PHYSICAL REVIEW B VOLUME 8, NUMBER 8 15 OCTOBER 1973

Hartree-Fock Lattice Constant and Bulk Modulus of Diamond

G. T. Surratt, R. N. Euwema, and D. L. Wilhite*

Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio 45433

(Received 8 December 1972; revised manuscript received 2 April 1973)

The equilibrium lattice constant and bulk modulus of diamond are calculated in the Hartree-Fock approximation to be 3.545 Å and 4.38×10^{12} dyn/cm^2, respectively. These values compare very well with the experimental values of 3.567 Å and 4.42×10^{12} dyn/cm^2. A comparison of the bulk modulus obtained from the pressure-volume product and from the total energy is made. The results are compared with other calculations which use local-density exchange operators. In addition, a new procedure for handling the two-electron integrals is presented with a computational test of the method.

I. INTRODUCTION

While there is great interest in understanding such things as phonon spectra, electron-phonon interactions, and the effects of phonons on optical transitions, very little serious attention has been paid to the ground-state energetics of solids. Until recently the main area of interest in computational solid-state physics has been the description of the energy band structure and optical properties.[1] While Löwdin[2] performed pioneering calculations on ground-state energetics (total energy as a function of nuclear position) using an exact linear-combination-of-atomic-orbitals (LCAO) method, most recent calculations have been based on the currently used band-structure methods. These methods employ local-density-exchange approximations in some form.[3-5] The success of these methods can only be described as moderate. The energy expression in each case is dependent on the choice of the coefficient which multiplies the local-exchange operator.[6,7] Either some convenient choice of this parameter is made, or some auxiliary condition on the energy expression is invoked.[8,9] Recently, however, methods have been developed by Kunz[10] and by the present authors[11] (Ref. 11 is hereafter referred to as I) which allow one to solve the Hartree–Fock equations for crystalline materials. The formalism of Kunz is based on the use of the Adams–Gilbert local-orbital formalism,[12,13] while that of the authors is a canonical Hartree–Fock technique patterned after the self-consistent-field (SCF) methods pioneered by Roothaan.[14] In these methods there is no adjustable-exchange-coefficient problem since the exchange is done exactly. The problem does remain, however, as to whether or not a Hartree–Fock calculation could be expected to give good ground-state properties. Calculations on diatomic molecules would seem to indicate that one was doomed to failure.[15] While occasional good agreement is obtained for molecular force constants, some results differ from experiment by as much as 60%. However, a few recent calculations on polyatomic systems have given quite good agreement with experiment for totally symmetric motion.[16]

In this work, the basic method outlined in I is used with modifications as discussed in detail in the Appendix. First, two methods of determining the bulk modulus and lattice constant are presented. The computational procedure is then outlined and the results are discussed. The results from the two methods are compared and a comparison with other calculations and with experiment is made. Overall, the agreement with experiment is quite good. Moreover, there is no ambiguity here due to the choice of an exchange parameter.

II. BULK MODULUS AND PRESSURE-VOLUME PRODUCT

The bulk modulus B is defined by the relation

$$U(a)=\tfrac{1}{2}B\delta^2, \tag{1}$$

where $U(a)$ is the energy per unit cell, δ is the dilation, and a is the lattice constant. We can also express $U(a)$ as

$$U(a)=\frac{1}{2}\,\frac{d^2U(a)}{da^2}\bigg|_{(a-a_0)^2} \tag{2}$$

near equilibrium. Using the relation for cubic crystals

$$\delta=3(a-a_0)/a_0\,, \tag{3}$$

one obtains the usual relation for B:

$$B=\frac{a_0^{\,2}}{9}\,\frac{d^2U(a)}{da^2}\bigg|_{a=a_0}. \tag{4}$$

Thus one direct way of obtaining the bulk modulus is to determine the energy per unit cell for a number of lattice constants, fit this data to some curve, and then determine the second derivative at equilibrium. There is an alternative method, however, based on the pressure-volume (pv) product. The derivation of this result follows most easily from the scaling arguments of Löwdin.[17] As he has shown, the scaling of the kinetic (T) and potential (V) energies with the scaling of the coordinates, $\vec{r}_i'=\lambda\vec{r}_i$, is given by

$$T(\lambda)=T(1)/\lambda^2,$$
$$V(\lambda)=V(1)/\lambda. \tag{5}$$

Thus

$$U(\lambda)=T(\lambda)+V(\lambda)=T(1)/\lambda^2+V(1)/\lambda. \tag{6}$$

In addition, the volume scales by the relation

$$v(\lambda)=\lambda^3 v(1). \tag{7}$$

Therefore one obtains

$$p=-\frac{dU}{dv}=-\frac{dU/d\lambda}{dv/d\lambda}=\frac{2T+V}{3v}, \tag{8}$$

$$pv=\tfrac{1}{3}(2T+V)\ . \tag{9}$$

The last relation is obtained by pointing out that for the optimum wave function, no scaling is necessary. Therefore $\lambda=1$ will be the stationary point of the energy. We will return to this scaling argument later. Now, taking the volume derivative of the energy expression (1) and solving as above, we obtain

$$pv=-3B\left(\frac{a-a_0}{a_0}\right), \tag{10}$$

$$B=-\frac{pv}{3}\left(\frac{a_0}{a-a_0}\right). \tag{11}$$

Equation (11) is a second means of determining the bulk modulus and provides a consistency check on the results.

III. COMPUTATIONAL TECHNIQUES

The computational formalism used in the present work is basically the same as that presented in I. The analytic basis set consists of four s- and three p-symmetry contracted-Gaussian-lobe functions for each carbon atom. These functions are used as a basis for Bloch functions,

$$\Phi_{\mu i}^{\vec{k}}(\vec{r})=\frac{1}{\sqrt{N}}\sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}}\phi_\mu(\vec{r}-\vec{R}_c-\vec{T}), \tag{12}$$

the first-order density matrix,

$$\rho(\vec{r},\vec{r}\,')=\sum_{ab\alpha\beta} A_{\alpha\beta}^{ab}\phi_\alpha(\vec{r}-\vec{R}_a)\,\phi_\beta(\vec{r}\,'-\vec{R}_b), \tag{13}$$

and the second-order density matrix,

$$\rho(\vec{r}_1,\vec{r}_2\,|\,\vec{r}_3,\vec{r}_4)=\sum_{\substack{abcd\\ \alpha\beta\gamma\delta}} B_{\alpha\beta\gamma\delta}^{abcd}\phi_\alpha(\vec{r}_1-\vec{R}_a)\times\phi_\beta(\vec{r}_2-\vec{R}_b)\,\phi_\gamma(\vec{r}_3-\vec{R}_c)\phi_\delta(\vec{r}_4-\vec{R}_d). \tag{14}$$

In the above equations, $\vec{k}$ labels a Brillouin zone point, the $\vec{T}$ sum is over all crystal translations, and N (which does not appear in the working equations) gives the number of cells in the crystal. The use of crystalline symmetry—rotations, inversions, and translations—greatly reduces the number of independent A's and B's. Only one two-electron integral need be evaluated for each independent B, while one-electron overlap, kinetic and nuclear integrals need only be done for each independent A. The SCF procedure of Roothaan[14] is used. The Hamiltonian and overlap matrices are constructed in terms of the Bloch basis functions, zone point by zone point. The resulting eigenfunctions then determine new A's.

In I, an approximation procedure is given for some of the smaller two-electron Coulomb integrals. Each local-basis-function (LBF) product charge distribution for every lobe-lobe pair is approximated by a single Gaussion located at the center of charge with the correct total charge. The Gaussian exponent is least-squares fit to the correct charge distribution. Thus the procedure is exact for uncontracted Gaussians, and is charge conserving for contracted Gaussians. Only one least-squares fit need be made for each lobe-lobe pair for each independent A. In our previous work, complicated criteria involving the number of centers were used to decide which three- and four-center integrals would be done exactly and which would be approximated. In the present work, only the magnitude of the integrals is considered. All two-electron integrals less than 10^{-6} are zeroed, all between 10^{-4} and 10^{-6} in magnitude are calculated approximately, all greater than 10^{-4} are calculated exactly. A more complete discussion of this approximation, as well as a computational test of the parameters involved, is given in the Appendix.

In the present calculation, LBF products are ne-

TABLE I. Contracted Gaussian LBF exponents (in a.u.) and coefficients. The contraction coefficients multiply normalized individual s and p Gaussians. This is the basis for 3.56 Å. The scaled exponents of the two outer Gaussians are given in Table II.

LBF	α	C
$1s$	16371.074	0.00022939
	2439.1239	0.00177527
	545.1677	0.00946479
	151.0038	0.03962765
	47.80399	0.131291
	16.43566	0.32055634
$2s$	5.949118	0.7252186
	2.215878	0.3104604
$3s$	0.85	1.0
$4s$	0.36	1.0
$1p$	24.17881	0.04081133
	5.7634925	0.23370981
	1.7994821	0.8158967
$2p$	0.85	1.0
$3p$	0.36	1.0

TABLE II. The effect of scaling the two outer Gaussian exponents on the determinant of the overlap matrix. The determinants are in units of 10^{-6}.

Lattice constant (Å)		3.46	3.51	3.56	3.61	3.66
Scaled exponents		0.89984	0.87439	0.8500	0.82662	0.80419
		0.38111	0.37033	0.3600	0.350097	0.34060
Zone point						
1	5th NN[a]	0.27514	0.34421	0.42641	0.52337	0.63666
	Exact	0.26665	0.33374	0.41364	0.50792	0.61815
	% Difference	3.18	3.14	3.09	3.04	3.00
2	5th NN	0.51719	0.64296	0.79127	0.96450	1.1650
	Exact	0.53726	0.66760	0.82122	1.0006	1.2080
	% Difference	3.74	3.69	3.64	3.61	3.56

[a] Calculated including interactions to fifth-nearest neighbors.

glected in (13) and (14) when they are separated by more than the fifth-nearest-neighbor distance. To compensate numerically for this neglect, monopole and dipole compensation terms are introduced exactly as in I. A further discussion of these computational boundary corrections can be found there.

As in I, 19 inequivalent Brillouin-zone points corresponding to 256 mesh points in the first Brillouin zone were used to determine the first-order density matrix coefficients A. It was demonstrated in I that this is a more than adequate sampling of the zone.

The basis set for a lattice constant of 3.56 Å is given in Table I. For other lattice constants, the exponents of the two outer uncontracted s- and p-symmetry Gaussians were then scaled so that the exponent times the lattice constant squared was constant. This procedure assured that the overlap matrices were converged to the same extent at the various lattice constants. The effect for the determinants of the overlap matrices for the Γ and X points is illustrated in Table II. The determinants are not fully converged since overlap integrals are only done for LBF's within the fifth-nearest-neighbor distance of each other. The determinants of the overlap matrices for the 19 Brillouin-zone points used in this calculation were typically 1.5% from convergence, Γ and X being the worst cases at about 3% from convergence.

TABLE III. Hartree–Fock results for the various lattice constants. Energies are in Ry. Other units are as noted.

Lattice constant (Å)	3.46	3.51	3.56	3.61	3.66
Eigenvalues					
$\Gamma_{25'v}$	−0.36441	−0.39017	−0.41835	−0.45530	−0.46364
Γ_{1v}	−2.63759	−2.61577	−2.59145	−2.56694	−2.54637
Γ_{15c}	0.70452	0.66590	0.63574	0.62196	0.57179
X_{4v}	−1.03440	−1.03557	−1.03742	−1.03363	−1.03590
X_{1v}	−1.77631	−1.77015	−1.76743	−1.76287	−1.75929
X_{1c}	0.91612	0.86470	0.81978	0.77400	0.73034
$L_{3'v}$	−0.67306	−0.69057	−0.70638	−0.72054	−0.72799
L_{3c}	1.09667	1.05080	1.01031	0.96935	0.92120
Δ_{1c} (min)	0.66374	0.62245	0.59167	0.56857	0.52317
Position of Δ_{1c} (min)[a]	0.5169	0.4964	0.4759	0.4965	0.4853
Total energy	−75.71218	−75.71485	−75.71484	−75.71422	−75.70975
$-2T/V$	1.002716	1.001523	1.0004226	0.999499	0.998435
pv	0.13749	0.07982	0.02134	−0.02527	−0.0788
$\rho(111)$[b]	3.2076	3.2316	3.2559	3.2812	3.3034
$\rho(222)$	0.07899	0.07982	0.08065	0.08201	0.08200

[a] Position of Δ_{1c}(min) in terms of α in the expression $(2\pi/a)$ $(\alpha,\ 0,\ 0)$.

[b] Units of electrons per crystallographic unit cell.

TABLE IV. Least-squares fits to the total energy and the pressure-volume product. The coefficients are for the polynomial $P(x) = C_0 + C_1x + C_2x^2$.

Fit to		C_0	C_1	C_2	a_0 (Å)	B (10^{12} dyn/cm^2)
Energy	5 point	−70.362672	−3.018071	0.425429	3.547	4.647
Energy	3^5 point	−70.365186	−3.016579	0.425208	3.547 ± 0.0019	4.644 ± 0.271
Energy	4 point	−70.678065	−2.84243	0.40100	3.544	4.384
Energy	3^4 point	−70.721038	−2.817778	0.397463	3.545 ± 0.003	4.385 ± 0.306
pv	5 point	3.83441	−1.06968	0.0	3.5846	5.5714
Experiment					3.567[a]	4.42[b]

[a] Reference 18.

[b] Reference 17.

IV. RESULTS

The experimental value for the bulk modulus is determined from the elastic constants by the standard formula $B = (c_{11} + 2c_{12})/3$. The elastic constants are those of McSkimin and Bond.[18] The experimental lattice constant is 3.567 Å, determined by Thewlis and Davey.[19]

The calculation was performed for five different lattice constants, as described above. These results are given in Table III. The total energy per atom was then least-squares fitted to a parabola and the pv product was least-squares fitted to a straight line. These results are given in Table IV. The energy curve was further analyzed in the following way. It was noted that a few points differed from the least-squares curve by about 0.0003 Ry. This tolerance was added to and subtracted from each energy, and the resulting 3^5 sets of points were each least-squares fitted to a parabola. The equilibrium lattice constant a_0 and bulk modulus B were also determined for each parabolic fit. The resulting a_0's and B's were then averaged using a weighting factor which was inversely proportional to the deviation of the parabola from the particular set of points. The resulting mean values and standard deviations are given in Table IV. The apparent disagreement between the direct determination of B and the pv product determination will be discussed in Sec. V.

On examining the eigenvalues as a function of lattice constant, a discrepancy was noted in the results for 3.61 Å. The occupied states were all shifted down in energy while the unoccupied states were shifted up. The determinant of the overlap matrix showed no unusual effects. The point was completely recalculated with the same results. However, in both cases the charge-density coefficients oscillated in the SCF cycle and were averaged to force convergence. No apparent reason for this numerical instability was discovered, so the data was reanalyzed, this time excluding the point at 3.61 Å. These results are also given in Table IV. The plots of the fitted curves are given in Fig. 1. The curves are for the 3^5 and 3^4 fits. The five- and four-point fits superimpose within the width of the line.

In Figs. 2 and 3 we also present the variation of the eigenvalues and eigenvalue differences as a function of lattice constant. The data is fit to a straight line in each case excluding the point at 3.61 Å. The energy and location of the minimum in the conduction band Δ_{1c} was found by fitting the three Δ_1-point eigenvalues to a parabola.[20] The slight disagreement at 3.61 Å can be seen in both figures.

V. DISCUSSION

The first point that should be treated is the obvious discrepancy between the bulk modulus obtained from the energy curve and that obtained from the pv product. Basically the problem is that while the basis set employed here is sufficiently flexible to give a reasonably good minimum energy, it is not complete enough to allow wave-function scaling.

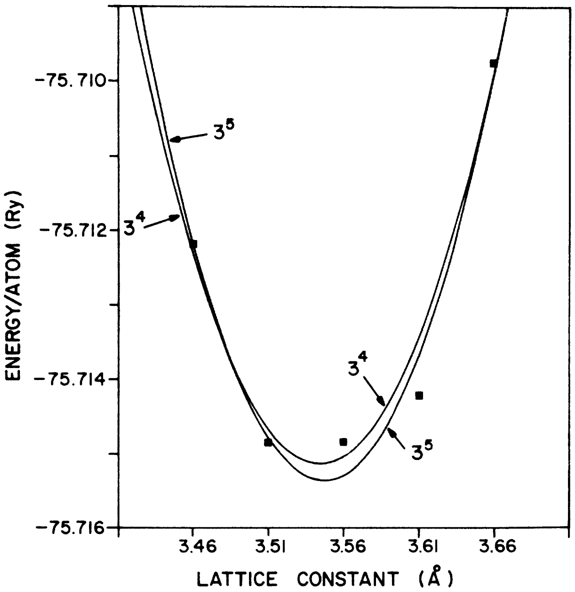

FIG. 1. The least-squares-fitted parabolas for 3^4 and 3^5 points. The calculated points are denoted by ■.

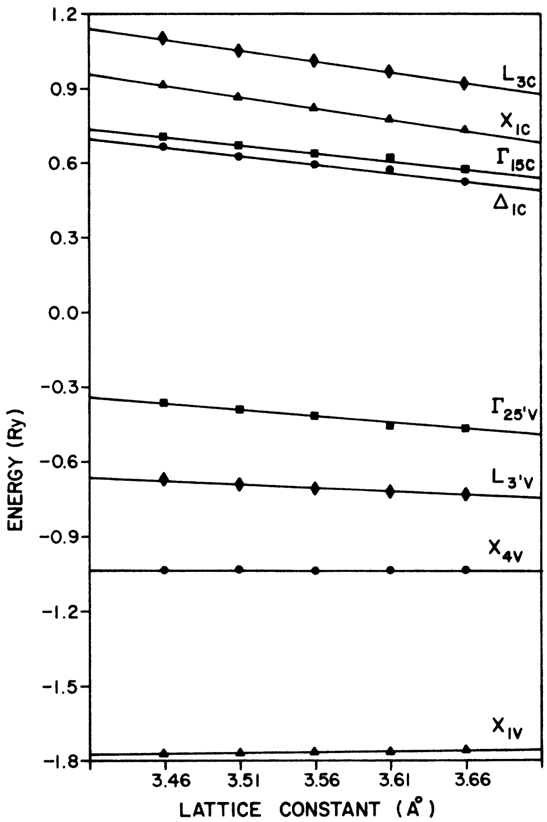

FIG. 2. Hartree–Fock eigenvalues as a function of lattice constant. The symbols represent the calculated points. The lines were fitted excluding the point at 3.61 Å.

One way out of the dilemma is to increase the size of the basis set in the hope that the extra variational freedom will provide the necessary scaling. This, too, fast becomes intractible in a system of this size. One is therefore forced to rely on the fact that the energy is a relatively insensitive quantity (corrections to it being of second order for the true Hartree–Fock wave function).

We have reported two values for the bulk modulus and the lattice constant as derived from the total energy, and so one might ask which one is correct. The answer, of course, is neither. The values obtained from the five-point fit are probably close to the true Hartree–Fock values. This guess is based on the fact that force constants calculated for molecules are almost always slightly higher and the bond lengths are usually slightly less than experiment.[15] The values obtained from the four-point fit are probably indicative of the correct answer for this level of calculation, with the various computational boundary corrections, as discussed in I. In any event, both results are within 1 standard deviation of each other, and within 5% of experiment.

The only other bulk modulus calculation for diamond is that of Goroff and Kleinman.[4] Their orthogonalized-plane-wave (OPW) calculation used Slater's exchange potential. Their results are compared with those of this work in Table V. A few points about their calculation should be made. First, only 133 OPW's were used in their calculation. In light of later OPW studies,[21] the convergence of this calculation with respect to the plane-wave basis is poor. Second, Goroff and Kleinman include a correlation correction in their calculation. They obtain a result for both Nozieres–Bohm–Pines and Gell-Mann–Breuckner correlation corrections. The use of a correlation correction in addition to Slater's exchange, which presumably includes some correlation, is questionable. In fact, in their work, unlike the present work, the correlation correction is necessary to obtain a reasonable description of the bulk modulus and lattice constant. We have redone the Goroff–Kleinman bulk modulus by fitting the uncorrelated energies to a parabola in the same manner that we treated our data. This result is also given in Table V. This probably represents a more accurate OPW value.

One important point which should be made is that

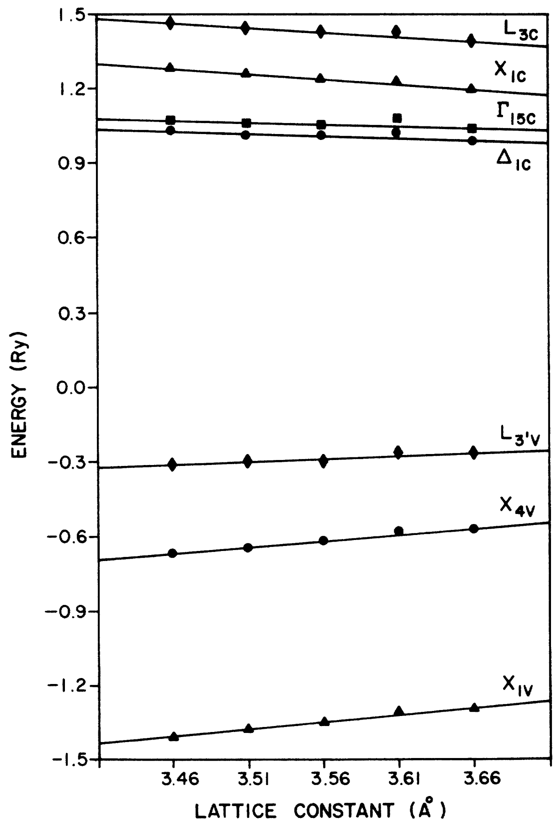

FIG. 3. Hartree–Fock eigenvalues relative to the $\Gamma_{25'v}$ state as a function of lattice constant. The symbols represent the calculated points. The lines were fitted excluding the point at 3.61 Å.

TABLE V. Comparison of calculated and experimental lattice constants and bulk moduli.

	a_0 (Å)	B (10^{12} dyn/cm^2)
GK[a] (Nozières–Bohm–Pines correlation)	3.515[b] 3.544	3.04 4.69
GK (Gell-Mann–Brueckner correlation)	3.569 3.576	3.16 4.69
GK (Slater exchange only)[c]	3.611	3.74
This work 4-point	3.544	4.38
5-point	3.547	4.64
Experiment	3.567[d]	4.42[e]

[a] Reference 3.

[b] The two numbers are for the two different results for each correlation correction obtained by Goroff and Kleinman depending upon the points used to determine the energy parabola.

[c] Determined from Goroff and Kleinman data by least-squares fitting a parabola to all data points.

[d] Reference 18.

[e] Reference 17.

there are no adjustable parameters in the present calculations. This is not the case with the previous determinations of the bulk modulus. These calculations all used some form of the local-density-exchange approximation. Particularly the work of Rudge[3] explicitly shows the scaling of the lattice constant and bulk modulus with the coefficient multiplying the exchange interaction. The recent work of Averill[5] shows this problem as well. He used two reasonable choices for the exchange coefficient and, even though a direct effect on B and a can be seen, neither choice produces the uniformly good agreement with experiment obtained in the present calculation.

VI. CONCLUSIONS

Even though this is the first Hartree–Fock study of ground-state energetics, the results are surprisingly good. While in I we demonstrated that the charge densities were good, this computational test reconfirms the integrity of the method. The new procedure for calculating two-electron integrals proves to be accurate as well as fast. In addition there is no arbitrariness due to the choices of a local-density exchange coefficient.

These results seem to indicate that correlation is not a major factor in the properties calculated for diamond. The effect of correlation on other properties and in other systems remains open until calculations are performed.

ACKNOWLEDGMENT

The authors wish to acknowledge helpful discussions with Dr. A. B. Kunz.

APPENDIX

One major problem, studied in I, is the development of a criterion for choosing which two-electron integrals can be safely approximated and which can be zeroed (and therefore not further processed). In I, the integrals were approximated or zeroed depending solely upon how many different centers for the LBF's were involved. If all three-center integrals were done exactly, for instance, then many small integrals involving essentially nonoverlapping core functions must be done. These integrals could just as easily be done approximately or zeroed. Rather than develop some criterion based on overlap, number of centers, and distance between centers (which was one possibility), it was decided to calculate all integrals approximately, then to zero all integrals smaller than a certain tolerance, T_{zero}, and to recalculate exactly all integrals above a higher tolerance, T_{exact}. This procedure is based on the assumption that the small integrals are multiplied by small charge-density coefficients and so contribute little to the Hamiltonian matrix. This assumption is justified only by showing that the method works. The two-electron integral computation proceeds in the following manner. After deciding how many nearest neighbors to include, the integrals are symmetry analyzed in the manner described in I. This procedure is equivalent to symmetry analyzing the second-order density matrix. All of the symmetry independent integrals

TABLE VI. Test of the integral computation parameters.

T_{exact} T_{zero}	10^{-4} 10^{-8}	10^{-4} 10^{-7}	10^{-4} 10^{-6}	10^{-4} 10^{-5}	10^{-4} 10^{-4}	10^{-5} 10^{-6}	10^{-6} 10^{-6}
$\Gamma_{25'v}$	−0.41822	−0.41830	−0.41849	−0.43241	−0.44023	−0.42072	−0.42087
$\Gamma_{1c}-\Gamma_{25'v}$	1.05241	1.05271	1.05344	1.08385	1.13847	1.05932	1.06025
$X_{4v}-\Gamma_{25'v}$	1.00819	1.00883	1.00950	1.03656	1.08713	1.01224	1.01283
$\Delta_{1c}(.5)-\Gamma_{25'v}$	3.256	3.256	3.256	3.257	3.262	3.255	3.255
Total Energy	−75.71483	−75.71485	−75.71486	−75.71531	−75.70576	−75.71474	−75.71483
$-2T/V$	1.00042	1.00042	1.00042	1.00048	1.00063	1.00041	1.00041
pv	0.0213	0.0212	0.0213	0.0242	0.0216	0.0209	0.0209

TABLE VII. Number of two-electron integrals for basis set in Table I, including interactions to fifth-nearest-neighbor distance.

Number of integrals greater than 10^{-n}	Number in decade	Sum to decade
0	50	50
1	3 346	3 396
2	22 730	26 176
3	96 853	123 029
4	227 799	350 828
5	366 718	717 546
6	457 179	1 174 725
7	497 921	1 672 646
8	501 636	2 174 282
15	···	6 875 548

$$(ab\alpha\beta : cd\gamma\delta) = \int \phi_\alpha(\vec{r}_1 - \vec{R}_a)\phi_\beta(\vec{r}_1 - \vec{R}_b)$$

$$\times 1/r_{12}\phi_\gamma(\vec{r}_2 - \vec{R}_c)\,\Phi_\delta(\vec{r}_2 - \vec{R}_d)\, d\vec{r}_1 d\vec{r}_2$$

are calculated in some standard order using the integral approximation of I. All of the integrals larger than the tolerance $T_{\rm zero}$ are saved (on magnetic tape or disk). The integral set is then reprocessed; this time all of the remaining integrals which are larger than a second tolerance, $T_{\rm exact}$, are recalculated exactly. This second integral set is then transformed into the form of Eq. (44) of I by summing the appropriate integrals and multiplying by the necessary charge-density coefficients. This method, while requiring more steps, actually decreases the integral computation time by a factor of 2 over the previous method. This is mainly due to the speed of the approximate procedure. In addition, the integral set after the second pass contains all of the integrals necessary to go beyond the Hartree–Fock stage, since they are in fact computed and stored according to the symmetry properties of the second-order density matrix.

A computational test of this technique was done in the following manner. A reasonable value of $T_{\rm exact}$ and a low value of $T_{\rm zero}$ were chosen. (The reasonable $T_{\rm exact}$ was determined by small initial calculations.) The results are given in column 1 of Table VI. $T_{\rm zero}$ was then increased until it was equal to $T_{\rm exact}$. The results of these calculations are given in columns 2 thru 5 of Table VI. It is quite evident that there is a "break" above 10^{-6}. The value of $T_{\rm zero}$ was then set at 10^{-6} and $T_{\rm exact}$ was decreased to this value. The results of these calculations are given in columns 6 and 7. In this case there is very little change observed. The parameters were chosen to be $T_{\rm zero} = 10^{-6}$ and $T_{\rm exact} = 10^{-4}$ for subsequent calculations. All of the above calculations were performed using a lattice constant of 3.56 Å, the basis set given in Table I and including interactions to fifth nearest neighbors.

An idea of the time savings involved can readily be deduced from Table VII. Here we see the number of two-electron integrals in each decade, as well as the total number including that decade. As can readily be seen, we save for future processing only $\frac{1}{6}$ of the integrals and recalculate only $\frac{1}{24}$ of the total number. (In fact, the approximate integral calculation need not be carried to completion for every integral since it has a prefactor multiplying an error function. Since the erf is less than or equal to 1, if the prefactor is less than $T_{\rm zero}$, the erf need not be calculated.)

---

[1] *Computational Methods in Energy Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971).

[2] P. O. Löwdin, J. Chem. Phys. **19**, 1570 (1951); J. Chem. Phys. **19**, 1579 (1951) and references therein.

[3] W. E. Rudge, Phys. Rev. **181**, 1033 (1969).

[4] I. Goroff and L. Kleinman, Phys. Rev. **131**, 2574 (1970).

[5] F. W. Averill, Phys. Rev. B **6**, 3637 (1972).

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

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

[8] M. Berrondo, and O. Goscinski, Phys. Rev. **184**, 10 (1969).

[9] K. Schwarz, Phys. Rev. B **5**, 2466 (1972).

[10] A. B. Kunz, Phys. Status Solidi **36**, 301 (1969); J. Phys. C **3**, 1542 (1970).

[11] R. N. Euwema, D. L. Wilhite, and G. T. Surratt, Phys. Rev. B **7**, 818 (1973).

[12] W. H. Adams, J. Chem. Phys. **34**, 89 (1961).

[13] T. L. Gilbert, in *Molecular Orbitals in Chemistry, Physics, and Biology*, edited by P. O. Löwdin and B. Pullman (Academic, New York, 1964); and in *Sigma Molecular Orbital Theory*, edited by O. Sinanoglu and K. B. Wiberg (Yale U. P., New Haven, Conn., 1970).

[14] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).

[15] M. Krauss, *Compendium of ab initio Calculations of Molecular Energies and Properties*, NBS Technical Note No. 438 (U.S. GPO, Washington, D.C. 1967).

[16] R. M. Pitzer, J. Chem. Phys. **46**, 4871 (1967); R. M. Pitzer and D. P. Merrifield, J. Chem. Phys. **52**, 9782 (1970); W. E. Palke, Chem. Phys. Lett. **12**, 150 (1971).

[17] P. O. Löwdin, J. Mol. Spectrosc. **3**, 46 (1959).

[18] H. J. McSkimin and W. L. Bond, Phys. Rev. **105**, 116 (1957).

[19] J. Thewlis and A. R. Davey, Philos. Mag. **1**, 409 (1958).

[20] In units of $2\pi/a$ the Δ points were ((1/4), 0, 0), ((1/2), 0, 0), ((3/4), 0, 0).

[21] R. N. Euwema and D. J. Stukel, Phys. Rev. B **1**, 4692 (1970).