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First-principles linear combination of atomic orbitals method for the cohesive and structural properties of solids: Application to diamond

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We present a new method for the *ab initio* calculation of the cohesive and structural properties of solids. The method is based upon a linear combination of atomiclike orbitals (LCAO). Thus it possesses the physical appeal of traditional LCAO approaches. The method is a "first principles" one in the sense that no adjustable parameters enter the calculation. The required overlap integrals are calculated directly in real space. The one-electron potentials are derived from atomic properties and correspond to "*ab initio*" pseudopotentials. Another aspect of the method is that it does not involve a fully-self-consistent-field solution of the Schrödinger equation. Rather, the total energy of the system is obtained by using a noniterative approach based explicitly on the variational principle in the density-functional formalism. The method is applied to an archtypical covalent system: the diamond crystal. Several ground-state properties—including the cohesive energy, lattice constant, the bulk modulus, and the derivative of the bulk modulus with pressure—are computed. The computed lattice constant and bulk modulus are within 1–2 % of the experimental values and the computed cohesive energy is within 10% of the experimental value. Also, we present a frozen-phonon calculation for the optical phonons at the Brillouin-zone center and obtain agreement to within 1% of the experimental value.

I. INTRODUCTION

If one were to ask what the most significant unsolved problem in solid-state physics is, several issues could be raised. Presumably a list of these issues would include the problem of determining the atomic or structural coordinates for nonperiodic systems or partially periodic system. The structure is not known or poorly known for a larger number of such systems. Examples of these include solid-solid interfaces, solid surfaces, extended or point defects in solids, amorphous materials, etc. Without knowledge of the structure, our understanding of these systems is at best limited. Another related issue, perhaps more global in nature, is the calculation of the energetics of solid-state systems. Obviously, if one knew the energy as a function of atomic positions for solid-state systems, one could calculate the preferred crystal structure, the mechanical properties, the phonon spectra, etc. Moreover, one would like to know the total energy of the system itself in order to compute the cohesive energy or the heat of formation for compound solids. This latter issue has been raised as "the problem" of solid-state physics in the sense that given a solution, one could predict solid-state properties of any material, real or hypothetical, from theory.

With respect to these two issues, a major effort in a search for a solution has centered on empirical methods. These methods include such chemical coordinates as atomic size, orbital radii, electronegativity, etc.[1] These approaches have great strengths in that they can be widely applied without the need of a large computational framework. For example, often it is possible using atomic size considerations to rule out hypothetical crystal structures or to rationalize existing structures. Contemporary examples of these methods include the Phillips—Van Vechten dielectric theory of semiconductors,[2] the Bloch-Simons orbital radii,[3] the metallurgical scheme of Miedema,[4] etc. While these schemes are quite valuable, often they reside in a completely empirical framework and it is not possible to attach a "definitive" physical interpretation of their significance.[5]

It is in this sense that the recent use of "*ab initio*" methods to compute the structural and cohesive properties of elemental solids and simple compounds is so promising.[6–16] It is now possible to compute the following with good accuracy (e.g., to within a few percent): the cohesive energy, the crystal structure, the lattice parameters, the mechanical properties, and the phonon spectrum. However, many complex solids and most compound solids reside outside of the "state of the art" with respect to energetics. Moreover, the question of examining nonperiodic systems has been only touched upon.[17] In this paper we present a method which should be applicable to some of these questions and move our capabilities for calculating energetics beyond the current state of the art.

The chief thrust of our effort is to avoid complications associated with the solution of the single-particle Schrödinger's equation rather than improve upon existing many-body formulations for exchange-correlation effects. In most respects for the ground-state properties, a practical method for the solution of Schrödinger's equation resides at the center of difficulty. In our method we shall follow the approach of a number of workers and use a

Gaussian orbital description.[11,18–22] Gaussian bases can be very efficient, especially in conjunction with pseudopotentials. In addition to the physical appeal of a local basis, once the potential is expanded in Gaussians all the needed matrix elements can be computed in an analytical fashion, which leads to enormous gain in computation speed. However, the price paid for the gain is the necessity of fitting the potential in terms of a Gaussian expansion. For self-consistent methods, if an equation-of-state curve is to be calculated, a fully self-consistent band structure must be determined at each volume point in question. Not only is this procedure computationally time consuming, it requires a full reexpansion of the potential in terms of Gaussians for each volume and for each iteration within that volume parameter. To date, the fitting of potentials with Gaussians (which is a multidimensional parameter-space nonlinear least-squares fitting problem) remains one of the difficult features of the Gaussian basis approach. Small fitting errors in percentage in the potential can lead to large errors in the cohesive and structural properties. In our approach we eliminate the need for the full self-consistency iteration cycle by making use explicitly of the variational principle in the density-functional formalism.[23] The density-functional formalism states that the ground-state energy E_{total} of the system for a given set of nuclear potentials is a unique functional of the charge density $\rho(\vec{r})$, and $E_{\text{total}}[\rho]$ is a minimum for the ground-state charge-density function. We demonstrate that one can obtain a highly accurate E_{total} with a reasonable $\rho(\vec{r})$, provided that the correct functional $E_{\text{total}}[\rho]$ is employed. For the case of diamond, $\rho(\vec{r})$ is taken to be the first iteration output charge density.

In developing our method we sought a system which would test the approximations of our method, yet would not be unnecessarily complex. We have chosen the diamond crystal for our prototypical system. The system is sufficiently complex that the pseudopotential requires a large *s-p* nonlocal component. Also, the wave functions are sufficiently localized, and the charge density is so highly directional, that a plane-wave expansion will not be as efficient as a Gaussian expansion. Thus the localized basis with a highly nonlocal potential will be tested in a significant fashion. However, the system does not contain strong *d*-wave components, and we will not have to be concerned with this additional complexity.

With respect to having an experimental and theoretical data base for comparison purposes, the diamond crystal is a good choice. A number of band structures exist and recent state-of-the-art calculations exist for the total energy of the diamond crystal.[9,10,24] Experimental data exist for most ground-state and optical properties of diamond. On the basis of this existing data, the method appears very promising. Our calculated cohesive energy for diamond is within 4% of the state-of-the-art theoretical calculations and within about 10% of the experimental value. Our calculated lattice constant and bulk modulus are within 1–2% of both calculated and experimental values. We have also performed the first *ab initio* calculation of the optical-phonon frequency for diamond at the Brillouin-zone center; our value is within 1% of the experimental value. The typical deviation of 1–2% from the most recent theories indicates that our method is probably just as accurate; however, the computational effort is reduced by at least an order of magnitude.

We will divide our discussion as follows: In Sec. II the method of calculating the electronic charge density will be discussed. The potential construction and the solution of the Schrödinger equation will be outlined. In Sec. III the method of calculating the total energy of the system will be discussed. In Sec. IV results will be presented for the diamond system with respect to the band structure, equation of state, and phonon spectra. In Sec. V we will present some concluding remarks.

II. ELECTRONIC-CHARGE-DENSITY CALCULATIONS

In this section we describe our method for obtaining an electronic charge density which is then used for calculating the total energy of the system of interest.

A. Construction of the one-electron potential

Traditionally one of the most difficult aspects of any electronic structure discussion for the solid state was the construction of an accurate one-electron potential. Fortunately, over the last several years a number of advances have been made. It has been shown, at least for ground-state properties, that the local-density approximation in the density-functional formalism is very accurate in treating exchange-correlation effects in solids. The advance of *ab initio* pseudopotentials[25–28] has greatly facilitated electronic structure calculations both in terms of accuracy and precision.

From an atomic structure calculation, an ionic pseudopotential may be determined which can be employed for highly accurate solid-state or molecular calculations. The essential feature of these potentials is that no parameters are fit to bulk properties. Our work on diamond employs an ionic pseudopotential which is based on the "Hamann-Schlüter-Chiang" formalism.[27] The potential has been used successfully in the description of graphite and intercalated graphite.[29]

With the ionic pseudopotential fixed, we form a total-input potential V_T with a local-density approximation for exchange and correlation:

$$V_T(\vec{r}) = V_{\text{ion}}(\vec{r}) + V_H(\vec{r}) + \mu_{\text{xc}}[\rho(\vec{r})] \ , \tag{1}$$

where V_{ion} is the ionic component which in the pseudopotential framework may have multiple l components, V_H is the Hartree or electron-electron electrostatic potential from Poisson's equation, and μ_{xc} is the effective exchange-correlation potential, which is a function of the charge density $\rho(\vec{r})$.[30]

As a first step in forming the total-input potential, we constructed a solid-state charge density by superposing atomic charge densities. This step is necessary to handle the effective exchange-correlation potential. Unlike the Hartree or ionic potentials which can be formed by a superposition of atomic potentials, we must first superpose the atomic charge densities and then form an exchange-correlation potential for the solid state. For diamond, we used pseudoatomic sp^3 wave functions for this purpose and expanded the pseudoatomic wave functions in Gaussians. As we shall demonstrate, our results are at worst weakly dependent on the initial charge density used;[31] an atomic s^2p^2 configuration would work equally well. Using four Gaussians we were able to obtain a properly normalized wave function fit to within 1% of the actual wave function. This accuracy was achieved over a range of several angstroms near the radial distribution function maximum. The coefficients for the wave function are given in Table I. With these wave functions, we constructed a charge density in the diamond structure, calculated an exchange-correlation potential, and fit the exchange-correlation potential with Gaussians localized on each site. It should be noted that off-site Gaussians are not required for an accurate description of the exchange-correlation potential from the atomic charge-density superposition.

In Fig. 1 we display a charge-density contour map from the superposed Gaussian wave functions. This density was constructed with a plane-wave expansion via a Fourier transform of the Gaussian wave functions. The plane-wave expansion does not rapidly converge owing to the localized nature of the carbon wave functions. However, since the Fourier transform of a Gaussian is trivial, and since many plane waves can easily be handled for such maps, this is not a serious problem. For reasonable convergence, we took all the reciprocal-lattice vectors whose lengths were less than 12 $(\text{a.u.})^{-1}$. For the known lattice constant of diamond, this corresponds to 2229 plane waves.

One obvious problem with the charge density in Fig. 1 is that it has no bond charge associated with the solid state, i.e., no charge-density local maximum exists along the bonding direction. If one examines the Fourier coefficients of our superposed charge density, the coefficient corresponding to the $(2\pi/a)(2,2,2)$ component vanishes, contrary to x-ray experimental data. This discrepancy is well understood and arises from the absence of any bond charge from a superposition of on-site densities. Thus this zeroth iteration density would not be adequate for the total energy evaluation.

Given the ionic pseudopotential from the Hamann-Schlüter-Chiang scheme,[27] the Hartree potential from the atomic charges, and the exchange-correlation potential from the superposed atomic charges, we can then form the total "crystalline" potential. Owing to the nonlocal or l-dependent nature of the pseudopotential, we may have s, p, d, f, etc. potentials. For carbon only s and p potentials are required, and we may write the total crystalline potential as

$$V_T(\vec{r})=V_L(\vec{r})+P_0^{\dagger}[V_s(\vec{r})-V_L(\vec{r})]P_0\,, \tag{2}$$

where P_0 is a projection operator for s-wave symmetry, V_s is the s component of the potential, and V_L is the local potential, i.e., the p or higher l component of the potential. As the screening potential is local, we may think of V_L as containing all the electron-electron potential terms enumerated in Eq. (1).

In order to expedite the evaluation of various matrix elements, it is necessary for us to expand accurately the potential in terms of on-site Gaussians. We do this by fitting V_L and V_s-V_L separately. V_s-V_L can be difficult to fit, since often its dependence with distance is almost "exponential" in character. We do not use the usual gradient methods for global minimization problems, but rather a Monte Carlo simulated annealing method as outlined by Vanderbilt and Louie.[32] The expansion coefficients are given in Table II for both V_L and V_s-V_L. In Fig. 2 we present the components of the potentials. The total potential can contain errors in fitting which in our approach are formulated as uncertainties in the trial screening potential, $V_{H\text{xc}}[\rho_{\text{in}}]$. As will be discussed in detail in Sec. III, when

TABLE I. Atomic wave functions expanded in Gaussians for an isolated carbon atom. The atomic configuration is for an sp^3 atom. The expansion has the form $rR=r^{l+1}\sum_i a_i \exp(-b_i r^2)/4\pi$. Normalization is such that $4\pi\int_0^\infty (rR)^2 dr=1$.

s state		p state	
a	b	a	b
−0.632 27	0.605 19	20.380 79	0.374 54
−0.479 52	0.251 49	0.885 44	1.063 46
−0.101 09	0.100 88	1.847 16	3.444 80
0.612 95	2.673 38	0.075 78	0.116 27

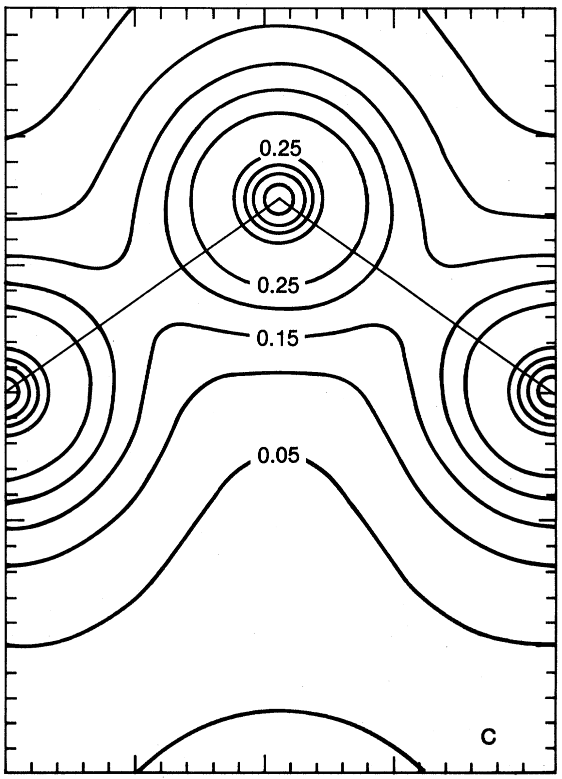

FIG. 1. Superposed charge density of atomic carbon (sp^3 configuration) in the diamond structure. The charge density is in units of $e/(\text{a.u.})^3$. The contour spacing is 0.05. The bonding directions are illustrated by the straight lines.

correctly formulated E_{total} of a system is solely a function of the density ρ and the external ionic potential, V_{ext}, i.e.,

$$E_{\text{total}} = E_{\text{total}}[V_{\text{ext}}, \rho] \ , \tag{3}$$

any errors in V_T (either in terms of our approximations in the construction of the screening potentials or in the fitting procedures) will only result in second-order influences in E_{total}.

B. Solution of the Schrödinger equation with the use of local basis

Given the expansion for the total-input pseudopotential in Table II, we can proceed to solve the Kohn-Sham equations. Our basis consists of Bloch sums of Gaussian orbitals.[20,33] The orbitals are taken to have s- and p-like symmetry. For materials with significant higher l components, e.g., d character, we could take d, f, g, etc., orbitals also. Thus our wave function has the form:

$$\begin{aligned} \psi_{n,\vec{k}}(\vec{r}) &= \sum_{l,m,\mu,\nu} \alpha_{l,m,\mu,\nu}(n,\vec{k})\phi_{l,m,\mu,\nu}(\vec{k},\vec{r}) \ , \\ \phi_{l,m,\mu,\nu}(\vec{k},\vec{r}) &= \frac{1}{\sqrt{\Omega}} \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R}) f_{l,m,\nu}(\vec{r}-\vec{R}-\vec{\tau}_{\mu}) \ , \end{aligned} \tag{4}$$

where

$$f_{l,m,\nu}(\vec{r}) = K_{l,m}(\theta,\phi)\exp(-\beta_{\nu} r^2) \ .$$

$K_{l,m}$ are cubic harmonics. The indices l,m,μ,ν label for the angular-momentum character of the orbital, l, the azimuthal quantum number m, the site within the unit cell, μ, and the decay constant (or Gaussian exponent) of the local orbital, ν. n is the band index; $\vec{k}$ is the wave vector. $\vec{R}$ is a lattice vector, $\vec{\tau}_{\mu}$ is a basis vector, and Ω is the crystal volume.[33] For simplicity in our discussion, we will use a generalized index $i = (l,m,\mu,\nu)$. Also, let us consider only one atom per unit cell and restrict the discussion to s and p states. Then our Gaussian orbitals within a normalization factor take the form

$$f_i(\vec{r}) = \begin{cases} \exp(-\beta_i r^2), & \text{for } s \text{ states} \\ (x,y,z)\exp(-\beta_i r^2), & \text{for } p \text{ states} \ . \end{cases} \tag{5}$$

TABLE II. Gaussian expansion for the carbon potential in the diamond structure. The expansion is of the form $V^a = \sum_i a_i \exp(-b_i r^2)$ with V in units of Ry. The expansion is for an on-site expansion of the total electronic potential within the diamond lattice. The total potential may be derived from $V_T = \sum_{\vec{R},\vec{\tau}_u} V^a(\vec{r}-\vec{R}-\vec{\tau}_{\mu})$, where $\vec{R}$ is the lattice vector and $\vec{\tau}_{\mu}$ is the basis vector.

V_L		$V_s - V_L$	
a	b	a	b
6.875 67	5.844 65	5.135 22	8.033 19
−44.157 66	2.385 96	−47.914 62	4.336 80
29.193 30	1.662 23	137.958 31	3.132 67
−10.291 19	0.973 35	−66.255 71	2.564 21
−1.091 53	0.231 37		

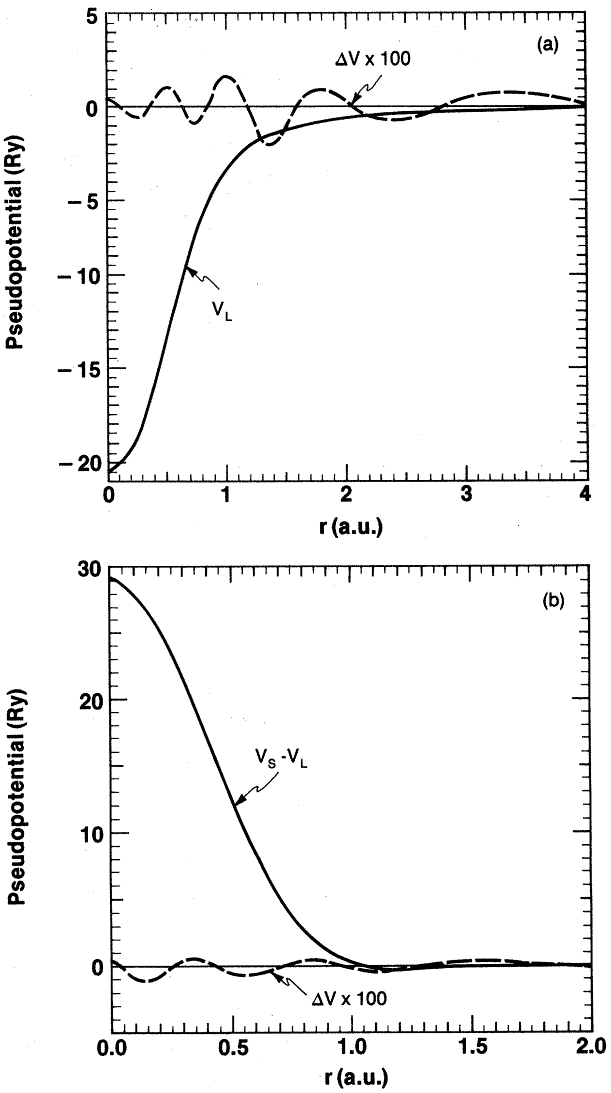

FIG. 2. Total "atom" potentials for carbon in the diamond structure. (a) Local potential or screened p-component of the total potential, (b) difference of the s and p components of the total potential. Also indicated are the errors in our Gaussian fits to these components. In order to display the error curve on the same scale, the error curve has been multiplied by 100. (Solid curves indicate total potentials; dashed curves indicate errors in the fit of Gaussians to the total potential.)

The Hamiltonian for one atom per unit cell is of the form

$$H = \frac{p^2}{2m} + V_L^c(\vec{r}) + \Delta V_{NL}^c(\vec{r}) \ , \tag{6}$$

where

$$V_L^c(\vec{r}) = \sum_{\vec{R}} V_L(\vec{r}-\vec{R}) \ ,$$

$$\Delta V_{NL}^c(\vec{r}) = \sum_{l,\vec{R}} P_l^{\dagger}[V^l(\vec{r}-\vec{R}) - V_L(\vec{r}-\vec{R})]P_l \ .$$

P_l is a projection operator and the sum over the l components of merit. As per our previous discussion, we take the local potential as the p potential and take the $l=0$

component as the *s*-*p* correction.

From our Hamiltonian and basis, we set up a matrix equation:

$$\underline{H}-E(\vec{k})\underline{S}=\underline{0}\,, \tag{7}$$

where

$$H_{ij}=\sum_{\vec{R}}\exp(i\vec{k}\cdot\vec{R})[t_{ij}(\vec{R})+v_{ij}(\vec{R})+v_{ij}^{NL}(\vec{R})]\,,$$

$$S_{ij}=\sum_{\vec{R}}\exp(i\vec{k}\cdot\vec{R})s_{ij}(\vec{R})\,,$$

with

$$t_{ij}(\vec{R})=\frac{-\hbar^2}{2m\Omega_c}\int f_i(\vec{r})\nabla^2 f_j(\vec{r}-\vec{R})d^3r\,,$$

$$v_{ij}(\vec{R})=\frac{1}{\Omega_c}\int f_i(\vec{r})V_L^c(\vec{r})f_j(\vec{r}-\vec{R})d^3r\,,$$

$$v_{ij}^{NL}(\vec{R})=\frac{1}{\Omega_c}\int f_i(\vec{r})\Delta V_{NL}^c(\vec{r})f_j(\vec{r}-\vec{R})d^3r\,,$$

$$s_{ij}(\vec{R})=\frac{1}{\Omega_c}\int f_i(\vec{r})f_j(\vec{r}-\vec{R})d^3r\,,$$

and Ω_c is the cell volume in the solid state. In writing this expression, we have interchanged the summation and integration order. This is acceptable provided we are certain that sufficient sites are included in the summations over lattice vectors. The chief advantage of the Hamiltonian is that the matrix elements, t_{ij}, v_{ij}, v_{ij}^{NL}, and s_{ij}, are analytical (given the expansion of the potential in Gaussians); the integrands consist of Gaussians and polynomials. While these matrix elements are analytic, the analytic expressions are not trivial. In particular, the nonlocal potential matrix elements involve three-center integrals with nonlocal projection operators in the integrands. Standard quantum-chemistry programs[34] have been developed to evaluate these integrals and are easily adapted for solid-state use. Another advantage of this formalism is that the matrix elements, $t_{ij}(\vec{R})$, $v_{ij}(\vec{R})$, $v_{ij}^{NL}(\vec{R})$, and $s_{ij}(\vec{R})$ are wave-vector independent. They need only be calculated once and stored for future use. Given a $\vec{k}$ point, the $\underline{H}$ and $\underline{S}$ matrices can be trivially evaluated by summing over lattice vectors with the appropriate phase factor. This is a great savings in computational effort and makes the method ideal for metallic systems where complex Fermi surfaces may be easily studied in some detail.

With the matrix elements evaluated, the secular equation may be solved by standard methods. The size of the matrix involved is quite small. For example, in the case of diamond with three decay constants for each of the s, p_x, p_y, p_z orbitals, the matrices in Eq. (7) are only 24×24. Thus essentially all the computational effort resides with the evaluation of the matrix elements. This is in contrast to plane-wave methods which may require a diagonalization of a matrix on the order of 450×450 to achieve comparable accuracy.[35]

As with any computational method, there can be questions involving so-called "hidden" parameters. For example, we do not sum over an infinite number of lattice sites, nor do we use an infinite basis. An unconverged cutoff can affect the results and we have attempted to study extensively how strong a role of the "cutoff" parameters play. With respect to the summation over lattice sites, the number of nearest-neighbor shells included in the overlap integrals, or the $t_{ij}(\vec{R})$ integrals, was six at a minimum for diamond. We have run our final results with ten shells to ensure well-converged results; for the diamond lattice, this corresponds to 146 neighbors.

The three-center integrals, e.g., $v_{ij}(\vec{R})$, involve a similar criterion. Given an orbital at site $\vec{R}_1$ and one at site $\vec{R}_2$, we consider all potential sites $\vec{R}_p$ which satisfy the criterion

$$|\vec{R}_1-\vec{R}_p|\le R_{\max},\quad |\vec{R}_2-\vec{R}_p|\le R_{\max}\,, \tag{8}$$

where $R_{\max}$ is the convergence parameter. If

$$|\vec{R}_1-\vec{R}_2|>R_{\max}\,,$$

we consider no potential overlaps for the two sites $\vec{R}_1,\vec{R}_2$. We note that $\vec{R}_{\max}$ corresponding to ten neighboring shells is more than sufficient. For diamond, the total energy difference is less than 30 meV between the six- and ten-shell results, and relative energy differences, i.e., changes in energy with the lattice constant, are much less.

Testing the basis is a more complex issue. We attempted to use a minimal basis and still maintain a high degree of accuracy. We tested our basis with and without *d* orbitals and found their inclusion unnecessary for diamond. Thus we included only *s* and *p* orbitals of the type indicated in Eq. (5). Choosing the decay constants is an important part of the calculation. In order to control the parameter space we examined, we fixed the basis so that the Gaussians we employed are "even tempered," i.e., given three decays, β_1, β_2, and β_3, we demand $\beta_2=(\beta_1\beta_3)^{1/2}$. We then varied β_1 and β_3 until the energy was at a minimum. Variation in β_2, once β_1 and β_3 were fixed, did not alter the energy in any significant fashion. Although our basis search was not exhaustive, it was extensive and we are confident that the basis is adequate for our purposes since the pseudo-wave-functions are relatively smooth. With the basis determined at a specific crystal volume, we use the same set at all other volumes. For diamond, the decays constants (in a.u.) used are $\beta_1=0.25$, $\beta_2=0.935$, $\beta_3=3.50$. Harmon *et al.*[11] have suggested that the basis should be scaled with the volume change. Apparently, this is to overcome deficiencies associated with an inadequate basis. We find that within our basis this problem does not arise for diamond and rescaling is not necessary.

For the case of diamond, we use only *s* and *p* orbitals. Determining the required matrix elements is such that given a decay constant one may compute all *l*-orbital overlaps with little savings over computing a specific *l*-orbital overlap. Thus with four types of orbitals (s,p_x,p_y,p_z) and three decay constants, we have a total of twelve orbitals per atom. Our matrix size with two atoms per unit cell is 24×24. Using only two decays will yield reasonable solid-state structural properties, but will not yield an accurate total energy, e.g., the total energy is about 0.5–1.0 eV above the three-decay results. Including *d* orbitals did not appear to enhance the basis as compared to adding more *s-p* orbitals. This is not surprising, since the *d* orbitals are known to play an insignificant role in the occupied states of carbon-derived crystals.

III. TOTAL-ENERGY CALCULATIONS

Virtually all modern first-principles methods on solid-state energetics are based upon the Hohenberg-Kohn-Sham density-functional formalism.[23] In this formalism it is shown that the ground-state total energy of a many-body system can be written in the form

$$E_{\text{total}}=\int V_{\text{ion}}(\vec{r})\rho(\vec{r})d^3r+\tfrac{1}{2}\int\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r\,d^3r' +G[\rho]+E_{\text{ion-ion}}\;, \tag{9}$$

where $\rho(\vec{r})$ is the electron density, $G[\rho]$ is a universal functional of the density, and $E_{\text{ion-ion}}$ is the electrostatic interaction energy among the bare ions. This expression is a minimum for the correct density function $\rho(\vec{r})$. Thus in principle, once the charge density is specified the total energy is uniquely determined. Owing to the complexity of solid-state systems, this is a powerful approach since one needs to concentrate on charge-density analyses alone.

Equation (9), in practical calculations, is usually further reduced to

$$E_{\text{total}}=\sum_{i=1}^{N}\epsilon_i-\tfrac{1}{2}\int\int\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r\,d^3r' +\int\rho(\vec{r})(\epsilon_{\text{xc}}[\rho]-\mu_{\text{xc}}[\rho])d^3r+E_{\text{ion-ion}}\;, \tag{10}$$

where ϵ_{xc} and μ_{xc} are, respectively, the exchange-correlation energy density and potential for the electrons.[23,30] The Kohn-Sham orbital density ρ and eigenvalues ϵ_i are determined self-consistently by solving the one-electron Schrödinger equation (in atomic units):

$$\{-\tfrac{1}{2}\nabla^2+V_{\text{ion}}(\vec{r})+V_H(\vec{r})+\mu_{\text{xc}}[\rho(\vec{r})]\}\psi_i(\vec{r})=\epsilon_i\psi_i(\vec{r})\;, \tag{11}$$

with

$$\rho(\vec{r})=\sum_{i=1}^{N}|\psi_i(\vec{r})|^2\;, \tag{12}$$

where N is the number of electrons, V_{ion} is the external potential seen by the electrons due to the nuclei, and V_H is the usual Hartree screening term:

$$V_H(\vec{r})=\int\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r'\;. \tag{13}$$

For accurate ground-state properties, $E_{\text{total}}[\rho]$ must be evaluated to a very high degree of precision.

In our approach, we eliminate the iterative self-consistency cycle by making explicit use of the variational principle in the density-functional formalism. Consider an approximate charge density $\tilde{\rho}$ which is nearly self-consistent. Then,

$$E_{\text{total}}[\rho]=E_{\text{total}}[\tilde{\rho}]+O((\rho-\tilde{\rho})^2)\;. \tag{14}$$

Thus all we need is to determine a scheme of exploiting this feature and obtaining $\tilde{\rho}$.

A careful reformulation of the conventional expression, Eq. (10), for the total energy is necessary for the direct use of the variational property of E_{total}. Equation (10) as written is only strictly correct for the final self-consistent Kohn-Sham orbital density $\rho(\vec{r})$ in a self-consistent calculation, i.e., $\rho_{\text{in}}(\vec{r})=\rho_{\text{out}}(\vec{r})$. The reason is that, as can be shown easily from Eq. (11),

$$\sum_i\epsilon_i=T[\rho_{\text{out}}]+\int V_{\text{ion}}(\vec{r})\rho_{\text{out}}(\vec{r})d^3r +\int V_H[\rho_{\text{in}}]\rho_{\text{out}}(\vec{r})d^3r +\int\mu_{\text{xc}}[\rho_{\text{in}}]\rho_{\text{out}}(\vec{r})d^3r\;, \tag{15}$$

where T is the kinetic energy functional of a noninteracting inhomogeneous electron gas of density ρ. Hence, a straightforward use of the conventional expression, Eq. (10), would not yield results which would be accurate to second order in $\Delta\rho=\rho-\tilde{\rho}$ because Eq. (15) is not a functional of a particular density.[36] It is possible to stop after one or two iterations by working with the correct functional. Namely, we replace the first term on the right-hand side of Eq. (10) by

$$\sum_{i=1}^{N}\epsilon_i-\int(V_H[\rho_{\text{in}}]-V_H[\rho_{\text{out}}])\rho_{\text{out}}(\vec{r})d^3r -\int(\mu_{\text{xc}}[\rho_{\text{in}}]-\mu_{\text{xc}}[\rho_{\text{out}}])\rho_{\text{out}}(\vec{r})d^3r\;. \tag{16}$$

The central equation in our method is

$$E_{\text{total}}=\sum_{i=1}^{N}\epsilon_i-\int V_H[\rho_{\text{in}}]\tilde{\rho}(\vec{r})d^3r+\tfrac{1}{2}\int V_H[\tilde{\rho}]\tilde{\rho}(\vec{r})d^3r -\int\mu_{\text{xc}}[\rho_{\text{in}}]\tilde{\rho}(\vec{r})d^3r+\int\epsilon_{\text{xc}}[\tilde{\rho}]\tilde{\rho}(\vec{r})d^3r +E_{\text{ion-ion}}\;. \tag{17}$$

For the diamond calculation ρ_{in} is taken to be the superposed atomic charge density and $\tilde{\rho}$ is the output charge calculated from a potential generated using ρ_{in}. We would like to emphasize several crucial points here. First, as formulated in Eq. (17), ρ_{in}, and hence the input Hartree and exchange-correlation potentials discussed in the preceding section, are explicitly removed from the total-energy expression. Thus its sole function in our approach is to provide a way of obtaining a good $\tilde{\rho}$ and $T[\tilde{\rho}]$. Second, the new E_{total} expression is now truly a functional of $\tilde{\rho}$ and, therefore, correct to second order in $\Delta\rho$. Moreover, as discussed in Sec. IV, $\tilde{\rho}$ is nearly equal to the self-consistent charge density ρ even though ρ_{in} may be quite different from ρ.

Although the above expressions are in real space, it is not advantageous to evaluate the energy in real space for crystalline solids. The central problem involves divergent terms, e.g., summing over an infinite number of longrange Coulomb interactions. (Of course, the total sum does not diverge.) It is convenient in this case to use the total-energy formalism of Ihm *et al.*[37] This formalism expresses the energy in momentum space and involves the Fourier transform of the potential and charge density. The energy per atom is written as (for the case of elemental solid with one atom per unit cell)

$$E_{\text{total}}=\frac{1}{N}\sum_{n,\vec{k}}\epsilon_{n,\vec{k}}-\Omega_a\sum_{\vec{G}\,(\neq\vec{0})}[V_H^{\text{in}}(\vec{G})+\mu_{\text{xc}}^{\text{in}}(\vec{G})]\tilde{\rho}(\vec{G})$$

$$+\tfrac{1}{2}\Omega_a\sum_{\vec{G}\,(\neq\vec{0})}\tilde{V}_H(\vec{G})\tilde{\rho}(\vec{G})+\Omega_a\sum_{\vec{G}}\tilde{\epsilon}_{\text{xc}}[\vec{G}]\tilde{\rho}(\vec{G})$$

$$+\gamma_{\text{Ewald}}+\alpha_1 Z\ , \tag{18}$$

where

$$\gamma_{\text{Ewald}}=\tfrac{1}{2}\sum_{\vec{R}\,(\neq\vec{0})}\frac{Z^2}{|\vec{R}|}-\lim_{\vec{G}\to\vec{0}}\frac{4\pi Z^2}{\Omega_a|\vec{G}|^2}\ ,$$

$$\alpha_1 Z=\frac{Z}{\Omega_a}\int\left[V_{\text{ion}}+\frac{Z}{r}\right]d^3r\ .$$

Here Ω_a is the atomic volume in the crystal, N is the number of atoms in the crystal, and the sum of the first term is over all occupied bands, n. We use atomic units where $e=1$, $\hbar=1$, $m=1$. $\tilde{\rho}(\vec{G})$ is the Fourier transform of $\tilde{\rho}(\vec{r})$, etc. To perform the required Fourier transform we use standard fast-Fourier-transform algorithms. Convergence was tested via the transform grid parameters and the total number of reciprocal-lattice vectors in the sum. Typically, the transform involved a grid size of 32 768 points in the real-space unit cell. However, we tested a grid of 4096 points and found only a 0.5-meV energy difference in the total energy. The number of reciprocal-lattice vectors tested was the same as the charge density, i.e., 2229 plane waves.

We remark here that it is extremely important to remove *exactly* all contributions from the input screening potentials from the sum of the eigenvalues. Thus, the $V_H^{\text{in}}+\mu_{\text{xc}}^{\text{in}}$ term used in Eq. (18) should be defined as

$$V_H^{\text{in}}+\mu_{\text{xc}}^{\text{in}}\equiv V_{\text{total}}^{\text{fit}}-V_{\text{ion}}\ .$$

In this way any numerical errors due to the fitting of the total potential to a sum of Gaussians are removed from E_{total} up to second order.

IV. RESULTS FOR THE DIAMOND CRYSTAL

A. Valence charge density

For the case of diamond, we have a classic covalent bonding configuration with the concurrent bond charge. In some sense, these systems present the greatest challenge to local-density methods in that they have a highly nonuniform density. In order to compute the theoretical density, we first solve the Schrödinger equation over a grid of $\vec{k}$ points. We have used the special point scheme of Chadi and Cohen for this purpose.[38] In order to test our accuracy, we used a 10-special-point and a 60-special-point grid. We did not find a significant change with the number of special points.

If we compare our atomic charge density arising from superposed atoms as shown in Fig. 1 with the calculated density in Fig. 3, the essential differences between "atomic" and "crystalline" environments become clear. The most gross change between the atomic and crystalline charge is that the atomic charge is diffuse with relatively little localization of the charge along the bonding directions. Conversely, the crystalline density has a well-defined bond charge and is highly anisotropic.

Our charge density seems to be in reasonable agreement with other calculations. Specifically, the work of Holzwarth *et al.*[29] yields two bond-charge maxima along the bonding direction and the size of the electron density at the maxima is in good agreement with our results. Also, our results are in accord with the work of Yin and Cohen.[24] They find a charge-density maximum within a few percent of our value, although their bond charge would appear to be slightly larger. The chief point here is that our crystalline density is far closer to the self-consistent density than is the superposition of the atomic charge densities.

B. Band structure

The band structure of diamond is well understood with respect to its valence-band structure and its lower conduction bands. We have calculated the band structure using both an s^2p^2 and an sp^3 charge configuration to screen the core potential. We will concentrate only on the sp^3 results since the s^2p^2 calculation yielded nearly identical results. We determined the lattice constant for our band structure by minimizing the total crystal energy. Details of the procedure will be given in the next section. No parameters entered our calculation for the band structure except the atomic number and the crystal structure. The lattice constant determined was within 0.01 Å of the experimental value. In Fig. 4 we display our band structure along high-symmetry lines.

For purposes of comparison, we tabulate eigenvalues at high-symmetry $\vec{k}$ points for two other theoretical calculations in Table III. These calculations also use local orbitals; however, one uses a pseudopotential similar to ours, the other uses the full-electron potential. Interestingly, our results reside within the values from these two calculations, and overall the agreement between the calculations is remarkable.

The greatest discrepancy occurs for the all-electron calculation of Zunger and Freeman[10] at point X_1. This value is much larger than our value or the value obtained by Bachelet *et al.*[9] It might be supposed that the discrepancy is related to the use of an all-electron potential versus a pseudopotential; however, Bachelet *et al.* have checked their numbers by using an all-electron potential with a linearized-augmented-plane-wave basis. They obtain nearly identical results to the pseudopotential work with a Gaussian basis.

We summarize in Table IV the known experimental values for various high-symmetry points and compare them with our work. We obtain rather good agreement

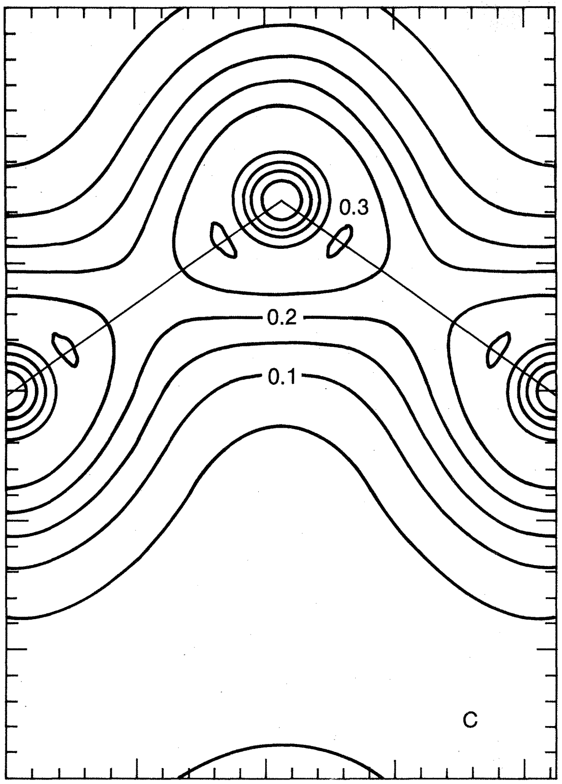

FIG. 3. Crystalline charge density for diamond using the wave function determined from the potential in Table II. The charge density is in united of $e/(\mathrm{a.u.})^3$. The contour spacing is 0.05. The bonding directions are illustrated by the straight lines.

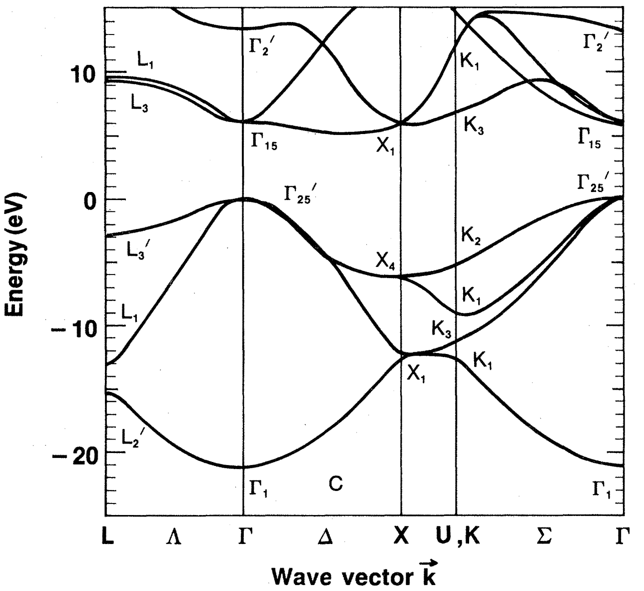

FIG. 4. Band structure for carbon in the diamond structure. The top of the valence band is taken as the zero of energy. Several high-symmetry directions are indicated. The band structure was determined from the potential in Table II, with the lattice constant determined by minimizing the total energy.

TABLE III. Eigenvalues in units of eV at high-symmetry points. Two other theoretical calculations are tabulated for comparison purposes: an all-electron calculation and a fully self-consistent pseudopotential calculation. The valence-band maximum is taken as the energy zero.

Symmetry point	Present work	All-electron local orbital (Ref. 10)	Pseudopotential local orbital (Ref. 9)
Γ_1	−21.03	−20.44	−21.68
Γ'_{25}	0.00	0.00	0.00
Γ_{15}	6.02	6.33	5.59
Γ'_2	13.41	14.07	13.07
X_1	−12.43	−12.17	−12.90
X_4	−6.27	−6.09	−6.43
X_1	5.91	8.96	4.65
X_4	16.77	16.69	16.87
L'_2	−15.29	−15.17	−15.79
L_1	−13.09	−12.18	−13.73
L'_3	−2.82	−2.82	−2.86
L_3	9.23	10.38	8.47
L_1	9.58	10.50	8.90

with the known experimental transitions. The occupied states are reproduced almost exactly by our calculated value. In addition, given that local-density-functional theory does not, in general, yield accurate values for the virtual states, our values for the unoccupied states are surprisingly good. We should note that data exist for unoccupied states at even higher energies, e.g., there exist estimates of transition energies at Γ up to 50 eV above the valence-band maximum.[39] We do not attempt to compare such data with our values for two reasons. First, our basis has been checked by achieving the lowest ground-state energy, and we have no reason to believe that it will replicate accurately high-energy unoccupied states which play no role in the total energy. Second, as mentioned, it is well known that local-density calculations do not yield accurate values for these states.

We have not computed a valence-band density of states or an optical-response function in that the thrust of our method and paper is on the ground-state properties of diamond. However, given that our band structure is nearly identical to those of previous attempts to compute these quantities, we see no reason for our results not being equally successful.

C. Equation of state for diamond

In this section we determine the equation of state for diamond at zero temperature. Using one of the simplest approaches,[40] we can assume that the bulk modulus of diamond near equilibrium varies only linearly with pressure,

$$B(P)=B_0+B'_0P\ , \qquad (19)$$

where B_0 is the equilibrium bulk modulus and P is the pressure. Upon integration, one obtains the Murnaghan[40] equation of state:

TABLE IV. Experimental critical points for diamond energy bands, in units of eV, compared to calculated values.

Symmetry point	Experimental[a]	Theory
Γ_1	-21 ± 1	-21.03
Γ_{15}	$6.0\ \pm0.2$	6.02
Γ_2'	15.3 ± 0.5	13.41
L_2'	-15.2 ± 0.3	-15.29
L_1	-12.8 ± 0.3	-13.09
$\Delta_1^{\min}$	$5.5\ \pm0.05$	5.05

[a] From F. J. Himpsel, J. F. van der Veen, and D. E. Eastman, Phys. Rev. B 22, 1967 (1980).

$$E(V)=\frac{B_0V}{B_0'(B_0'-1)}\left[B_0'\left[1-\frac{V_0}{V}\right]+\left[\frac{V_0}{V}\right]^{B_0'}-1\right]+E(V_0)\,, \tag{20}$$

where V_0 is the equilibrium volume. More sophisticated expressions exist for the equation of state, but this one is simple and sufficiently accurate for our purposes. If we solve for the energy as a function of volume and fit the Murnaghan equation of state to the calculated points, we may extract the equilibrium volume, the lowest total energy, the bulk modulus, and the derivative of the bulk modulus with pressure.

Let us briefly outline the steps in our method for evaluating the equation of state. As input we are given an atomic number and a crystal structure. From the atomic number we calculate a transferable ion-core pseudopotential. Within the given crystal structure, we must screen this ion core. At this stage, we guess at "reasonable" lattice parameters. For example, we might resort to Goldsmidt radii[41] for metals, or the Pauling radii[42] for covalent or ionic materials in order to obtain the bond lengths. With this hypothetical structure, we then form a screening potential using superposed atoms. In principle we should refit the screening potential at each lattice constant and use our total-energy expression to evaluate the energy at that volume. While this would still be an improvement over a self-consistent iteration which involves a number of iterations at each point, it is unnecessary. We find for the case at hand that once we have a potential at a reasonable crystal structure we may transfer it to other volumes without further alteration. Considering the variational nature of our approach, this result should not be surprising.

With respect to our calculated equation of state, we display in Fig. 5 the calculated energy versus volume equation of state using our sp^3 potential in Table II. The fit to the Murnaghan equation of state is outstanding. Over a 400-meV range, the largest deviation for the computed energies is less than 1 meV. In Table V we compile the extracted equation-of-state parameters. In Table VI we give the calculated volumes and total energies. The cohesive energy (7.84 eV/atom) is obtained from the difference between the bulk crystalline total energy, -155.29 eV/atom, including a zero-point motion correction of 0.18 eV/atom (Ref. 10) and the pseudoatom ground-state energy, -147.45 eV/atom, including the spin polarization energy, -1.40 eV/atom.[24]

A few total-energy calculations exist for the diamond crystal. Considering the different approaches used, the agreement is quite good. A possible exception to this statement is the work of Bachelet *et al.*[9] They find a cohesive energy several electron volts too small in comparison to other theories and experiment. We note that the cohesive energy is the most difficult property to compute since it involves a difference between the total energy of the atom and of the solid. A 1% error in either the atomic energy calculation or the solid-state energy calculation will result in as much as 30% error in the cohesive energy. Thus the discrepancy in cohesive energies may not be too surprising. Bachelet *et al.* attribute their poor value for the cohesive energy to an inadequate basis.

A key issue with respect to our results is the determination of the lattice constant, or as implied above, the transferability of our total potential. It could be argued that the calculated equation-of-state parameters are biased by the fact that we started with the known experimental lattice constant. Perhaps if we had started with a lattice constant considerably removed from the known value, we would not converge to the experimental value, but to some other lattice constant. This is not the case and we have done a number of tests to verify this fact.

We fit a series of potentials from -5% to $+5\%$ in the lattice constant. The total energy was independently calculated at each volume point with corresponding potential. The total energies for these points coincided with the energies for our fit from our original potential to within a few meV. As another test, we used the potentials fit at $\pm5\%$ differences to calculate the equation of state. Again, the equilibrium lattice constant obtained was within 0.01 Å of the experimental value. Thus we are confident that our formalism will not suffer from a par-

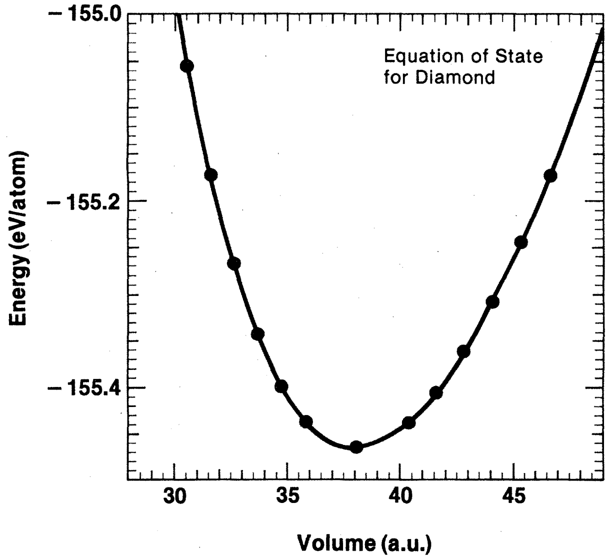

FIG. 5. Equation of state for carbon in the diamond structure. The continuous curve is the Murnaghan equation of state; the points are the calculated energies at the indicated volume. The zero-point motion energy is not included in this curve.

TABLE V. Ground-state properties of diamond from a fit to the Murnaghan equation of state (Ref. 40). We also compare our results to other contemporary self-consistent theories.

			Self-consistent field	
Ground state	Experiment	Present theory	Local orbitals (Ref. 9)	Plane waves (Ref. 24)
Cohesive energy (in eV)	7.37[a]	7.84	3.61	8.10
Lattice constant (in Å)	3.567[b]	3.560	3.69	3.60
Bulk modulus (in Mbar)	4.42[c]	4.37	4.56	4.33
Pressure derivative of bulk modulus	4[d]	3.54		

[a] L. Brewer, Lawrence Berkeley Laboratory Report No. LB-3720 (unpublished).

[b] J. Donohue, *The Structure of Elements* (Wiley, New York, 1974).

[c] H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. 43, 985 (1972).

[d] Estimated value from K. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).

ticular initial condition. Of course, if doubt exists in the obtained equilibrium lattice constant, the equilibrium point could be checked by refitting the input potential at several key volume points. The point to be made is that it is not necessary to refit the potential at each volume point in the calculation. Moreover, we have obtained an input potential for carbon in the graphite structure and applied it to the diamond structure. Again, results for the ground-state properties are virtually identical to those listed in Table V.

D. Lattice vibrations in the diamond crystal

Given the capacity to evaluate equation-of-state parameters, it is clear that we should be able to probe energy changes with atomic positions, e.g., we should be able to examine lattice-vibrational modes. To test this aspect of the problem, we have used the frozen-phonon approximation and attempted to calculate the optical-phonon frequencies at vanishing wave vector. This is a simple mode to examine, yet it will provide us with a sensitive test. Moreover, if we can evaluate the phonon frequencies at specific symmetry points, we can make use of new techniques which have been developed for obtaining the complete phonon spectrum.[43]

The atomic motions for this phonon mode are particularly simple. The motion corresponds to a constant volume uniaxial distortion of the diamond crystal along the $\langle 111 \rangle$ direction. To obtain the required energies, we displace the ion cores by a small amount and fit the displacement to the following form:

$$\Delta E = a(\Delta u)^2 + b(\Delta u)^3 , \qquad (21)$$

TABLE VI. Total crystal energy for diamond as a function of atomic volume.

Volume (a.u.^{3})	Energy (eV/atom)
46.670 72	−155.174 26
45.374 39	−155.244 95
44.102 28	−155.308 73
42.854 19	−155.361 64
41.629 85	−155.405 79
40.429 07	−155.437 56
38.097 21	−155.464 83
35.856 79	−155.436 53
34.770 30	−155.398 99
33.705 97	−155.342 75
32.663 59	−155.267 88
31.642 94	−155.173 64
30.643 75	−155.055 66

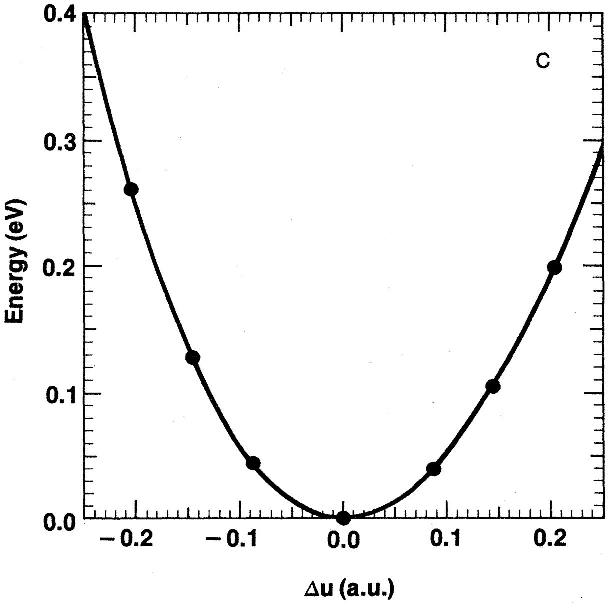

FIG. 6. Frozen-phonon energy vs bond displacement. From the quadratic term we calculate the phonon frequency to within 1% or better of the experimental value.

TABLE VII. Frozen-phonon parameters for the optical phonons in the diamond crystal lattice. Parameters *a* and *b* are as in Eq. (21). Also given is the total energy as a function of the bond-length displacement. The experimental phonon frequency is as tabulated in Ref. 2

Frozen phonon energy expansion parameters *a* [eV/(a.u.)^2]	*b* [eV/(a.u.)^3]	Optical phonon frequency (zone center) Theory (THz)	Experiment (THz)
5.55	−3.65	40.1	39.96

Displacement (a.u.)	Change in energy (eV)
0.203 37	0.198 98
0.145 26	0.105 92
0.087 16	0.039 48
−0.087 16	0.044 28
−0.145 26	0.128 24
−0.203 37	0.260 52

where *a* and *b* are expansion coefficients. Δu is the displacement in the bond length. From our fit, we obtain the phonon frequency f_{TO}:

$$f_{\mathrm{TO}}=\frac{\omega_{\mathrm{TO}}}{2\pi}=59.08\left[\frac{a}{M}\right]^{1/2}. \qquad (22)$$

M is the atomic mass of carbon. If a is in units of ev/(a.u.)^2, b units of eV/(a.u.)^3, M in units of gram-atom/mole, then the frequency is in units of THz.

In Fig. 6, we present our frozen-phonon energies for various displacements of the bond length. In Table VII we tabulate the calculated energy, the displacements, the fit expansion parameters (a,b), and the resulting phonon frequency from our theory and from experiment. The error we make in our calculated frequency is on the order of 1%. While this accuracy may seem surprising, compared with other calculations for semiconductors and our structural parameters, it is not.[43] Although we have not attempted a calculation of the full-phonon spectrum, there appear to be no inherent barriers to an accurate calculation.

V. CONCLUSION

We have presented in this paper a method which combines *ab initio* pseudopotentials and a Gaussian basis for evaluating the total energies of solids without resorting to a full self-consistent evaluation of the charge density. To demonstrate the utility of the method, we have concentrated on the structural properties of carbon in the diamond structure: an arch-typical covalent system. We calculated an energy band spectrum, an equation of state, and a fundamental phonon mode. Although our method is not as complex as the current state-of-the-art methods, we have obtained equally good results.

With respect to our energy bands, we found that either an s^2p^2- or an sp^3-derived screening potential led to an accurate critical point structure in the valence bands when compared to photoemission measurements. As typical of local-density results, our conduction bands were closer to the valence bands in energy than expected from experiment, i.e., the band gaps were too small.

With respect to the structural properties of diamond, we were able to reproduce the experimental values for the cohesive energy within 10%. The lattice constant and bulk modulus were determined to within 1% or 2%. We examined the sensitivity of these results to the basis and screening potentials and found negligible changes.

Our results for the optical-phonon mode at vanishing wave vector were within 1% of the experimental values. This result is consistent with the structural accuracy obtained for tetrahedral semiconductors and reaffirms the state-of-the-art accuracy for phonon calculations.

In summary, we have developed a method for examining the spectral and total energetics of solids which is easier to implement than methods currently available. Yet our method is as accurate as the current state of the art. Moreover, the method has the physical appeal of tight-binding or chemical orbital methods and can be applied to a wide variety of solid-state systems.

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[34] We use an edition of the POLYATOM program provided by T. H. Upton. (For details see C. F. Melius, Ph.D. Thesis, California Institute of Technology, 1972.)

[35] Private communication from M. T. Yin. This size matrix is required for a highly converged cohesive energy. For accurate structural properties, e.g., the lattice constant, a matrix size of 250×250 may be sufficient.

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