internal orthogonalization charge gives rise to the Coulomb potential

$$\begin{aligned} V_{\text{ortho}}^{\text{Coul}}(r) &= (2/r) \int_0^r 4\pi r'^2 \rho_{\text{ortho}}(r') dr' \\ &\quad + 2 \int_r^\infty 4\pi r' \rho_{\text{ortho}}(r') dr'. \end{aligned} \quad (4.8)$$

A discussion of $\rho_{\text{ortho}} [= B(r) + C(r)]$ appears in GKI. In practice (4.7) and (4.8) are evaluated together. In principle the space-averaged value of $V_{\text{ortho}}^{\text{Coul}}(\mathbf{r})$ should be subtracted from (4.8) (to give no $k+0$ Fourier transform), but the difference is numerically insignificant.

We now write the total Coulomb contribution to the $1s$ energy as

$$\begin{aligned} E_s^{\text{Coul}} &= \langle |\psi_c| (4,3+) [(4.5) + (4.6)] \frac{1}{4}(4+\epsilon) \\ &\quad + (4.7) + (4.8) |\psi_c \rangle, \end{aligned} \quad (4.9)$$

where the numbers in parentheses represent symbolically the right-hand sides of the corresponding equations.

The contribution of the exchange potential to E_s , given the exchange potential used in the one-electron valence Hamiltonian, presents no great problem. The exchange contribution to E_s due to the smooth part of the valence charge density is calculated in the same

¹⁷ L. Kleinman, Phys. Rev. **130**, 2283 (1963).

¹⁸ K. Fuchs, Proc. Roy. Soc. (London) **151**, 585 (1935).

¹⁹ R. Pick and G. Sarma, Phys. Rev. **135**, A1363 (1964).

TABLE IV. Contributions to the total crystal energy in Ry/atom. a_0 is taken to be 6.7238 Bohr units.

| a/a_0 | 0.98 | 1.00 | 1.02 | 1.04 | 1.06 |
|---------------------------------|----------|----------|----------|----------|----------|
| Weighted one-electron energy | - 0.2511 | - 0.4517 | - 0.6439 | - 0.8214 | - 0.9936 |
| $\frac{1}{2}E_{\text{val-val}}$ | 2.3672 | 2.3015 | 2.2410 | 2.1808 | 2.1255 |
| Point ion interaction | -13.0801 | -12.8185 | -12.5671 | -12.3255 | -12.0929 |
| GB Bruckner correlation | - 0.3211 | - 0.3161 | - 0.3112 | - 0.3063 | - 0.3015 |
| NBP correlation | - 0.4286 | - 0.4261 | - 0.4236 | - 0.4212 | - 0.4188 |
| Total crystal energy (GMB) | -11.2851 | -11.2848 | -11.2812 | -11.2725 | -11.2626 |
| Total crystal energy (NBP) | -11.3925 | -11.3948 | -11.3936 | -11.3873 | -11.3798 |

fashion as the valence Coulomb contribution in (4.3),

$$\langle \psi_s | V_{\text{val}}^{\text{exch}} | \psi_s \rangle = \sum_{\kappa} \rho_{1s}(\mathbf{r}) V_{\text{val}}^{\text{exch}}(\mathbf{r}), \quad (4.10)$$

where the sum is over all κ (including $\kappa=0$).

The core exchange potential is taken from (3.12), and the exchange potential due to the orthogonalization charge density is taken from (3.13').

The remaining contribution to E_s is the kinetic energy. Since we are assuming rigid cores, the kinetic energy does not change from the atom. Herman and Skillman list both the atomic core eigenvalue and the self-consistent potential used in their calculation, and the kinetic-energy contribution to E_s is just

$$\langle \psi_s | T | \psi_s \rangle = E_{\text{H-S}}^{\text{C}1s} - \langle \psi_c | V_{\text{H-S}} | \psi_c \rangle. \quad (4.11)$$

We now write all the contributions to E_s .

$$E_s = (4.9) + (4.10) + (4.11) + \langle \psi_s | (3.12) + (3.13b) | \psi_s \rangle, \quad (4.12)$$

where the numbers in parentheses refer symbolically to the right-hand sides of the corresponding equations.

V. RESULTS AND CONCLUSIONS

We list the contributions to the total crystal energy in terms of Ry/atom.

A. Weighted One-Electron Energy

This is the sum of the one-electron energies of four electrons, weighted as described in GKI. Included in this energy are the $\kappa=0$ exchange potentials, both

valence-valence and core valence as well as the $\kappa=0$ neutral ion potential defined in Sec. V C which follows. About 133 OPW's are used. The matrices range in size from 8×8 (for Γ) to 40×40 (at Σ).

B. Minus One-Half the Valence-Valence Contribution

The way in which the doubly counted valence-valence interactions are calculated deserves some mention here. The valence-valence interaction energy per atom is

$$E_{\text{val-val}} = \frac{1}{8} a^3 \langle \rho_{\text{val}} V_{\text{val}} \rangle, \quad (5.1a)$$

where $(a^3/8)$ is the volume of the atomic cell and ρ_{val} is the charge density of all the valence electrons. The potential includes both direct Coulomb and exchange. In order to calculate $\langle \rho_{\text{val}} V_{\text{val}} \rangle$ to sufficient accuracy it is necessary to split the calculation into three parts

$$E_{\text{val-val}} = \left\{ \sum_{\kappa} [A(\mathbf{r}) V_{\text{val}}(\mathbf{r}) + (B(\mathbf{r}) + C(\mathbf{r})) V_{\text{val sm}}(\mathbf{r})] + \int [B(r) + C(r)] V_{\text{val wiggle}}(r) d^3r \right\}. \quad (5.1b)$$

A , B , and C are in units of electrons per atom. $V_{\text{val sm}}$ is due to A , the smooth part of the valence charge density, and $V_{\text{val wiggle}}$ is due to $B+C$. As in Sec. II, the reason for rewriting (5.1a) into (5.1b) is to avoid the slow convergence of the Fourier transform of squared wiggle charge densities. $V_{\text{val wiggle}}^{\text{Coul}}$ should be taken with respect to its average value, but the difference is numerically insignificant. And also as in Sec. IV, we

TABLE V. Lattice constant, bulk modulus, and binding energy of diamond with a parabolic energy approximation.

| Points sampled | | 0.98, 1.00 1.02 | 1.00, 1.02 1.04 | Expt |
|--|-----------|--|--|------------------------------------|
| Equilibrium lattice spacing (in units of a/a_0) | GB NBP | 0.988 1.003 | 0.996 1.005 | 1.0013 ^a |
| Bulk modulus (in dyn/cm) | GB NBP | 3.04×10^{12} 3.16×10^{12} | 4.69×10^{12} 4.69×10^{12} | 4.42×10^{12} ^b |
| Minimum total crystal energy (in Ry) | GB NBP | -11.288 -11.395 | -11.285 -11.395 | -11.42 ^c |

^a J. Thewlis and A. R. Davey, Phil. Mag. **1**, 409 (1956). The value of a_0 in this reference is for $T=123^\circ\text{K}$. The value originally used in the calculation (i.e., the reason why a_0/a_0 experimentally is not = 1) was taken from L. Kleinmann and J. C. Phillips, Phys. Rev. **116**, 880 (1959).

^b H. J. McSkimin and W. L. Bond, Phys. Rev. **105**, 116 (1957).

^c D. D. Wagman *et al.*, *Selected Values of Chemical Thermodynamic Properties* (National Bureau of Standards Tech. Note No. 270-3, U. S. Government Printing Office, Washington, D. C., 1968).

must include both the Coulomb potential due to the wiggle in the i,ν atomic cell and that due to the wiggles outside the i,ν cell. The potential due to the exterior wiggles is just a Madelung-like term, whereas the potential due to the interior wiggle is just an atomiclike term.

C. Point-Ion Interaction

This is the energy of a diamond lattice of 4+ point ions in Ry/atom. This contribution is

$$= -4 \times 21.5472/a. \tag{5.2}$$

Although the ions are not point particles, their interaction energy is the same as for point charges, since the ions are nonoverlapping spheres. However, in calculating the Madelung energies (see Sec. IV) the result is not finite unless one includes the effect of the constant background of negative charge, i.e., the $\kappa=0$ Fourier transform of the valence charge density.

The resulting valence-core interaction is different for point ions than for the real 4+ C ions, and this interaction has been discussed in Sec. IV in connection with (4.6). This core valence energy per atomic site is $-2\langle\psi_c|\alpha r^2|\psi_c\rangle$, where α is that which appears in (4.6). In line with our discussion in GKI we have decided to include this term with the other core valence terms, i.e., $-1/2\langle\psi_c|\alpha r^2|\psi_c\rangle$ appears on the diagonal of the Hamiltonian matrix of each valence state, and, therefore, does not appear as a separate contribution here.

D. Correlation Energy

The Gell-Mann-Brueckner (BG)²⁰ formula for correlation is supposed to apply for $r_s < 1$. The Nozières-Bohm-Pines (NBP)²¹ formula is applicable for $r_s > 2$. These are free-electron formulas, but at present there is no other way to estimate the correlation energy. There is no formula for $1 < r_s < 2$. r_s for diamond is 1.3. Therefore, we write both formulas in Ry/atom:

$$\text{GB} = 4 \times (0.0622 \ln r_s - 0.096), \tag{5.3}$$

$$\text{NBP} = 4 \times (0.0311 \ln r_s - 0.115). \tag{5.4}$$

Table IV lists these contributions and their sums for several values of the lattice constant a .

The equilibrium lattice constant, bulk modulus, and minimum total crystal energy are determined from the results listed in Table IV. We do this by fitting three

TABLE VI. Selected orthogonalization coefficients for $a/a_0=0.98, 1.00, 1.02, 1.04$ as a function of $h^2=(a/2\pi)^2k^2$.

| $16h^2$ | 0.98 | 1.00 | 1.02 | 1.04 |
|---------|--------|--------|--------|--------|
| 0 | 0.1836 | 0.1781 | 0.1729 | 0.1679 |
| 4 | 0.1807 | 0.1754 | 0.1704 | 0.1656 |
| 8 | 0.1779 | 0.1728 | 0.1680 | 0.1633 |
| 12 | 0.1752 | 0.1703 | 0.1656 | 0.1616 |
| 16 | 0.1725 | 0.1677 | 0.1632 | 0.1589 |
| 20 | 0.1699 | 0.1653 | 0.1609 | 0.1567 |
| 48 | 0.1532 | 0.1496 | 0.1462 | 0.1433 |
| 192 | 0.0975 | 0.0966 | 0.0957 | 0.0948 |
| 416 | 0.0573 | 0.0576 | 0.0577 | 0.0579 |

points to a parabola. We have used two sets of points; 0.98, 1.00, and 1.02 constitute one set, while 1.00, 1.02, and 1.04 constitute the other. These results are listed in Table V. Table VI shows some selected orthogonalization coefficients.

The results should not be interpreted as favoring the Nozières-Bohm-Pines correlation. It is not clear what is the convergence error in the electronic contribution due to the finite basis set (~ 133 POW's) in this calculation. The disconcerting decrease in the bulk modulus as a function of lattice constant may well be due to a lack of convergence, as it is reasonable to expect that in the denser crystal the electronic wave function will converge more rapidly than in the expanded crystal. There is also the possibility that the decrease in the bulk modulus is due to a neglect of the overlap of 1s electrons on neighboring atoms.

Future calculations should consider the recent alternative proposals to the Slater exchange, such as those offered by Gaspar,¹¹ Kohn and Sham,¹² and by Herman.¹⁰ In addition many of the difficulties arising from the OPW method might be better handled by going to one of the generalizations of the method.²²

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²⁰ M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1952).

²¹ P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).

²² See, e.g., F. A. Butler, F. K. Bloom, Jr., and E. Brown, Phys. Rev. **180**, 744 (1969).