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General Crystalline Hartree–Fock Formalism: Diamond Results

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A method is presented for performing crystalline Hartree–Fock calculations with a wave-function basis consisting of Gaussian lobe functions. The most important concepts involve (i) the utilization of crystal symmetry in characterizing the first-order density matrix, and in selective computation and efficient storage of the one- and two-electron integrals; (ii) the introduction of a charge-conserving approximation for some of the less important three- and four-center integrals over contracted Gaussian basis functions; and (iii) the imposition of monopole and dipole compensation for the most important neglected two-electron Coulomb integrals. The method is applied to diamond, and calculational results are given for various sets of parameters. The best results include a Hartree–Fock cohesive energy of 0.38 Ry/atom, a virial coefficient ($-2T/V$) of 1.0005 for a lattice constant of 3.56 Å, a direct band gap at Γ of 15 eV, and an indirect band gap from Γ to Δ of 13.7 eV. The (111) Fourier transform of the charge density is 3.29 electrons per crystallographic unit cell.

I. INTRODUCTION

The purpose of this paper is to present computational techniques for performing crystalline ground-state calculations in which the correct Hartree–Fock (HF) exchange operator is employed, and to illustrate the method by applying it to diamond and presenting calculated charge density Fourier transforms, uncorrelated energy bands, cohesive energies, virial coefficients, and pv products for various sets of calculational parameters.

The well-known alternative to performing a HF crystalline calculation is to utilize the formalism of Hohenberg, Kohn, and Sham.[1] This formalism establishes the existence of a ground-state Hamiltonian which is a functional only of the charge density $n(\vec{r})$. The sum over filled states of squared eigenfunctions of this operator gives the fully correlated charge density. Well-known homogeneous electron-gas approximations to this operator include the Kohn–Sham–Gaspar[2] and the Slater[3] exchange-correlation operators, generalized by Slater and co-workers[4] to the X_α operator. These exchange-correlation operators are all proportional to $n(r)$ to the one-third power. Hedin and Lundqvist[5] have determined a more complicated density-dependent exchange-correlation operator for the homogeneous free-electron gas. However, when these various operators are used to calculate crystalline charge densities, systematic discrepancies between calculation and experiment are observed. Three different self-consistent-field (SCF) calculational models, the orthogonalized plane wave (OPW), the augmented plane wave (APW), and the mixed-basis plane-wave Gaussian (PWG) have all yielded similar results.[6] These discrepancies suggest that either more complicated homogeneous electron-gas functions of $n(\vec{r})$ are necessary, or that inhomogeneous terms involving the gradient operator must be included. Herman and co-workers[7] have developed the form of some of these terms and have done atomic calculations with them. Ma and Brueckner[8] have performed many-body electron-gas calculations to establish the magnitude of the terms. They express strong doubts, however, about the convergence of any simple power-series expansion. Moreover, the formalism is much more complicated to work with in crystals than is the HF formalism presented here.

Similar difficulties arise in finding an excitation Hamiltonian,

$\mathcal{H}(n(\vec{r}), E_\mu)$

whose eigenvalues E_μ give excitation energies. The simplest of these operators is Slater's energy-independent exchange potential.[3] However, Slater-exchange eigenvalues do not match experimental excitation energies in semiconductors when relativistic effects are considered[9] and the comparison is even poorer in insulators.[10] Liberman's energy-dependent excitation Hamiltonian[11] does give eigenvalues close to those obtained from HF calculations for atoms. One important by-product from crystalline HF calculations is that one will be able to compare the HF eigenvalues with Liberman-exchange eigenvalues. If the Liberman-exchange eigenvalues do match the HF eigenvalues in a crystal, a Liberman or some kind of a screened Liberman energy-dependent local operator would show great promise in calculating energy bands for crystals for which a HF calculation is too expensive.

Crystalline HF calculations have been reported by many authors. Most calculations use free-atom HF wave functions to construct a crystal potential[12] and are consequently not self-consistent. Kunz[13] reported the first of several[14] self-consistent crystalline HF calculations. He employs the localized orbital formalism of Adams and Gilbert,[15] which was introduced in order to economically calculate the first-order density matrix. Kunz and co-workers then use this self-consistent charge density along with Kunz's mixed-basis formalism[16] to obtain crystalline HF energy bands. Electron correlation is then introduced by either the Mott-Littleton method,[17] or by the screened-exchange-plus-Coulomb-hole[18] method. The resulting correlated bands closely match experiment for the insulators which they have calculated.[19] Kunz[20] has formulated yet another method for applying correlation corrections to energy bands based upon Toyozawa's electronic polaron.[21] Early results seem very promising.

We present here a local-basis-function (LBF) method[22] which is very straightforward and should be applicable to a large variety of crystals. Crystal symmetry is fully utilized and an integral approximation procedure speeds up the computation of the less important two-electron integrals over contracted Gaussians. Monopole and dipole corrections help compensate for zeroed integrals.

One convenient feature of such a HF calculation is that the HF first-order density matrix $\rho(\vec{r}, \vec{r}\,')$, and hence the related charge density $\rho(\vec{r}, \vec{r})$, and the momentum distribution $\rho(\vec{k}, \vec{k})$, are stationary to first-order under correlation corrections.[23] Furthermore, various well-investigated and well-understood techniques have been developed and applied to atoms and molecules to improve upon the HF formalism, i.e., to include correlation. Examples are projected HF[24] and configuration interaction (CI)[25] methods. After the HF computational techniques are well mastered, it should be very interesting to apply them in modified form to the problem of electron correlation in crystals.

II. CRYSTALLINE HF FORMALISM

A. Contracted Gaussian Lobe Function Basis

In the LBF method, spatially localized basis functions centered at different locations in the atom, molecule, or crystal are used as the expansion set for the wave functions. We distinguish between LBF and linear combination of atomic orbitals (LCAO) in that we do not wish to imply that atomic functions are used as the expansion set for the wave functions. In addition, the positions of the LBF's are arbitrary, which means that we can put functions in the bonding region if we wish. Finally, the basis functions employed are local in character, unlike plane waves, for example. In a crystal, long-range functions are not needed owing to the periodicity of the lattice.

In this calculation we use only s and p LBF's. For s-symmetry LBF's, we use contracted[26] sets of primitive Gaussian functions centered on the various atom locations:

$$\phi(\vec{r}) = \sum_\alpha A_\alpha e^{-\alpha \vec{r}^2} . \tag{1}$$

For LBF's of p symmetry, we employ Gaussian lobe functions, originally proposed by Pruess[27] and later developed independently by Whitten.[28] Such functions have been successfully employed in a variety of *ab initio* HF calculations on molecules.[29]

The lobe functions of p symmetry are constructed as the difference of two contracted Gaussian lobes, centered a distance $\vec{R}_\alpha$ from the origin of the p function. The displacement is designed to reproduce the angular dependence of an atomic p function:

$$P_x(\vec{r}) = \sum_\alpha A_\alpha [e^{-\alpha(\vec{r}-\vec{R}_\alpha)^2} - e^{-\alpha(\vec{r}+\vec{R}_\alpha)^2}] , \tag{2}$$

where

$$|\vec{R}_\alpha| = C/\sqrt{\alpha} , \; 0.005 \le C \le 0.1 . \tag{3}$$

Atomic studies have established the lobe displacement range given in Eq. (3). A series of SCF calculations on the argon atom were performed,[30] allowing C to vary over the range indicated in Eq. (3). The resulting total energies were stable to 0.001 a.u. The value 0.09 is employed for C in this work.

Tables are available of optimized Gaussian fits to atomic HF wave functions, including contracted as well as fully uncontracted functions.[31] The short-range (large α) groups may, in general, be carried over for use in crystal calculations. The intermediate-range groups (those with appreciable overlap with neighboring sites) should be fully uncontracted to allow for maximal distortion from atomic character. The long-range groups, which in the atom are necessary to fit the exponential tail of the wave function, may be discarded for the crystal because of the existence of the intermediate range functions on neighboring sites.

B. Crystal Symmetry and $\rho(\vec{r},\vec{r}\,')$

Diamond has two atoms in the unit cell. The atom at (0, 0, 0) will be designated type 1, while the atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ will be designated type 2. The coordinates are with respect to the diamond basis vectors

$$\vec{t}_1 = \tfrac{1}{2}a(\vec{j}+\vec{k}), \quad \vec{t}_2 = \tfrac{1}{2}a(\vec{i}+\vec{k}), \quad \vec{t}_3 = \tfrac{1}{2}a(\vec{i}+\vec{j}). \tag{4}$$

Twenty-four rotation-reflection operators transform each atom into an equivalent atom. The inversion about the point $\vec{T} = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ interchanges atoms of type 1 with atoms of type 2.[32] In the remainder of this paper, the set $\{X\}$ will include all of the rotation-reflection and inversion operators. The symmetry discussion which follows will be couched in terms of diamond, but the ideas are applicable to other geometries as well.

As is well known, only the first-order density matrix

$$\rho(\vec{r}, \vec{r}\,') = \int \Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_n)\Psi^\dagger(\vec{r}\,', \vec{r}_2, \ldots, \vec{r}_n) \times d(\vec{r}_2)\ldots d(\vec{r}_n) \tag{5}$$

is needed in the HF formalism. Thus, we will limit our discussion of symmetry to the first-order density matrix. Should one want to extend this procedure beyond the HF formalism, then of course the symmetry properties of the second-order density matrix should be considered.

Given a set of LBF's $\{\phi_\alpha(\vec{r} - \vec{R}_a)\}$, the first-order density matrix can be expanded, using products of LBF's as a basis:

$$\rho(\vec{r}, \vec{r}\,') = \sum_{(ab\alpha\beta)} P^{ab}_{\alpha\beta}\phi_\alpha(\vec{r} - \vec{R}_a)\phi_\beta(\vec{r}\,' - \vec{R}_b). \tag{6}$$

We assume that the LBF's are real functions. For closed-shell ground states (semiconductors and insulators), the first-order density matrix has full crystal symmetry. Consequently,

$$\begin{aligned}\rho(\vec{r}, \vec{r}\,') &= \rho(\vec{r}\,', \vec{r}) = \rho(X\vec{r}, X\vec{r}\,') \\ &= \rho(\vec{T} - \vec{r}, \vec{T} - \vec{r}\,') \\ &= \rho(\vec{r} + \vec{A}, \vec{r}\,' + \vec{A}),\end{aligned} \tag{7}$$

where $\vec{A}$ is a translation which leaves the crystal invariant.

Now we know that operating on any product of two functions

$$\phi_\alpha(\vec{r} - \vec{R}_a)\phi_\beta(\vec{r} - \vec{R}_b),$$

with all of the symmetry operators of the crystal will produce a set of product functions. By taking all possible values of α and β on each site and by taking different values for $|\vec{R}_a - \vec{R}_b|$, we can generate distinct product sets containing all possible product pairs for $|\vec{R}_a - \vec{R}_b|$ less than a given value. Now we note several things. First, we only need to acquire information about one member of each product set, since information about all other members may then be generated by using crystal-symmetry operators. Second, the symmetry requirements (7) mean that the $P^{ab}_{\alpha\beta}$ in Eq. (6) will be the same (exclusive of sign) for all the pairs of functions of s and p character in one product set. Thus, Eq. (6) may be rewritten

$$\rho(\vec{r}, \vec{r}\,') = \sum_I P_I \sum_{(ab\alpha\beta)\in I} \phi_\alpha(\vec{r} - \vec{R}_a)\phi_\beta(\vec{r}\,' - \vec{R}_b), \tag{8}$$

where I runs over the different product sets which we call symmetry sets, and where $(ab\alpha\beta)$ labels the different product pairs of a symmetry set. This notation will be used throughout the paper with the addition that μ or ν will occasionally be used to denote the labels $(ab\alpha\beta)$. It should be noted that the P_I do not have complete variational freedom since ρ must be idempotent and must satisfy the normalization condition

$$\int \rho(\vec{r}, \vec{r})d^3r = 2NZ. \tag{9}$$

Table I lists the members of the first six symmetry sets. These sets include all of the one-cen-

TABLE I. First six symmetry sets for diamond symmetry. The s stands for an LBF of s symmetry, while x, y, and z are p-symmetry LBF's. The second atom's coordinates are (0, 0, 0), $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$, $(-\frac{1}{4}, \frac{1}{4}, -\frac{1}{4})$, and $(-\frac{1}{4}, -\frac{1}{4}, \frac{1}{4})$ relative to the basis vectors given in Eq. (4). The first atom is at (0, 0, 0).

Set	Atom	$\{\mu\nu\}$
1	1	$xx + yy + zz$
2	1	ss
3	2	$xx + yy + zz$
	3	$xx + yy + zz$
	4	$xx + yy + zz$
	5	$xx + yy + zz$
4	2	$xy + yx + xz + zx + yz + zy$
	3	$-xy - yx - xz - zx + yz + zy$
	4	$-xy - yx + xz + zx - yz - zy$
	5	$xy + yx - zx - xz - yz - zy$
5	2	$xs - sx + ys - sy + zs - sz$
	3	$xs - sx - ys + sy - zs + sz$
	4	$-xs + sx + ys - sy - zs + sz$
	5	$-xs + sx - ys + sy + zs - sz$
6	2	ss
	3	ss
	4	ss
	5	ss

TABLE II. Representative members of the diamond symmetry sets for the first six shells of atoms. The s stands for an s-symmetry LBF, while x, y, and z are p-symmetry LBF's. The coordinates are relative to the basis vectors given in Eq. (4).

Shell	Atom	$\{\mu\nu\}$
1	$(0, 0, 0)$	ss, xx
2	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	ss, sx, xx, xy
3	$(\frac{1}{2}, \frac{1}{2}, 0)$	ss, sx, sz
		xx, zz, xy, xz
4	$(\frac{3}{4}, \frac{1}{4}, -\frac{1}{4})$	ss, sx, sy
		xx, yy, xy, yz
5	$(1, 0, 0)$	ss, sx, sy
		xx, yy, xy, yz
6	$(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$	ss, sx, sz
		xx, zz, xy, xz

ter and nearest-neighbor two-center contributions to the first-order density matrix. As can be seen, the symmetry analysis reduces 68 coefficients to 6. Table II gives a representative member of each symmetry set for the first six shells[33] of atoms. The total number of symmetry-independent coefficients can be found by multiplying the number of symmetry-independent s-s LBF products by $\frac{1}{2}N_s(N_s+1)$, the s-p products by N_sN_p, etc., where there are $N_s(N_p)$ separate LBF's of $s(p)$ character.

For example, good calculations can be performed over the first six shells of atoms in diamond with four LBF's of s character and three LBF's of p character. Consequently, 270 symmetry-independent coefficients characterize the first-order density matrix. We shall see later that only 270 one-electron integrals of each type need be done, and that all of the two-electron integrals can be collected in an array dimensioned 270 by 270.

C. Hamiltonian and Overlap Matrices

In order to determine the symmetry-independent coefficients of the first-order density matrix, we use the method of Roothan.[34] For each LBF $\phi_\alpha(\vec{r}-\vec{R}_a)$, where ϕ_α is a contracted set of Gaussian lobe functions [Eqs. (1) and (2)], we construct a Bloch function

$$\Phi_\alpha^k(\vec{r}) = (1/\sqrt{N}) \sum_a e^{i\vec{k}\cdot\vec{R}_a}\phi_\alpha(\vec{r}-\vec{R}_a), \tag{10}$$

where k labels the Brillouin zone point and where N is the number of unit cells in the crystal. Separate Bloch functions are needed for each of the two atoms in the unit cell. The one-electron wave functions Ψ_n^k are then expanded in terms of the Bloch functions

$$\Psi_n^k(\vec{r}) = \sum_\alpha C_{n\alpha}^k \Phi_\alpha^k(\vec{r}), \tag{11}$$

where n is the band index. The coefficients $C_{n\alpha}^k$ are adjusted in the usual manner to minimize the total energy. One obtains the following Hamiltonian and overlap matrices, the total matrices being block diagonal in k:

$$\sum_\beta \mathcal{H}_{\alpha\beta}^k C_{n\beta}^k = \epsilon_n^k \sum_\beta \mathcal{U}_{\alpha\beta}^k C_{n\beta}^k, \tag{12}$$

$$\mathcal{U}_{\alpha\beta}^k = \int \Phi_\alpha^{k\dagger}(\vec{r})\Phi_\beta^k(\vec{r})\,d(\vec{r})$$

$$= \sum_b U_{\alpha\beta}(\vec{R}_a, \vec{R}_b)e^{i\vec{k}\cdot(\vec{R}_a-\vec{R}_b)}, \tag{13}$$

$$U_{\alpha\beta}(\vec{R}_a, \vec{R}_b) = \int \phi_\alpha(\vec{r}-\vec{R}_a)\phi_\beta(\vec{r}-\vec{R}_b)\,d(\vec{r}), \tag{14}$$

$$\mathcal{H}_{\alpha\beta}^k = \sum_b H_{\alpha\beta}(\vec{R}_a, \vec{R}_b)e^{i\vec{k}\cdot(\vec{R}_b-\vec{R}_a)}, \tag{15}$$

$$\begin{aligned} H_{\alpha\beta}(\vec{R}_a, \vec{R}_b) = \int & d(\vec{r}_1)\phi_2(\vec{r}_1-\vec{R}_a) \\ & \times\Big[-\nabla_1^2 - 2\sum_c \frac{Z}{|\vec{r}_1-\vec{R}_c|} + \int d(\vec{r}_2) \\ & \times\Big(2\frac{\rho(\vec{r}_2, \vec{r}_2)}{r_{12}} - \frac{\rho(\vec{r}_1, \vec{r}_2)}{r_{12}}P_{12}\Big)\Big] \\ & \times\phi_\beta(\vec{r}_1-\vec{R}_b). \end{aligned} \tag{16}$$

Equations (13) and (15) need only be summed over atoms b, not over atoms a, owing to translational symmetry. Note that the sum over b is over all atoms of type 1 or of type 2, depending on whether the Bloch function Φ_β^k, is for atom type 1 or type 2. In Eq. (16), the sum over c is over all atoms and P_{12} is the permutation operator which interchanges r_1 with r_2. Matrix elements where the atom at R_a is of type 2 can easily be obtained from those where the atom at R_a is of type 1 by application of the inversion operator about $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$.

The matrix eigenvalue problem [Eq. (12)] is then most conveniently solved by performing a Choleski decomposition[35] on each positive definite overlap matrix U^k.

$$\begin{aligned} & U = LL^\dagger, \\ & L_{ij} = 0 \quad \text{for } i<j, \end{aligned} \tag{17}$$

where L is a lower triangular matrix. After this decomposition is performed, a single-matrix diagonalization yields the desired eigenvalues and eigenvectors:

$$[L^{-1}HL^{-1\dagger}][L^\dagger C] = \lambda[L^\dagger C]. \tag{18}$$

In Eqs. (14) and (16), one can see that we have integrals which involve LBF product pairs just as in $\rho(\vec{r}, \vec{r}\,')$. Therefore, we should be able to use the same decomposition into symmetry sets to reduce the number of integrals which need be done. All of the operators in the Hamiltonian, as well as in the overlap matrix (the unit operator) have full crystalline symmetry. Therefore, none of the one-electron operators can change the symmetry of the function it operates on. Thus all of the one-electron integrals may be classified into the same symmetry sets as $\rho(\vec{r}, \vec{r}\,')$. Only a single one-electron integral of each type for each different symmetry set need be done. The two-electron integrals in Eq. (16) involve an LBF pair multiplying $\rho(\vec{r}, \vec{r}\,')$. Thus, if K symmetry-independent coefficients (symmetry sets) characterize $\rho(\vec{r}, \vec{r}\,')$ in Eq. (6), then all of the two-electron integrals can be stored in a K by K array. The two-electron part of Eq. (16) is summed over R_b, α and β for R_a fixed (to be zero usually) to give the array [using the notation of Eq. (8)]

$$A_{IJ}=\frac{1}{N}\sum_{(ab\alpha\beta)\in I}\;\sum_{(cd\gamma\delta)\in J}\times\int d(\vec{r}_1)\,d(\vec{r}_2)\,\phi_\alpha(\vec{r}_1-\vec{R}_a)\times\left(\phi_\gamma(\vec{r}_2-\vec{R}_c)\,\frac{(2-P_{12})}{r_{12}}\,\phi_\delta(\vec{r}_2-\vec{R}_d)\right)\times\phi_\beta(\vec{r}_1-\vec{R}_b)\,. \tag{19}$$

Element A_{IJ} is thus proportional to the total Coulomb-plus-exchange integral of all members (translated, rotated, and inverted) of symmetry set I with all members (translated, rotated, and inverted) of symmetry set J. The constant of proportionality is the reciprocal of the number of cells in the crystal. At this point we can see that the symmetry of Eq. (19) guarantees the symmetry of the array, so that

$$A_{IJ}=A_{JI}\,.$$

In practice, the centers for the atoms a, b, c, and d are chosen such that they all are within M shells of each other and atom a is taken at zero. The two-electron integral contribution in Eq. (16) is now given by

$$(1/W_I)\sum_J P_J A_{IJ}\,, \tag{20}$$

where W_I is the number of members of symmetry set I for fixed R_a. Here we again stress the fact that in evaluating Eq. (19), a single member of symmetry set I, say μ, can be chosen and the integral for that member can be multiplied by the number of members of I with R_a at zero. In addition, one can use the set of symmetry operations $\{X\}$ which leave μ invariant, for a further reduction. The members of symmetry set J can be decomposed into subsets which transform into each other under the operations $\{X\}$. Only integrals between μ and one member of each subset need be calculated. All of the rest within each subset are equal. Finally, one has the permutational symmetry that the Coulomb integral for $(ab\alpha\beta : cd\gamma\delta)$ is equal to the exchange integral for $(ac\alpha\gamma : bd\beta\delta)$ and $(ad\alpha\delta : bc\beta\gamma)$. All of these considerations, when used together, greatly reduce the number of one- and two-electron integrals which must be calculated.

D. Charge Density Average over the Brillouin Zone

In order to construct a new first-order density matrix from the SCF results, one in principle needs an integral over the occupied HF eigenfunctions in the first Brillouin zone[6]:

$$\rho(\vec{r}, \vec{r}\,')=\int_{\mathrm{B.Z.}} d(\vec{k})\sum_{n\ \mathrm{filled}}\Psi_n^k(\vec{r})\Psi_n^{k\dagger}(\vec{r}\,')\,. \tag{21}$$

In practice, one replaces the Brillouin-zone integral by a weighted sum over a numerical mesh in an irreducible sector of the Brillouin zone:

$$\rho(\vec{r}, \vec{r}\,')=\sum_k W_k\sum_{n\ \mathrm{filled}}\Psi_n^k(\vec{r})\Psi_n^{k\dagger}(\vec{r}\,')\,. \tag{22}$$

A natural weight to use for a given mesh point is one proportional to that volume of the first Brillouin zone which is closer to that mesh point than to any other mesh point. If a regular mesh is used, the weights are easy to determine. Table III gives zone-point coordinates in terms of the reciprocal crystal lattice, together with the nearest-volume weights. The generalization to finer meshes should be obvious.

It will be noted that only a part of the first Brillouin zone is represented in Table III. For example, the point $(\frac{1}{2}, 0, 0)$ occurs, but not $(0, \frac{1}{2}, 0)$ or $(-\frac{1}{2}, 0, 0)$. The zone-point weights are adjusted accordingly. In order to correctly project the correct crystal symmetry into $\rho(\vec{r}, \vec{r}\,')$ from these unsymmetrical zone samplings, one must again use the symmetry ideas discussed previous-

TABLE III. Brillouin-zone meshes and relative weightings. The Cartesian coordinates multiply $2\pi/a$, where a is the diamond lattice constant.

10 point	Weight	6–19 points	Weight	
$(0, 0, 0)$	1	$(0, 0, 0)$	1	
$(1, 0, 0)$	3	$(1, 0, 0)$	3	
$(\frac{1}{3}, 0, 0)$	6	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	4	
$(\frac{1}{3}, \frac{1}{3}, 0)$	12	$(1, \frac{1}{2}, 0)$	6	
$(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$	8	$(\frac{1}{2}, 0, 0)$	6	
$(\frac{2}{3}, 0, 0)$	6	$(\frac{1}{2}, \frac{1}{2}, 0)$	12	
$(\frac{2}{3}, \frac{1}{3}, 0)$	24	$(\frac{3}{4}, \frac{3}{4}, 0)$	12	32
$(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$	24	$(1, \frac{1}{4}, 0)$	12	
$(\frac{2}{3}, \frac{1}{3}, 0)$	12	$(\frac{3}{4}, \frac{1}{4}, 0)$	24	
$(1, \frac{1}{3}, 0)$	12	$(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$	24	
	108	$(\frac{3}{4}, \frac{1}{2}, 0)$	24	
		$(\frac{3}{4}, \frac{1}{2}, \frac{1}{4})$	24	
		$(\frac{3}{4}, 0, 0)$	6	
		$(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$	24	
		$(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$	24	
		$(\frac{1}{2}, \frac{1}{4}, 0)$	24	
		$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	8	
		$(\frac{1}{4}, \frac{1}{4}, 0)$	12	
		$(\frac{1}{4}, 0, 0)$	6	
			256	

ly. That is, one must average over the coefficients of LBF products belonging to a single symmetry set (with proper attention to sign) to get the correct common coefficient of the set.

We can illustrate this point with a simple example. Consider the symmetry set consisting of

$$(xx + yy + zz),$$

where atoms a and b are identical, x stands for an LBF of p_x symmetry, etc. If one calculates the contribution to this part of the first-order density matrix from the zone point (1, 0, 0), it will have the structure

$$A(xx) + B(yy + zz). \tag{23}$$

Similarly, the zone points (0, 1, 0) and (0, 0, 1) will contribute, respectively,

$$A(yy) + B(xx + zz) \tag{24}$$

and

$$A(zz) + B(xx + yy). \tag{25}$$

Averaging over these three zone points gives a total contribution of

$$\tfrac{1}{3}(A + 2B)(xx + yy + zz), \tag{26}$$

which we could have obtained more simply by averaging over the coefficients of xx, yy, and zz for any one of the zone points. For a closed-shell system, averaging over symmetry-connected Brillouin zone points is completely equivalent to averaging over the individual symmetry-connected coefficients of one representative point.

E. Two-Electron Integral Approximation

Another computational simplification that we have employed is the approximation of some of the less important two-electron integrals involving sets of contracted Gaussians. The corelike LBF's are usually contracted sets of Gaussians with coefficients chosen to help simulate the wave function behavior in the vicinity of the nucleus. Each two-electron integral over four LBF's thus involves many integrals over individual Gaussians. If each basis function consists of m_i Gaussians, $m_1m_2m_3m_4$ Coulomb integrals over individual Gaussian products must be done for each Coulomb integral over four basis functions.

We can, however, view each two-electron integral as representing the Coulomb interaction between two charge distributions:

$$I_{\mu\nu} = \int [n_\mu(\vec{r}_1) n_\nu(\vec{r}_2)/r_{12}]\, d(\vec{r}_1)\, d(\vec{r}_2). \tag{27}$$

For a contracted Gaussian lobe function basis, $n_\mu(\vec{r})$ is given by

$$n_\mu(\vec{r}) = \phi_\alpha(\vec{r} - \vec{R}_a)\phi_\beta(\vec{r} - \vec{R}_b) = \sum_{i=1}^{m_1m_2} C_i e^{-\alpha_i(\vec{r}-\vec{R}_i)^2}, \tag{28}$$

where we use the fact that the product of two Gaussians about different centers is again a Gaussian about some third center. The approximation is to replace the sum over m_1m_2 Gaussians by a single Gaussian

$$n_\mu(\vec{r}) \cong De^{-\delta(\vec{r}-\vec{R}_d)^2}, \tag{29}$$

such that the total charge of $n_i(\vec{r})$ is correct:

$$Q_\delta = D(\pi/\delta)^{3/2} = \sum_i Q_i, \qquad Q_i = C_i(\pi/\alpha_i)^{3/2}, \tag{30}$$

the center of charge is correct:

$$Q_\delta \vec{R}_d = \sum_i Q_i \vec{R}_i, \tag{31}$$

and δ is adjusted for a best least-squares fit to $n_i(\vec{r})$:

$$S(\delta) = \int \Big(De^{-\delta(\vec{r}-\vec{R}_d)^2} - \sum_i C_i e^{-\alpha_i(\vec{r}-\vec{R}_i)^2} \Big)^2 d(\vec{r}), \tag{32}$$

$$\frac{dS(\delta)}{d\delta} = 0. \tag{33}$$

When p-symmetry LBF's are involved, each lobe-lobe pair in $n_i(\vec{r})$ is treated independently; that is, two separate fits are made for s-p and four separate fits for p-p LBF pairs. This procedure maintains the predominant dipole character of the s-p charge density and the essential quadrupole character of the p-p charge density.

When all of the four-center integrals in ethylene were approximated in this fashion, the resulting total energy and one-electron eigenvalues changed less than 0.001 Ry, as compared to doing all of the integrals correctly. The same results were obtained for a fictitious C_4 molecule with the four C atoms in their nearest-neighbor diamond configuration. When all of the ethylene three-center integrals were approximated, the total energy and eigenvalues changed by several eV. Some of the three-center integrals must consequently be done properly.

F. Monopole and Dipole Charge Balance Corrections

In principle, nuclear and two-electron integrals should be done over all the atoms in the crystal. In fact, there is complete cancellation between nuclear and two-electron Coulomb integrals at large distances from the two atoms belonging to the symmetry set of electron one [Eqs. (14) and (16)]. In practice, we specify at the beginning the number of shells of atoms M that we wish to consider. All symmetry sets, taking one atom at the origin and the second within the M shells, are determined. The integral approximation least-squares fits are made for this group of LBF pairs. All one-electron integrals are calculated for LBF pairs contained in these symmetry sets and are zeroed for all other LBF pairs. For two-electron integrals, we include all contributions for which all four atom locations are within M shells of each other.

Although the above prescription is the natural one to use in conjunction with our method of utilizing symmetry sets and of handling the integral approximations, it does introduce numerical difficulties. If the third atom is just inside the Mth shell boundary of the first or second atom, the two-electron Coulomb integrals will be zeroed for all fourth atoms just outside the same Mth shell boundary. Substantial amounts of charge and dipole moment are associated with these atom pairs in $\rho(\vec{r}, \vec{r}\,')$ [Eq. (6)]. If the nuclear charge of each atom is taken to be Z (6 for diamond) in the electron-nuclear integral [Eq. (16)], we find that we have lost charge balance between the electron-nuclear and the electron-electron Coulomb integrals. The electron eigenvalues sink and the crystal charge density distorts because of the neglected electron-charge distribution. We shall see this effect illustrated in Sec. III.

In order to minimize the effects of these computational boundaries we find that we must reduce the nuclear charge on each atom by the amount of the electronic charge we effectively ignore in the Coulomb integrals. From Eq. (6), we have that the charge density $n(\vec{r})$ is

$$\begin{aligned} n(\vec{r}) &= -\rho(\vec{r}, \vec{r}) \\ &= -\sum_{I} P_I \sum_{(ab\alpha\beta)\in I} \phi_\alpha(\vec{r}-\vec{R}_a)\phi_\beta(\vec{r}-\vec{R}_b). \end{aligned} \tag{34}$$

We now recall Eq. (9), which relates the nuclear charge to P_I:

$$Z = \sum_{I} P_I W_I O_I , \tag{35}$$

$$O_I = \int \phi_\alpha(\vec{r}-\vec{R}_a)\phi_\beta(\vec{r}-\vec{R}_b)\, d(\vec{r}), \quad (ab\alpha\beta)\in I \tag{36}$$

where W_I is the number of members in symmetry set I for which R_a is at zero, and where we have used the fact that all of the integrals for members of a symmetry set are the same, exclusive of sign. However, when we impose the M-shell boundary on Eq. (19), we limit the $(cd\gamma\delta)$ sum to be over just those members of symmetry set J for which both atoms c and d are within M shells of a and b, for each choice of $(ab\alpha\beta)$. We then use Eq. (20) to get the Hamiltonian matrix element for the electron-electron interaction. Focusing on the Coulomb part, we find that it can be written

$$\int \phi_\alpha(\vec{r}_1)\Bigg(\sum_{J} P_J \sum_{\substack{(cd\gamma\delta)\in J \\ \text{limited}}} \phi_\gamma(\vec{r}_a-\vec{R}_c)\phi_\delta(\vec{r}_2-\vec{R}_d)\Bigg) \times \phi_\beta(\vec{r}_1-\vec{R}_b)\, d(\vec{r}_1)\, d(\vec{r}_2), \tag{37}$$

where the limited $(cd\gamma\delta)$ sum has just the M-shell limitation discussed above. The point is that the quantity in large parentheses is no longer the full electronic charge density. Instead of Eq. (35), we now have

$$\sum_{J} P_J \sum_{\substack{\nu \\ \text{limited}}} O_\nu = \sum_{i=1}^{2N} Z_i^{\text{eff}} , \tag{38}$$

where i labels the atom position. The Z_i^{eff} are determined by accumulating a charge $\frac{1}{2}O_\nu$ on site c and on site d, while ν goes through its limited values for each J. The Z_i^{eff} are thus different for each choice of $(ab\alpha\beta)$.

When we accumulate the nuclear charge associated with the distributed electronic charge for symmetry set member $(cd\gamma\delta)$ in Eq. (37), we end up with predominantly positive charge close to the computational boundaries and with the negative electronic charge systematically further from the boundaries. We introduce so-called dipole corrections to compensate for this artificial bias. We do this in the following way: From Eq. (37) the extended electronic charge associated with $(cd\gamma\delta)$ is

$$-\phi_\gamma(\vec{r}-\vec{R}_c)\phi_\delta(\vec{r}-\vec{R}_d), \tag{39}$$

while the associated nuclear charge is

$$q = \tfrac{1}{2}\int \phi_\gamma(\vec{r}-\vec{R}_c)\phi_\delta(\vec{r}-\vec{R}_d)\, d(\vec{r}) \tag{40}$$

on atom c and also on atom d. This charge distribution can be very roughly approximated by the charge distribution consisting of charges q on c and on d, and two charges of $-q$ at $\frac{1}{2}(\vec{R}_c+\vec{R}_d)$. This distribution then consists of two finite dipoles of strength

$$\tfrac{1}{2}q(\vec{R}_c-\vec{R}_d), \tag{41}$$

one associated with c and one of opposite direction associated with d. To eliminate the bias in charge distribution owing to our artificial computational boundary, we then associate point dipoles at c and at d of equal strength and opposite direction to these. If all possible crystal rotations of d about c are included within the computational boundaries, the dipoles at c will add to zero because of the properties of the cubic point group (this procedure will thus not work for all crystal point groups). However, the accumulated dipole moments on atoms near a computational boundary will not add to zero, but will simulate the neglected electronic distributions, and will thus help to remove the bias of positive charge at the boundary.

Monopole and dipole corrections are thus applied every time one performs a two-electron integral [Eq. (37)]. With every such two-electron integral that is calculated, we also calculate a one-electron integral over $(ab\alpha\beta)$ for the potential due to point nuclear charges on c and d of strength q, and we also do a one-electron integral for the potential due to the compensating point dipoles on c and d.

G. Working Equations

We are finally in a position to write down a set of equations which we can program for a digital computer. The Hamiltonian matrix for the SCF is given by

$$H^I = T^I + V^I_{\text{el-el}} + V^I_{\text{el-}z} + V^I_{\text{el-dp}} , \tag{42}$$

$$T^I = \int d(\vec{r})\phi_\alpha(\vec{r} - \vec{R}_a)(-\nabla^2)\phi_\beta(\vec{r} - \vec{R}_b) , \tag{43}$$

$$V^I_{\text{el-el}} = (1/W_I)\sum_J P_J A_{IJ} , \tag{44}$$

$$V^I_{\text{el-}z} = -\int d(\vec{r})\phi_\alpha(\vec{r} - \vec{R}_a)\sum_J P_J \tfrac{1}{2}O_J \times \sum_{\substack{(cd\gamma\delta)\in J\\ \text{limited}}}\left(\frac{2}{|\vec{r} - \vec{R}_c|} + \frac{2}{|\vec{r} - \vec{R}_d|}\right)\phi_\beta(\vec{r} - \vec{R}_b) , \tag{45}$$

$$V^I_{\text{el-dp}} = \int d(\vec{r})\,\phi_\alpha(\vec{r} - \vec{R}_a)\sum_J P_J \tfrac{1}{2}O_J \times \sum_{\substack{(cd\gamma\delta)\in J\\ \text{limited}}}\left(\frac{\vec{R}_{cd}\cdot\vec{r}}{|\vec{r} - \vec{R}_c|^3} - \frac{\vec{R}_{cd}\cdot\vec{r}}{|\vec{r} - \vec{R}_d|^3}\right)\phi_\beta(\vec{r} - \vec{R}_b) , \tag{46}$$

$$\vec{R}_{cd} = \vec{R}_c - \vec{R}_d .$$

For the calculation of the total energy per atom, the dipole term is viewed as another electron term as its purpose is to compensate for missing electron bonds. The total energy per atom is thus

$$\mathcal{E} = \sum_I W_I P_I\left(T^I + \tfrac{1}{2}V^I_{\text{el-el}} + V^I_{\text{el-}z} + \tfrac{1}{2}V^I_{\text{el-dp}} + \tfrac{1}{2}V^I_{z\text{-}z} + V^I_{z\text{-dp}}\right) , \tag{47}$$

where the last terms are

$$V^I_{zz} = \tfrac{1}{2}O_I \sum_J P_J \tfrac{1}{2}O_J \times \sum_{\substack{(cd\gamma\delta)\in J\\ \text{limited}}}\left(\frac{2}{|\vec{R}_a - \vec{R}_c|} + \frac{2}{|\vec{R}_a - \vec{R}_d|} + \frac{2}{|\vec{R}_b - \vec{R}_c|} + \frac{2}{|\vec{R}_b - \vec{R}_d|}\right) , \tag{48}$$

$$V^I_{z\text{-dp}} = \tfrac{1}{2}O_I \sum_J P_J \tfrac{1}{2}O_J \times \sum_{\substack{(cd\gamma\delta)\in J\\ \text{limited}}}\left(\frac{\vec{R}_{cd}\cdot\vec{R}_a}{|\vec{R}_a - \vec{R}_c|^3} + \frac{\vec{R}_{cd}\cdot\vec{R}_b}{|\vec{R}_b - \vec{R}_c|^3} - \frac{\vec{R}_{cd}\cdot\vec{R}_a}{|\vec{R}_a - \vec{R}_d|^3} - \frac{\vec{R}_{cd}\cdot\vec{R}_b}{|\vec{R}_b - \vec{R}_d|^3}\right) . \tag{49}$$

The above procedure may seem complicated, but it is necessary for numerical integrity. The procedure smooths the transition across the computational boundary between doing and zeroing integrals for atoms *c* and *d*. It allows one to ignore many integrals without having to worry about loss of charge or dipole balance. It is necessary in this formalism because of the coulomb interaction.

III. COMPUTATIONS

In discussing the computational results, we shall first present the relevant experimental information on diamond, along with our guesses as to the effects of correlation on each quantity. Subtracting out the estimated correlation effects, we then get our best estimates for good HF results. Next, we discuss the results of various parameter studies to determine optimal choices of the parameters: choice of basis, Brillouin-zone averaging, approximating three-center and zeroing four-center integrals. Finally we present results for the best choices of these parameters.

A. Experimental Information of Diamond

The available experimental information which is relevant for this work is presented in column 1 of Table IV. After estimating the size of the correlation corrections, our best guesses at reasonable HF results are given in column 2. We shall now discuss the entries to these columns in some detail. These discussions will provide a reference from which to view the actual computational results.

The experimental width[36] of the valence bands corresponds to the $\Gamma_{25'v} - \Gamma_{1v}$ energy difference. The experimental width[37] of the p-like valence bands should very roughly correspond to the $\Gamma_{25'v} - X_{1v}$ energy difference. We obtain the corresponding entries in column 2 by using the fact that the HF bands are approximately 50% wider than experiment.

The direct band gap at Γ is 0.54 Ry, while the indirect gap from $\Gamma_{25'v}$ at (0, 0, 0) to Δ_{1c} near (0.75, 0, 0) is around 0.40 Ry.[38] The bottom conduction band thus dips in going from Γ along (x, 0, 0) to a minimum somewhere between (0.5, 0, 0) and (0.75, 0, 0) and then rises again to the X point (1.0, 0, 0). To monitor this shape, Table V contains results for the bottom conduction band for three intermediate zone points between Γ and X. Kunz and co-workers[19] find in alkali halides that correlation corrections raise the valence band by roughly 2 eV and lower the conduction bands by 2 eV, giving a net narrowing of the band gap of roughly 4 eV. Correlation corrections are expected to be larger in a covalent material such as diamond. Thus we estimate that the correlation corrections will narrow the diamond HF band gaps by somewhat more—say 4–8 eV.

The first-order density matrix is stationary through first order under correlation corrections. We consequently expect only small changes in the Fourier transforms of the charge density from the experimental values.[39]

TABLE IV. Diamond HF calculational results. Column 1 gives some cogent experimental information on diamond. Column 2 contains our best estimates of HF properties of diamond. The Gaussian exponents are of the $4s$-$3p$ LBF's, except for the last column, where the $3s$-$2p$ LBF exponent is also given. The three- and four-center parameters give the shells from the atom at zero through which three-center integrals are done exactly rather than approximated, and within four-center integrals are approximated rather than zeroed. The n and y indicate whether monopole and dipole corrections are not (no) or are (yes) included. The SCF row gives the eigenvalue for the top of the valence band as it comes from the SCF. All other band eigenvalues are then given relative to this level. The Fourier transform of the charge density are in electrons per crystallographic unit cell. The last rows give the total energy ϵ per atom, the binding energy BE per atom, the virial coefficient, and the pressure-volume product. All energies are in rydbergs.

	1	2	3	4	5	6	7	8	9	10	11	12	13
α	Expt.	Uncorr.	0.45	0.45	0.45	0.40	0.40	0.36	0.36	0.40	0.45	0.317	0.65/0.40
N atoms			29	29	29	29	29	47	47	47	47	47	47
3 center			2	2	2	2	2	2	3	3	3	3	3
4 center			4	4	4	0	4	4	7	7	7	7	7
monopole			n	y	y	y	y	y	y	y	y	y	y
dipole			n	n	y	y	y	y	y	y	y	y	y
SCF $\Gamma_{25'v}$			−5.36	0.44	−0.21	−0.21	−0.20	−0.32	−0.40	−0.36	−0.30	−0.42	−0.41
$1s$			−21.89	−22.01	−22.05	−22.11	−22.09	−21.94	−21.97	−21.97	−21.96	−21.95	−21.97
Γ_{1v}	−1.5	−2.2	−3.43	−2.17	−2.11	−2.20	−2.15	−2.06	−2.17	−2.17	−2.15	−2.16	−2.15
$\Gamma_{25'v}$			0	0	0	0	0	0	0	0	0	0	0
X_{1v}	−0.7	−1.1	−2.52	−1.44	−1.42	−1.51	−1.46	−1.23	−1.34	−1.36	−1.36	−1.32	−1.34
X_{4v}			−1.84	−0.79	−0.73	−0.70	−0.72	−0.48	−0.61	−0.64	−0.65	−0.58	−0.61
Γ_{15c}	0.54	0.8 − 1.2	2.58	0.91	0.75	0.83	0.68	0.81	1.10	1.07	1.06	1.10	1.10
$\Delta_{(0.25)c}$			2.73	0.97	0.78	0.84	0.74	0.82	1.08	1.07	1.05	1.07	1.08
$\Delta_{(0.5)c}$			2.81	1.11	0.83	0.84	0.83	0.82	1.01	1.02	1.06	1.03	1.00
$\Delta_{(0.75)c}$	0.4	0.7 − 1.0	2.80	1.32	0.86	0.77	0.78	0.81	1.04	1.09	1.16	1.07	1.02
X_{1c}			2.85	1.63	0.93	0.61	0.73	0.84	1.27	1.33	1.42	1.25	1.22
$\Gamma_{2'c}$			3.02	2.16	1.64	1.85	1.83	1.65	1.93	1.91	1.91	1.97	1.93
$\rho(111)$	3.32	3.32	3.08	3.37	3.39	3.32	3.33	3.28	3.29	3.33	3.38	3.25	3.29
$\rho(220)$	1.98	1.98	1.74	1.91	1.93	1.93	1.93	1.93	1.93	1.93	1.92	1.94	1.93
$\rho(311)$	1.66	1.66	1.57	1.64	1.65	1.67	1.66	1.67	1.68	1.67	1.65	1.69	1.68
$\rho(222)$	0.14	0.14	0.10	0.10	0.10	0.04	0.08	0.08	0.08	0.09	0.11	0.08	0.09
ϵ	−76.23	75.5 − 75.7			−75.648	−75.658	−75.667	−75.647	−75.736	−75.715	−75.670	−75.752	−75.728
BE	0.56	0.2−0.4			0.27	0.28	0.29	0.27	0.36	0.34	0.30	0.38	0.35
$-2T/V$	1.	1.			1.004	1.002	1.002	1.002	1.0005	1.001	1.003	1.0001	1.0006
pv	0.	0.			0.19	0.11	0.12	0.10	0.024	0.066	0.14	0.006	0.029

TABLE V. Contracted Gaussian LBF exponents (in a.u.) and coefficients. The coefficients multiply normalized individual *s* or *p* Gaussians. Parameters are given for the two 1*p* LBF's used in this work. The 3*s*-2*p* Gaussian exponents are taken as 1.0 unless otherwise specified, while the outer 4*s*-3*p* Gaussian exponents are varied.

LBF	α	C
1*s*	16371.074	0.000 229 39
	2439.1239	0.001 775 27
	545.1677	0.009 464 79
	151.0038	0.039 627 65
	47.803 99	0.131 291
	16.435 66	0.320 556 34
2*s*	5.949 118	0.725 218 6
	2.215 878	0.310 460 4
1*p* (I)	40.790 42	0.004 096 98
	9.503 463	0.027 584 77
	2.940 836	0.106 354 35
1*p* (II)	24.178 81	0.040 811 33
	5.763 492 5	0.233 709 81
	1.799 482 1	0.815 896 7

The diamond experimental binding energy of 7.6 eV/atom is well known.[40] The free-atom correlation energy has been calculated to be 0.316 Ry for the atomic configuration $^3P_0$.[41] One would expect an increase in correlation energy in going from the atom to the crystal. In the C_2 molecule, the correlation energy is 0.415 Ry/atom,[42] an increase of 0.1 Ry/atom over the atomic correlation energy. This gives us very roughly the correlation correction for one C-C bond, so that for the four diamond bonds we could expect an increase in correlation energy of from 0.2 to 0.4 Ry/atom over the atomic correlation energy. Subtracting out this correlation enhancement, we arrive at an estimated range of from 0.16 to 0.36 Ry/atom for the crystalline HF binding or cohesive energy. Adding this to the HF energy for the atom of 75.375 Ry,[31] we get the estimated total energy per atom given in Table IV.

A good measure of the quality of a HF calculation is the degree to which the virial theorem

$$-2(\langle T\rangle/\langle V\rangle)=1.0 \tag{50}$$

is satisfied for the experimental lattice constant. Because the electrons and nuclei comprise a system in equilibrium, the virial theorem for the combined system should be satisfied. The expectation value of the potential energy $\langle V\rangle$ can easily be calculated. The expectation value of the kinetic energy $\langle T\rangle$ is that of the electrons alone when the nuclear masses are assumed infinite. The virial theorem should thus be satisfied at the equilibrium lattice constant, and the *pv* (pressure-volume) product

$$pv=\tfrac{2}{3}\langle T\rangle+\tfrac{1}{3}\langle V\rangle\ , \tag{51}$$

which reflects the nonequilibrium forces on the nuclei,[43] should also vanish there. Since the equilibrium lattice constant is stationary to first order under correlation corrections, we can expect a good HF calculation to give a virial ratio close to 1.0 and a *pv* product close to 0.0 when the total electronic energy is minimized at the experimental lattice constant. In all of these calculations, we use a lattice constant of 3.56 Å.

B. Study of Computational Parameters

The LBF basis set parameters were chosen from the unpublished tables of Huzinaga,[31] who compiled an extensive collection of optimized atomic basis sets for both Gaussian and Slater LBF's. Our choices for the 1*s*, 2*s*, and 1*p* LBF's consist of sets of 6, 2, and 3 contracted Gaussians, respectively. Here 1*p* refers to the first *p* LBF rather than to principle quantum number 1. The coefficients and exponents are given in Table V. The coefficients for normalized spherical harmonic Gaussians can be directly used as coefficients for normalized Gaussian lobe functions. Individual Gaussians were chosen for the 3*s*, 4*s*, 2*p*, and 3*p* LBF's in order to allow maximal variational freedom in the bonding region. The 3*s* and 2*p* Gaussian exponents are fixed at 1.0 for most of the calculations to maintain approximate even-temperedness for the exponents. The 4*s* and 3*p* Gaussian exponents are varied in the range from 0.36 to 0.45, but are kept equal to each other to aid them in joining together to make an *s*-*p* bonding wave function

The number of shells of atoms over which integrals are performed and over which symmetry sets are constructed depends upon the Gaussian basis chosen. Loose Gaussians overlap considerably, requiring one to use more shells of atoms than is necessary with tighter Gaussians. A convenient way of determining the required number of shells of atoms is to calculate the determinant of the Bloch-function overlap matrix for each of 19 Brillouin zone points for increasing numbers of shells. The more nearly converged the determinants are, the more reliable are the calculational results. For example, for our choice of basis, the overlap determinants for four shells (29 atoms) are converged to within 10% of the fully converged determinants for outer *s* and *p* exponents of 0.40; to within 25% for an outer exponent of 0.36; and several determinants are negative for an exponent of 0.32. When six shells (47 atoms) are included, the Bloch-function overlap determinants are converged to within 0.5%, 2%, and 5%, respectively, for the same series of exponents. In the first calculations, we use four shells in order in inexpensive study computational questions. We then use six shells for the calculations which follow.

We find that between five and ten SCF iterations at 19 zone points are necessary to converge the eigenvalues to 0.002 Ry. Initially, however, we use six iterations at six zone points to get the SCF started. We find that it is quite helpful to update the first-order density matrix coefficients after each zone point is calculated, rather than at the end of each full iteration. This has the effect of speeding up convergence by reducing the oscillations in the coefficients which would otherwise occur.

We have studied the dependence of the calculational results upon the number of Brillouin zone points over which the first-order density matrix coefficients are averaged. We have done SCF calculations for 6, 10, 19, and 28 symmetry-independent zone points in $\frac{1}{48}$ of the first Brillouin zone. The eigenvalues for six zone points differ around 0.02 Ry from those for 28 zone points. However, the eigenvalues for 19 zone points and those for 28 zone points agree to within 0.003 Ry. The charge-density Fourier coefficients vary in the third decimal place from 6 to 28 zone points. Consequently, for the results reported in this paper, we have always averaged the first-order density matrix coefficients over 19 Brillouin zone points.

Next, let us consider the importance of monopole and dipole corrections. Results for which both monopole and dipole corrections are ignored are given in column 3 of Table IV. The full nuclear charge was used for all nuclei within four shells of both atoms *a* and *b* in the electron-nuclear integrals. The resulting electron eigenvalues are 5 Ry too low because of this uncompensated nuclear charge. The direct band gap is 2 Ry too wide, the valence band is much too wide, and the charge density is extremely warped. The results are completely unacceptable.

Monopole corrections have been applied in column 4 of Table IV. Note that the charge density is greatly improved and that the band gap now has a reasonable value. However, the eigenvalue corresponding to the top of the valence band has apparently overshot, since it is now positive. This is physically unreasonable as it implies a negative work function. Moreover, although we do not illustrate it in the tables, when the outer Gaussians are made progressively looser, the band gap gets continuously smaller, almost reaching the experimental value for an outer Gaussian exponent of 0.32.

The dipole corrections, applied in column 5 of Table IV, compensate for the imbalance noted above. We can no longer decrease the band gap by decreasing the exponent of the outermost Gaussians. The top valence band is now at a negative absolute energy (relative to infinity). The bottom conduction band from Γ to X has leveled off somewhat, although its minimum is still incorrectly at Γ. Thus the dipole corrections, while much smaller than the monopole corrections, are still very significant, and cannot be ignored. However, they are so much smaller than the monopole corrections that higher-order corrections can safely be ignored. They are sufficiently large, however, that more care should be exercised in calculating them. Our prescription in this paper is a casual one, in that we assume all of the distributed electron charge to be concentrated halfway between the two atoms of the associated symmetry set. This clearly gives an overestimate of the dipole moments.

Two parameters determine the way in which we treat three- and four-center integrals. The shell of the center which is furthest from the atom at zero is found and compared to the three- or the four-center parameter. The three-center parameter gives the shell beyond which three-center integrals are approximated. The four-center parameter gives the shell within which four-center integrals are approximated rather than zeroed. We never zero three-center integrals (within the shells of atoms specified) and never do any four-center integrals exactly. However, we do not recommend the above method for deciding how the three- and four-center integrals are to be calculated and, in fact, we intend to abandon it. It is not a symmetric criterion in terms of the four atoms comprising the two symmetry sets, focusing as it does on the atom at zero. Furthermore, a good criterion would not always treat all *s* and *p* functions alike. We now feel that the decision to approximate three-center or to zero four-center integrals should depend on the looseness of the functions as well as on the relative location of their centers. We intend to address this problem in the near future. However, let us now consider the results as we have calculated them with this criterion.

Columns 6 and 7 of Table IV demonstrate the unimportance of the four-center integrals. In column 6, all of the four-center integrals are zeroed. In column 7, the four-center integrals are approximated when all four centers are within three shells of the atom at zero. We see that the charge density is unaffected. The valence bands also show only small changes, while slightly larger differences occur in the conduction band. We conclude that the four-center integrals can be safely approximated, and that the outer shell four-center integrals can be safely zeroed. Dipole and monopole corrections should, in fact, help compensate for the loss of these integrals.

The importance of the three-center integrals is illustrated in columns 8 and 9 of Table IV. When three-center integrals involving atoms in the third shell are done correctly rather than approximately, the band gap changes 0.3 Ry to a more reasonable value, and the conduction band from Γ to X obtains the correct dip. The changes in the results from exactly calculating integrals through two shells compared with those in which integrals are calculated exactly through three shells are sufficiently large that we cannot dismiss the possibility that parts of the fourth shell are also important. However a better method for determining which integrals can be approximated must be developed before this investigation will be economically feasible.

The statements regarding the effects of three- and four-center integrals in the preceding two paragraphs may seem unduly strong since the effect on the results in the two cases is about the same. However, we contend that zeroing all four-center integrals over the inner three shells is a much more drastic step than computing three-center integrals involving atoms in the third shell exactly rather than approximately. Thus we feel justified in calling one effect small and the other large.

C. HF Diamond Results

In this section we present results for the best sets of computational parameters, as determined from Secs. III A and III B. Integrals are calculated over six shells of atoms (47 atoms). All four-center integrals are approximated, while three-center integrals are calculated exactly through the third shell. The first-order density matrix coefficients are averaged over 19 zone points.

The outer $4s$-$3p$ Gaussian exponent is varied in columns 9 through 11 of Table IV from 0.36 to 0.45. The total energy per atom is lowest at 0.36, and the virial theorem is closest to being satisfied. However, the (111) Fourier coefficient of the charge density has moved slightly below the experimental value, crossing at 0.40. The dip in the conduction band from Γ to X also gets increasingly better as the outer Gaussians get looser. When we fit the total energy versus the $4s$-$3p$ Gaussian exponent to a parabola, we find that the predicted exponent for which the total energy is a minimum is 0.317. In column 12, we present results for 0.317. We caution the reader, however, that the determinants of the overlap matrices are not well converged here, being off by as much as 10% at the X point. We consequently do not consider these results as being as reliable as the others.

In column 13 of Table IV, variational freedom has been given to the low-density region of the crystal in a different way. The basis now contains the second $1p$ LBF contracted Gaussian set given in Table V, Gaussians with exponents of 0.65 and 0.40 are used for the $3s$-$2p$ and the $4s$-$3p$ LBF's, respectively. The reason for using the second $1p$ LBF rather than the first is to maintain approximate even-temperedness in the Gaussian exponents. The total energy and virial are not quite as good as we obtained with the (1, 0.36) exponents, but are better than with the (1, 0.40) exponents. The charge density matches the (1, 0.36) results. The valence and low conduction band energies match the (1, 0.317) column closely. There seems to be an over-all uncertainty in the valence and low conduction band energies of about 0.05 Ry from run to run. Several of the higher conduction bands (not shown in the table) come down as much as 1 Ry from the (1, x) exponent set to (0.65, 0.40). For example, the second nondegenerate conduction band at Γ moves from 4.44 Ry at (1, 0.317) to 3.38 Ry at (0.65, 0.40). The extra variational freedom in the low-density region has much more effect on the conduction bands than on the ground-state results.

We see from the table that more variational freedom is still called for in the interstitial regions. Neither the (1, 0.317) nor the (0.65, 0.40) supplied enough variational freedom to produce a minimum in the total energy. (Extrapolating the 0.40, 0.36, and 0.317 results predicts a still lower total energy for an outer exponent less than 0.317.) However, using looser Gaussians would require more than six shells of atoms. It would probably be more efficient to introduce LBF's centered away from atom sites in the bonding region.

The over-all results are quite good, although they are surely not the definitive last word on the HF band structure of diamond. The ground-state results vary little when the Gaussian exponents are varied. The closeness of the virial coefficient to 1.0 and the smallness of the pv product at the experimental lattice constant are reassurance that the computational model has integrity. The band gap is reasonable. The dip in the bottom conduction band from Γ to X is less than experiment, but the shape is correct, and the detailed effects of correlation are unknown. The HF binding energy is reasonable, but is on the high side. The charge densities are fairly good, although the (111) charge density seems low. The total widths of the valence bands are about 50% enhanced, as they should be.

IV. CONCLUSIONS

Good crystalline HF calculations are a necessary step towards highly refined crystal calculations on ground-state and excited-state properties. We have developed a HF formalism which utilizes crystalline symmetry to store integrals economically, and which reduces the number of integrals which must be done to a minimum. We described an approximation procedure for two-electron integrals which works well for four-center integrals, but which must be applied with caution to three-center integrals. We have demonstrated that a good HF calculation can be done on diamond if we neglect one- and two-electron integrals over atoms separated by more than six shells. Monopole and dipole compensation make the zeroing of these integrals unimportant. Our best results on diamond agree well with our expectations.

Work must still be done to better treat the dipole compensation, and to develop better criteria for approximating and zeroing two-electron integrals. A by-product of this work will hopefully be an economical treatment of multicenter integrals involving core LBF's. This would allow reasonable HF calculations to be done further down in the periodic table. Additionally, it seems that interstitial LBF's should be included in the basis to increase the variational freedom in the bonding region.

We have done all of the integrals which are necessary for a correlated crystalline calculation. However, we have thrown away information by storing them according to the symmetry sets of the first-order density matrix. If these same integrals are stored according to the symmetry sets of the second-order density matrix, correlated crystalline calculations involving perhaps CI methods should be feasible.

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PHYSICAL REVIEW B VOLUME 7, NUMBER 2 15 JANUARY 1973

Hole Transport in Pure NiO Crystals

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The drift mobility of excess holes has been investigated in undoped NiO crystals using a transient technique with electron-beam excitation. Specimens with low-impurity content were grown epitaxially from the gas phase. At room temperature μ_h lies between 20 and 50 cm^2 V^{-1} sec^{-1}, and its temperature dependence shows that scattering by optical modes predominates. The results lead to a phonon energy of 0.055 eV, a polaron effective mass of $1.5m_0$, and a coupling constant of 1.6.

In spite of a great deal of work during the last two decades, the detailed nature of the electronic transport properties of NiO and of other transition metal oxides, is by no means clear. Most of the interpretable transport data on NiO have been obtained from dc conductivity and thermoelectric power measurements on Li-doped and undoped crystals[1,2] and ceramic specimens.[3] In the exhaustion range of the Li acceptors ($\simeq$ 1200 K), a hole drift mobility μ_h of about 0.4 cm^{2}V^{-1}sec^{-1} has been deduced by several authors, whereas room-temperature determinations have led to values between 0.5 and 5 cm^{2}V^{-1}sec^{-1}. The form of the temperature dependence of μ_h is not well established and depends largely on the assumptions made concerning the temperature dependence of the density of states. A detailed analysis of available transport data, and of the Hall mobility problem, has recently been carried out by Bosman and van Daal.[4] It led to the conclusion that the transport of free holes in NiO takes place in a relatively wide band and is describable on the basis of the large-polaron model. This is also in general agreement with the discussion of Adler and Feinleib.[5]

In the present state of the subject it appeared of some interest to provide independent transport results by an essentially different experimental method. Transient drift-mobility techniques are a very direct approach, which have been widely used in transport studies on molecular crystals and liquids and on amorphous solids.[6] Two previous attempts have been made to determine the drift mobility of photogenerated holes in NiO.[7,8] A value of about 0.3 cm^{2}V^{-1}sec^{-1} was obtained at room temperature, which must be regarded as a lower limit; however, in the absence of any measurements on the temperature dependence of μ_h, no further conclusions could be drawn.

The present work was stimulated by the fact that NiO crystals of considerably improved purity had become available. The crystals were produced by epitaxial deposition from the gas phase and further details are given in the paper by Lubezky and Tannhauser.[9] Analysis by emission spectroscopy showed that in the specimens used here the total metal impurities lay below 50 ppm (by weight). Neutron-activation analysis indicated a bromine content of 25 ppm or less.

In the following experiments an electron-beam technique was used[6] in which excess carriers were generated within a few μm of the specimen's top electrode by a 45-keV electron pulse of 15-nsec duration. Holes were extracted from this region by a synchronized field pulse, and their transit