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Exact-exchange Hartree-Fock calculations for periodic systems. III. Ground-state properties of diamond

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The linear-combination-of-atomic-orbitals self-consistent field *ab initio* Hartree-Fock method previously presented [Int. J. Quantum Chem. **17**, 501 (1980)] is here applied to diamond. Using a minimal basis set, total, binding, and correlation energy, equilibrium lattice constant, bulk modulus, band structure, population analysis, x-ray factors, and directional Compton profiles have been calculated. The results are compared with those previously obtained with Hartree-Fock and local-exchange Hamiltonians. A comparison is made for some properties with results for graphite obtained using the same approximation.

I. INTRODUCTION

In a preceding work,[1] hereafter referred to as I, we presented an *ab initio* linear-combination-of-atomic-orbitals self-consistent exact-exchange Hartree-Fock (HF) method for the study of the electronic properties of two- and three-dimensional periodic systems in their ground state. There are essentially three reasons that suggest the use of an HF Hamiltonian: First, it generally provides a good description of the ground state and its properties; second, an extensive HF literature exists, especially concerning atoms and molecules: detailed information is thus available about the quality of the results to be expected with a given basis set, and unambiguous reference data can be used for differential quantities[2]; third, the HF solution is, if not unique, the most natural starting point for further improvements using many-body techniques such as have been applied with success in the study of molecular systems[3] or, in a simplified form, of periodic structures.[4] Our method was first tested with monolayers of graphite and hexagonal boron nitride (see Ref. 5, hereafter referred to as II); the computational problems were discussed, and it was shown that satisfactory results can be obtained for some ground-state properties, even with a minimal basis set.

In this work we present the results for diamond, which allows very accurate comparisons to be made with other *ab initio* calculations[6-10] and with experimental findings.[11-16] After recalling the essential characteristics of the calculation method the results are presented and discussed. They concern total and binding energy, bulk modulus, lattice parameter, population analysis, x-ray factors, Compton profiles, and band structure. The possibility of correcting energy data by means of a density-dependent correlation term is also considered. In many cases a comparison with the corresponding results for graphite is performed: it appears that while the method works well in both cases, the basis set we adopted is particularly well-suited for the more symmetric structure of diamond.

II. THE CALCULATION METHOD

The calculation method has been described in detail in I; we recall here only its most significant aspects. The problem essentially lies in the self-consistent solution of the matrix equations $F(\vec{k})A(\vec{k})=S(\vec{k})A(\vec{k})E(\vec{k})$, one for each $\vec{k}$ sampling point in the irreducible part of the first Brillouin zone (IBZ). $F(\vec{k})$ and $S(\vec{k})$ are the Fock and overlap matrices in the basis set of the Bloch functions obtained from the atomic orbitals in the zero cell by applying the projection operator of the translation group, corresponding to the $\vec{k}$ irreducible representation; $A(\vec{k})$ and $E(\vec{k})$ are the eigenvector and eigenvalue matrices. The general element of $F(\vec{k})$ can be written, indicating by H the one-electron part of the Hamiltonian:

$$F_{12}(\vec{k})=\sum_{\vec{g}} e^{i\vec{k}\cdot\vec{g}} F_{12}^{\vec{g}} =\sum_{\vec{g}} e^{i\vec{k}\cdot\vec{g}}\left(\langle\chi_1^{\vec{0}}|H|\chi_2^{\vec{g}}\rangle+\sum_{\vec{l},3,4}\Pi_{3,4}^{\vec{l}} D_{1,2,3,4}^{\vec{g},\vec{l}}\right). \quad (1)$$

Here 1, 2, 3, 4 are general basis functions indices, $\vec{g}$, $\vec{l}$, $\vec{m}$ are translation vectors of the direct lattice, $\chi_2^{\vec{g}}\equiv\chi_2(\vec{r}-\vec{g}-\vec{s}_2)$ is the atomic orbital with index 2, belonging to the atom identified by fractionary translation vector $\vec{s}_2$ in the $\vec{g}$ cell. $\Pi_{3,4}$ is a pseudodensity matrix defined as follows for a closed shell system:

$$\Pi_{3,4}^{\vec{l}}=2\int_{\mathrm{IBZ}} d\vec{k}\exp(i\vec{k}\cdot\vec{l})\sum_i a_{3i}^*(\vec{k})a_{4i}(\vec{k})\Theta(\epsilon_F-\epsilon_i(\vec{k})), \quad (2)$$

where Θ is the step function, a_{1i} and ϵ_i are elements of the A and E matrices, respectively, and ϵ_F is the Fermi energy. The quantities $D^{\vec{g},\vec{l}}$ appearing in Eq. (1) are symmetrized sums of two-electron integrals which can be obtained as a linear combination, with coefficients depending on the point group of the crystal (see I), of the Coulomb and exchange sums:

$$d^{\vec{g},\vec{l}}_{1,2,3,4}=\sum_{\vec{m}}(\chi_1^{\vec{0}}\chi_2^{\vec{g}}|\chi_3^{\vec{m}}\chi_4^{\vec{m}+\vec{l}})-\tfrac{1}{2}\sum_{\vec{m}}(\chi_1^{\vec{0}}\chi_3^{\vec{m}}|\chi_2^{\vec{g}}\chi_4^{\vec{m}+\vec{l}}). \tag{3}$$

In summary, according to our scheme, symmetry is fully exploited in the preliminary part of the program, when preparing the symmetrized $D^{\vec{g},\vec{l}}$ quantities. In the self-consistent step it is then possible to be confined in the irreducible part of the Brillouin zone by using the pseudodensity matrix $\Pi^{\vec{l}}$, thus avoiding the necessity of reconstructing the eigenvectors throughout the BZ.

When applying the above scheme, one must deal with infinite sums over direct lattice vectors, as shown in Eqs. (1) and (3). Since individual terms in these sums can be far from negligible even for vectors of large modulus, the truncation criteria must be very carefully designed in order to reach a good convergency with minimum computational effort. Three such criteria have been adopted in our work:

(i) Exclusion of interactions between negligible pseudocharges. The general two-electron Coulomb integral in Eq. (3) of the form

$$\begin{aligned}(\chi_1^{\vec{0}}\chi_2^{\vec{g}}|\chi_3^{\vec{m}}\chi_4^{\vec{m}+\vec{l}})\\ &=\iint d\vec{r}\,d\vec{r}\,'\,\chi_1(\vec{r}-\vec{s}_1)\,\chi_2(\vec{r}-\vec{g}-\vec{s}_2)\,\frac{1}{|\vec{r}-\vec{r}\,'|}\\ &\quad\times\chi_3(\vec{r}\,'-\vec{m}-\vec{s}_3)\,\chi_4(\vec{r}\,'-\vec{m}-\vec{l}-\vec{s}_4).\end{aligned} \tag{4}$$

The densities of the two interacting pseudocharges at $\vec{r}$ and $\vec{r}\,'$ vanish exponentially with increasing values of $|\vec{g}+\vec{s}_2-\vec{s}_1|$ and $|\vec{l}+\vec{s}_4-\vec{s}_3|$, respectively. In the sums over $\vec{g}$ and $\vec{l}$ we have therefore retained those $\vec{g}$ and $\vec{l}$ values which are associated with pseudocharges above a certain tolerance. A similar criterion has been adopted by Euwema *et al.*[7] in their HF calculations. The same criterion provides a limit to the sum over $\vec{g}$ in the one-electron Hamiltonian [see Eq. (1)] and to the sum over $\vec{m}$ in the exchange term.

(ii) Taking into account the short-range character of exchange interactions. The above criterion is unable to limit the sum over $\vec{l}$ and $\vec{g}$ in the exchange term; in fact, in exchange integrals, the distance $|\vec{m}+\vec{l}+\vec{s}_4-\vec{g}-\vec{s}_2|$, determining the entity of the pseudocharge at $\vec{r}\,'$, may be near zero for arbitrarily large values of $|\vec{l}|$. However, if the sums over $\vec{l}$ and $\vec{g}$ are effected by including in succession complete stars of all symmetry-related lattice vectors, the short-range character of the exchange interactions comes immediately to light. In fact, when multiplying these sums by $\Pi^{\vec{l}}_{3,4}$ [in the reconstruction of $F^{\vec{g}}$, see Eq. (1)] or by $\Pi^{\vec{g}}_{1,2}$ (in the calculation of total energy), interference effects rapidly destroy the overall contribution of outer stars. The data reported in II and similar tests performed with diamond have shown that if we limit exchange sums over $\vec{l}$ and $\vec{g}$ to three complete stars, the error in total energy is less than 0.001 a.u.: such an error has been taken as a standard to fix the level of the different approximations in the present computations.

(iii) Multipolar expansion of Coulomb interactions. We must finally discuss the criterion adopted to truncate the sums over $\vec{m}$ in the Coulomb term [see Eq. (3)]. To this purpose we first associate to each shell λ of atomic orbitals on a given atom in the general $\vec{m}$ cell a charge distribution defined according to a Mulliken partition of the total charge:

$$\rho_{\lambda,\vec{m}}(\vec{r}\,')=\sum_{3\in\lambda}\sum_{4,l}P^{\vec{l}}_{3,4}\,\chi_3(\vec{r}\,'-\vec{m}-\vec{s}_3)\,\chi_4(\vec{r}\,'-\vec{m}-\vec{l}-\vec{s}_4). \tag{5}$$

Due to the localized character of atomic orbitals, such a distribution is localized around the *m*th cell; at an external point $\vec{r}$, the potential it creates can be evaluated by means of a multipolar expansion. In a preceding work,[17] it was shown that such a partition of the charge makes the multipolar expansion rapidly convergent, so that only dipole terms need to be retained:

$$V_{\lambda,\vec{m}}(\vec{r})=\int d\vec{r}\,'\,\rho_{\lambda,\vec{m}}(\vec{r}\,')/|\vec{r}-\vec{r}\,'|\simeq q_\lambda|\vec{r}-\vec{m}-\vec{s}_\lambda|^{-1}+\vec{\gamma}_\lambda\vec{r}\,|\vec{r}-\vec{m}-\vec{s}_\lambda|^{-3}=V'_{\lambda,\vec{m}}(\vec{r}). \tag{6}$$

Using Eqs. (5) and (6), the set of all Coulomb integrals associated with the indices $3\in\lambda$, $4,\vec{l}$ (with fixed $1\vec{0}$, $2\vec{g}$, $\vec{m}$) is substituted by the one-electron integrals:

$$H'^{\vec{g}}_{1,2}(\lambda,\vec{m})=\langle\chi_1^{\vec{0}}\,|V'_{\lambda,\vec{m}}|\chi_2^{\vec{g}}\rangle. \tag{7}$$

In II it was shown that calculating Coulomb interactions by means of Eq. (7) when $|\vec{m}|\geqslant 10$ a.u. involves errors in total energy which are less than 0.001 a.u. in the case of graphite; note that in that case the first nonzero term that is neglected is a quadrupole term, while for diamond it is an octupole term. In summary, Coulomb interactions are evaluated exactly for small $|\vec{m}|$; in the surrounding region Eq. (7) is used up to a given distance ($|\vec{m}| \leq M$; for diamond $M = 13.4$ a.u.); Coulomb terms from the external region are neglected for what concerns their influence on eigenvectors, while their contribution to energy is evaluated by introducing a Madelung term relative to a system of point net charges $\delta_\lambda = q_\lambda - Z_\lambda$. For diamond, of course, net charges are zero and the Madelung term is absent. From the above description, it is evident that all quantities of interest are calculated in direct space and the transformation from $F^{\vec{g}}$ to $F(\vec{k})$ [see Eq. (1)] is performed just before the diagonalization. On the contrary, many authors[9,18-20] represent all quantities, in particular basis functions and Coulomb and exchange potentials, in reciprocal space so that their sums are extended to all translation vectors of the reciprocal lattice. The speed of convergency is surely different with the two approaches, but it depends on many features of the system under study (number of basis functions to be used, degree of localization of valence electrons, number of core electrons, etc.), so that we do not think it possible to claim at this time the absolute superiority of either approach.

The computations to be presented in the following were performed using a minimal basis set [five atomic orbitals (AO) per carbon atom], each AO being an STO-3G, that is, a least-squares representation of a Slater-type orbital as a sum of three Gaussian-type orbitals.[2] The use of Gaussian functions is known to simplify the evaluation of one- and two-electron integrals, and it also makes it possible to analytically perform all tests associated with the truncation criteria and the evaluation of x-ray factors and Compton profiles.

III. RESULTS AND DISCUSSION

A. Binding energy and bulk modulus

Total energy was calculated for five different values of the lattice parameter of diamond, in the range 3.48–3.68 Å. The calculated minimum lies at 3.59 Å, against an experimental value of 3.57 Å.[16] Euwema *et al.*,[7] using the HF method and a basis set comprising 13 variational functions, localized the minimum at 3.54 Å. Zunger,[8] using a local density method, obtained an equilibrium distance of 3.66 Å when including only the exchange $\rho^{1/3}$ term, and of 3.58 Å when a correlation term was added to the Hamiltonian. When comparing the latter results with the good performance of HF exact-exchange noncorrelated calculations, we find a confirmation of the fact that in local density Hamiltonians the correlation term contains an important contribution which partly corrects the shortcomings of the local exchange term.

As is well known (see Ref. 2 and related work), using a minimal STO-3G basis involves an appreciable error in total energy because of the limited variational freedom, but especially because of the poor representation of the peak of 1*s* core functions near the nuclei. So, our total energy per cell is 74.874 a.u. against a value of 75.71 a.u. as obtained by Euwema.[21] However, bond energies can be accurately calculated because the errors associated with core functions are entirely translated from isolated atoms to compounds. By making reference to the atomic energy of carbon, calculated with the same basis set,[2] we obtain a binding energy of 5.69 eV per atom against an experimental value of 7.62 eV.[8] Two slightly different binding energies are reported in the two Euwema papers[7,21]; the more recent estimation is 5.03 eV. The evaluation of this quantity by Zunger[8] is difficult because of the lack of an atomic reference term, which would require a spin-polarized calculation; the author reports three values: 11.92, 5.7, 7.8 eV, the first referring to a nonpolarized atomic calculation, the other two based on privately communicated spin-polarized atomic energy data. The difference of 1.93 eV between experimental binding energy and that resulting from our calculation is considerably less than that reported for graphite in II (2.48 eV per atom); as a result, the calculated diamond structure appears to be more stable than that of graphite, contrary to experimental evidence. Two other results are indicative of the fact that the present basis set is more adequate for diamond than for the lamellar structure of graphite: First, the error in equilibrium distance is appreciably different in the two cases (0.56% and 2.4%, respectively); second, the virial coefficient for diamond is by 5×10^{-4} nearer to 1 than that for graphite. From these observations and from a comparison with Euwema's results we derive the belief that the basis set we used is substantially adequate for diamond, and that most of the difference between calculated and experimental binding energies is attributable to correlation effects. The coefficient of the second-order term of the best-fit parabola to the energy-versus-distance data is 0.55 a.u.$^{-2}$ corresponding to a bulk modulus of 5.9×10^{12} dyn/cm^2 to be compared with an experimental value of 4.42×10^{12} dyn/cm^2 as obtainable from the elastic constants[22] according to the formula $B = (C_{11} + 2C_{12})/3$. Of the other authors that have performed diamond calculations, only Surratt, Euwema, and Wilhite[23] report a computed value of the bulk modulus, which was comprised of between 4.4 and 4.6×10^{12} dyn/cm^2. Such an excellent agreement with experiment is perhaps partly fortuitous: HF calculations of molecules usually involve appreciable errors in force constants (of the order of 20%)[24,25]; an uncertainty in Euwema's energy data is related to a correction those authors must add to compensate for a loss of translational symmetry due to their truncation criteria; still, the evaluation of the quadratic coefficient is a very delicate task, since it involves energy differences of a few thousandths of a.u. To this purpose, when repeating with higher accuracy the data for graphite reported in II, we obtained the same values for the equilibrium distance and the corresponding energy, but the computed force constant for the C-C bond changed from the reported value of 13.6 to 7.9 mdyn/Å, against an experimental value[26] of 8.5 mdyn/Å.

B. Correlation energy

The correlation energy E_c represents only a minor part (0.5%) of the total energy of diamond, even if it appreciably contributes to binding energy. The HF electronic distribution should therefore be adequate for calculating E_c *a posteriori* (that is, outside the self-consistent process) using a density functional technique. Among the many proposals, the local exchange and correlation functional proposed by Gunnarsson and Lundqvist (GL)[27] for spin-polarized systems has provided good results for a number of ground-state properties of atoms and molecules, in particular, their total energy. However, it is well known that such success is partly due to a happy cancellation of errors in the exchange and correlation terms, since this functional and similar ones[28] overestimate E_c[29-31] by as much as 100%. It is for this reason that Stoll, Pavlidou, and Preuss (SPP)[32] have recently proposed the following functional to calculate E_c with HF atomic and molecular densities:

$$E_c^{\mathrm{SPP}} = \int (\rho_+ + \rho_-)\,\epsilon_c(\rho_+,\rho_-)\,d\tau - \int \rho_+\epsilon_c(\rho_+,0)\,d\tau - \int \rho_-\epsilon_c(\rho_-,0)\,d\tau, \quad (8)$$

where $\epsilon_c(\rho_+,\rho_-)$ is the GL correlation function for a spin-polarized system. The first term is therefore E_c^{GL}, which is the approximation for E_c as proposed by GL; the other two terms represent the correlation energies of the two pure spin subsystems, which are subtracted in order to preserve only the correlation of motions between electrons of different spin. In this way, most correlation effects should be taken into account at least for systems of limited dimensions[33]; in fact, for such systems, there are no long-range correlations, while in an HF solution electrons of the same spin are kept away by the exchange interaction. For a closed-shell system, Eq. (8) becomes

$$E_c^{\mathrm{SPP}} = \int \rho\,[\epsilon_c(\rho/2,\rho/2) - \epsilon_c(0,\rho/2)]\,d\tau \equiv \int \rho\,\epsilon_c'(\rho)\,d\tau\,. \quad (9)$$

It is interesting to compare the values of $\epsilon_c(\rho/2;\rho/2)$ and $\epsilon_c'(\rho)$ at different densities (see Table I). It clearly shows that in a closed-shell system, no matter how complicated the electronic density function is, the SPP expression for the correlation energy will lead to a result that is about one-third of that obtained according to GL. Starting from the HF charge density we have evaluated the two functions. The integration was performed numerically. Within a sphere surrounding the nuclei and containing exactly two electrons, the distribution was assumed to be spherically symmetric and 700 sampling points were taken along the radial axis. Within the residual volume of the irreducible part of the elementary cell, the integral was effected by a random sampling technique (4000 points); the error in the calculated correlation energies may be estimated to be of the order of 0.1 eV. The value obtained using the SPP functional is of 4.95 eV per atom from which the atomic correlation energy calculated in the same approximation must be subtracted, which is practically coincident with the experimental one.[34] As a result, a contribution to binding energy of 0.73 eV per atom is obtained, which is less than half the expected value. On the contrary, by subtracting from the calculated E_c^{GL} value of 13.45 eV the experimental atomic correlation energy, one obtains a contribution to binding energy of 9.2 eV per atom. If, however, we take as a reference the atomic correlation energy calculated in the same approximation,[31] a value of 1.3 eV is obtained. While the latter result is better than the

TABLE I. Values of the correlation energy density functions for a closed-shell system, $\epsilon_c(\rho/2,\rho/2)$ (Ref. 27) and $\epsilon_c'(\rho)$ (Ref. 32), as a function of the electronic density ρ. r_s is defined as usual $[r_s = (\frac{4}{3}\pi\rho)^{-1/3}]$. All quantities are in atomic units.

ρ	r_s	ϵ_c	ϵ_c'	ϵ_c/ϵ_c'
10^{+3}	0.062	−0.326	−0.123	2.65
10^{+2}	0.134	−0.275	−0.103	2.66
10	0.288	−0.226	−0.084	2.68
1	0.620	−0.177	−0.065	2.71
10^{-1}	1.337	−0.131	−0.048	2.75
10^{-2}	2.879	−0.090	−0.032	2.81
10^{-3}	6.204	−0.057	−0.020	2.87
10^{-4}	13.365	−0.033	−0.011	2.94

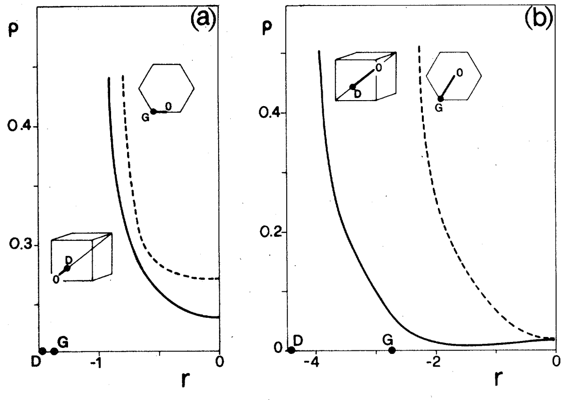

FIG. 1. Total charge density in diamond (——) and graphite (---) along the bonding (a) and antibonding (b) directions. ρ and r are in a.u.

SPP one, it is dubious that a difference between largely overestimated values may in general provide reasonable results. In summary, it appears that the modification to the GL formula suggested by SPP is in the correct direction, but perhaps too drastic. It is possible that further work at a molecular scale will eventually lead to an effective expression to be used also with HF solutions for nonconducting periodic systems.

C. Population analysis and charge distributions

Diamond and graphite lend themselves particularly well as covalent systems to a population analysis according to Mulliken. The six electrons of each carbon atom are subdivided into a proper atomic population (4.87 electrons for diamond, 4.76 for graphite) and a bond population. Each bond between nearest neighbors contains 0.74 and 0.96 electrons in the two cases; the two populations are in a proportion which is very near to the theoretical $\frac{3}{4}$ value estimated according to a classical valence-bond scheme. The higher charge density along bonds in graphite is evident from Fig. 1: at the midpoint between nearest neighbors it is 0.27 $e/(\text{a.u.})^3$ for graphite and 0.24 $e/(\text{a.u.})^3$ for diamond; note also that in both cases the density falls practically to zero in the direction opposite to bonds. The antibonding character of the non-nearest-neighbor interactions is revealed by the negative bond populations with second and third neighbors. A final observation concerns the hybridization ratios, that is, the ratio between p and s electrons in tetrahedral and planar hybrids of diamond and graphite: they are 2.4 and 1.7, respectively, to be compared with the values of 3 and 2 corresponding to pure sp^3 and sp^2 hybrids.

D. X-ray structure factors

The x-ray-structure factors computed in this work are presented in the third column of Table II. The experimental data,[13,14] corrected for the effect of isotropic thermal vibration with a Debye-Waller parameter $B=0.2007$,[13] are given in column 2. The HF results of Euwema *et al.*,[7,21] the "$\rho^{1/3}$ exchange" data of Heaton and Lafon,[10] and the local spin-density ones of Zunger and Freeman[8] are shown in columns 3–6. In column 7, the structure factors obtained from a superposition of atomic HF charge distributions[13] are finally given. The last row supplies the agreement factor[10] corresponding to each calculation: $R=\sum|F_{\text{expt}}-F_{\text{theory}}|/\sum|F_{\text{expt}}|$. The excellent quality of Zunger and Freeman's data[8] is not related to the presence of a correlation term, since their noncorrelated Hamiltonian performed nearly as

TABLE II. Experimental and calculated x-ray factors for diamond.

hkl	Expt.[a]	Hartree-Fock[b]	Hartree-Fock[c]	Local exchange[d]	Local exch. and correl.[e]	Atomic superp.[a]
111	3.321	3.274	3.298	3.349	3.281	3.056
220	1.972	1.925	1.931	2.023	1.995	1.951
311	1.663	1.659	1.671	1.748	1.692	1.755
222	0.144	0.088	0.086	0.075	0.139	0.000
400	1.480	1.535	1.545	1.590	1.493	1.555
331	1.579	1.533	1.527	1.564	1.605	1.509
422	1.443	1.443	1.417	1.452	1.408	1.430
511	1.418	1.386		1.401	1.392	1.391
333	1.418	1.382		1.394	1.392	1.391
R		0.023	0.024	0.028	0.015	0.051

[a] References 13 and 14.

[b] Present work.

[c] References 7 and 21.

[d] Reference 10.

[e] Reference 8.

well, but is due, in our opinion, to the correctness of the formal scheme and to the quality of the basis set, which is a decisive factor for the detailed description of electron density distributions. In this respect, it is surprising that our results are better than previous calculations[21,10] using much richer basis sets; it is possible that some deficiencies of those calculation schemes, especially concerning translational invariance, are made evident when calculating this kind of Fourier transform. All results here reported relating to low-index reflexes are, of course, better than those obtainable by simple superposition of atomic distributions; for higher indices, the structure factors are associated with the distribution of core electrons and only the quality of the atomic basis set becomes important.

E. Compton profiles

We have calculated Compton profiles for diamond, using the impulse approximation[35] along five directions for which experimental data are available[11,12]; use of a Gaussian basis set makes such a computation very fast. Our results, together with those of Wepfer *et al.*,[36] also obtained with an HF method, and with the experimental ones by Weiss and Phillips,[11] are reported in Table III. The two calculated data are very similar with an overestimation at low moments with respect to experiment, more markedly so in our case; this general behavior is observed also in the local exchange data by Heaton.[10] Such a similarity of results with different approaches to, and a different extent of the basis sets might suggest that the main source of discrepancies is attributable to the use of the impulse approximation. More interesting characteristics of the different computations are revealed by the differential curves, measuring the degree of anisotropy of moment distributions. In Fig. 2 such data are reported for the present and previous[8,10,36] theoretical calculations, together with recent accurate experimental results[12] concerning the anisotropy of distribution of momenta.[11] It is still not clear how much the quality of the results depends on the extent of the basis set and on the type of Hamiltonian that has been employed. In particular the importance of including correlation interactions

TABLE III. Experimental and calculated Compton profiles $J(q)$ along five directions. Values of J and q are in atomic units.

hkl	*q*	Experimental[a]	Hartree-Fock[b]	Hartree-Fock[c]
100	0.0	2.09	2.22	2.18
	0.4	1.91	2.05	2.05
	0.8	1.46	1.54	1.55
	1.2	0.86	0.88	0.88
	1.6	0.47	0.46	0.46
111	0.0	2.05	2.09	2.08
	0.4	1.89	1.99	1.97
	0.8	1.50	1.62	1.64
	1.2	0.88	0.97	0.97
	1.6	0.47	0.45	0.45
110	0.0	2.11	2.19	2.21
	0.4	1.93	2.00	1.96
	0.8	1.44	1.55	1.58
	1.2	0.91	0.98	0.98
	1.6	0.47	0.42	0.43
211	0.0	2.04	2.13	2.12
	0.4	1.91	2.00	1.99
	0.8	1.48	1.61	1.62
	1.2	0.89	0.94	0.95
	1.6	0.47	0.44	0.44
221	0.0	2.02	2.12	2.12
	0.4	1.92	2.00	1.97
	0.8	1.49	1.60	1.62
	1.2	0.87	0.97	0.97
	1.6	0.47	0.43	0.44

[a] Reference 11.

[b] This work.

[c] Reference 36.

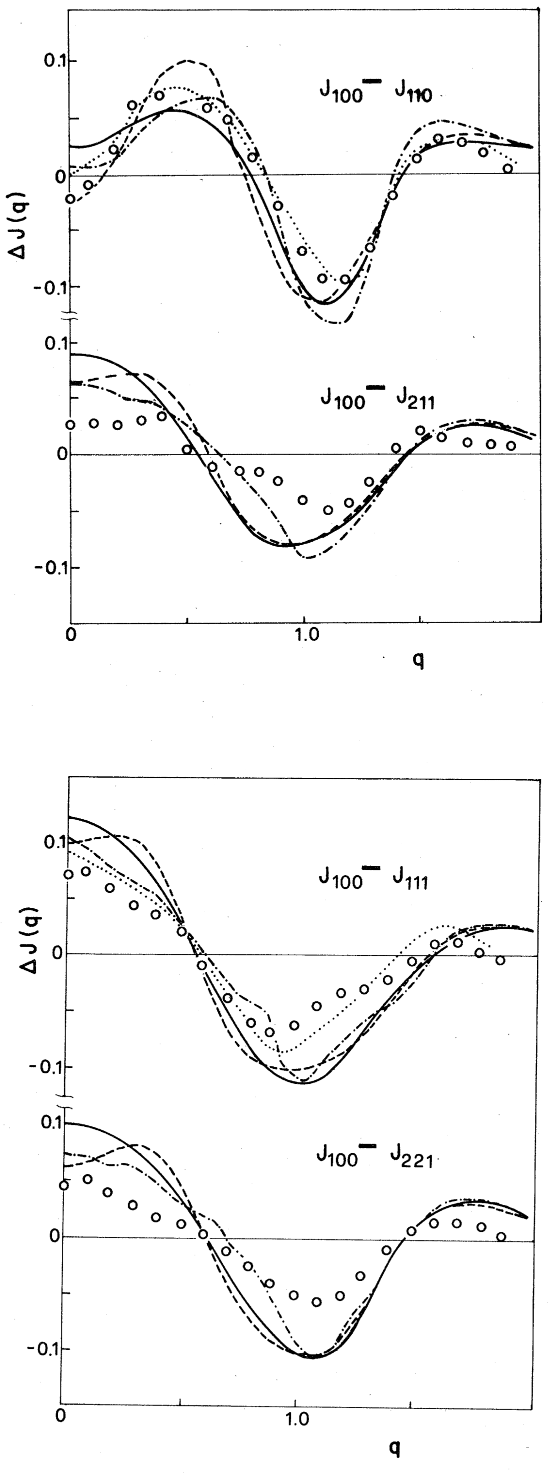

FIG. 2. Anisotropy of the Compton profiles for diamond. q and ΔJ are in a.u. ○ represents the experimental data (Ref. 12); —— HF calculations, this work; ---- HF calculations (Ref. 36); -·-·- local exchange calculations (Ref. 10); ······ local exchange and correlation calculations (Ref. 8).

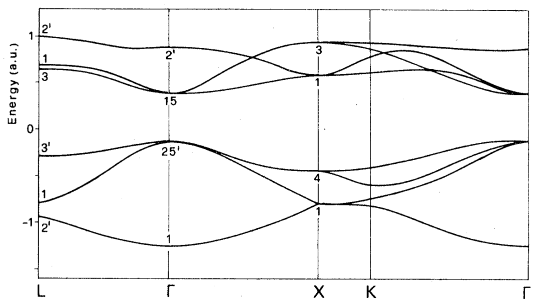

FIG. 3. Self-consistent band structure of diamond. The symmetry type of the eigenvectors at L, Γ, and X points is reported.

in moment distribution calculations (which might justify the good performance of Zunger's method) has been debated[37, 38]: from very accurate atomic calculations with atomic systems ,[39] it comes out that correlation is extremely important for open-shell systems, much less for closed ones, thus in-

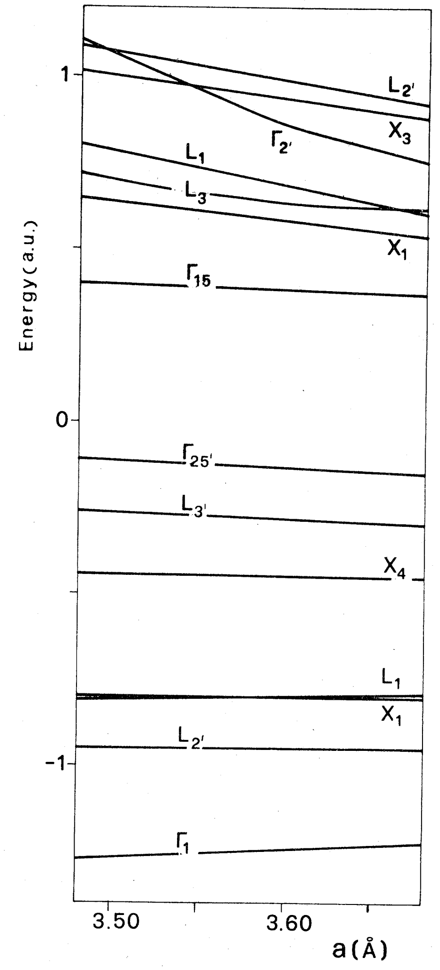

FIG. 4. Hartree-Fock eigenvalues as a function of lattice constant.

creasing the difference between experimental and calculated data. Calculations are in progress with other systems (graphite, silicon, and aluminum) which will permit us to judge on a wider basis the quality of the information obtainable with our method about this important observable quantity.

F. Band structure

The diamond band structure is shown in Fig. 3; its qualitative features are very similar to previous results.[10,8] On the other hand, it is known that HF bands are wider by a factor 1.5 to 2 with respect to "experimental" ones, as obtained from optical excitation data. So, the calculated $\Gamma_{25}-\Gamma_{15}$ gap is 13.9 eV, practically coincident with that reported by Euwema,[7] against an experimental value of 5.4 eV (Ref. 40); the total calculated and experimental[41,42] valence bandwidths are 37 and 21–24 eV, respectively. Recently, Brener[4] has corrected HF bands for diamond[7] to take correlation into account; his results are encouraging and indicate that an *a posteriori* correction on HF bands can introduce substantial improvements. In Fig. 4 we finally report the variation of eigenvalues at special $\vec{k}$ points with the lattice parameter. The behavior is very similar to that published by Surratt *et al.*[23]: the valence eigenvalues are slightly lowered with decreasing pressure (with the only exception of Γ_1 and L_1) and conduction levels are lowered at a much higher rate, so that the overall effect is a narrowing of the gap and an overall compression of the band structure. In Zunger's work[8] such effect is enhanced because of the fact that in his computation valence levels are increased with increasing pressure.

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