PHYSICAL REVIEW B VOLUME 24, NUMBER 8 15 OCTOBER 1981

Exact-exchange Hartree-Fock calculations for periodic systems. IV. Ground-state properties of cubic boron nitride.

R. Dovesi, C. Pisani, C. Roetti, and P. Dellarole
Institute of Theoretical Chemistry, University of Torino, Via Pietro Giuria, 5, I-10125 Torino, Italy

(Received 23 October 1980)

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 cubic boron nitride. We use a minimal basis set to calculate total and binding energies, band structure, population analysis, x-ray factors, and directional Compton profiles. By referring to the results of previous calculations, we have been able to discuss the quality of the ground-state properties of the four isoelectronic compounds: graphite, diamond, and hexagonal and cubic boron nitride, as obtained in the same approximation and using the same computational technique.

I. INTRODUCTION

The four isoelectronic compounds, graphite, diamond, and hexagonal and cubic boron nitride, are ideally suited to test the adequacy of a computational scheme designed for the study of periodic systems. In fact, they have been studied in detail from an experimental point of view and, in spite of their simplicity, they cover a range of structural and electronic situations (two- and three-dimensional systems, covalent and partially ionic compounds). They have therefore been the object of many theoretical calculations performed with both *ab initio* and semiempirical or parametric methods. Nonetheless, to our knowledge, a homogeneous set of computations performed with the same technique for the four compounds does not exist.

In two preceding papers we reported about Hartree-Fock (HF) studies of graphite, hexagonal boron nitride (HBN) (Ref. 1), and diamond.[2] In this paper the same computational technique is applied to cubic boron nitride (CBN); in addition we provide new data for graphite and HBN. In all cases a standard minimal STO-3*G* basis set[3] was used. More severe tolerances have been adopted in the choice of computational parameters so that energies are now determined to within 0.1 eV/cell.

Our exact-exchange linear-combination-of-atomic-orbitals, self-consistent-field method[4] was described at length in previous publications. It follows a real-space approach[5,6] in the sense that the integrals and all the intermediate quantities are calculated in $\vec{r}$ space. The criteria adopted to truncate Coulomb and exchange series play a fundamental role in the method. Up till now, the influence of those criteria have been discussed with reference to the graphite monolayer[1] and to diamond.[2] Owing to the homonuclear character of those compounds, however, long-range Coulomb interactions did not enter into the evaluation of total energy, whose expression is as follows [Ref. 4, Eq. (34)]:

$$E = \tfrac{1}{2}\,\mathrm{Tr}[P(H_M + H'_M + B')] + \tfrac{1}{2} \sum_{\substack{\lambda_1 \lambda_2 \vec{\mathrm{m}} \\ (\vec{\mathrm{m}} < M)}}{}' Z_{\lambda_1} Z_{\lambda_2} \,|\vec{S}_1 - \vec{S}_2 - \vec{\mathrm{m}}|^{-1} + E^{\mathrm{Mad}}(M) .$$

The first two terms define the total electronic plus electrostatic nuclear energy per unit cell, excluding, however, the Coulomb interactions between cells which are separated by a distance greater than a certain radius *M*. These long-range interactions are taken classically into account by the last term. It has the form of a Madelung series, where each nuclear position is assigned a net charge evaluated after subdividing the electronic distribution into atomic gross charges, according to a Mulliken population analysis. It is known that such subdivisions suffer from a large degree of arbitrariness, and the question can be raised how effective the correction term is and how important it is in the study of an appreciably ionic compound such as the one treated in the present work. In order to answer these questions we performed a series of computations with HBN (which is more ionic and requires much less computational effort than CBN) by letting the radius *M* separating the "quantum" from the "classical" zone vary from 7.5 to 19 Å. The results are reported in Table I. The

Madelung correction term appears to be rather effective in that it accounts for about 70% of the total energy variation in the explored range, and it has therefore been included in all the present computations. Note that the residual uncertainty is well below the level of precision ($\Delta E < 0.1$ eV) which has been chosen to fix the computational parameters.

II. RESULTS AND DISCUSSION

In Table II, total and binding energies for CBN are reported and compared with the results from previous HF (Ref. 7) and local exchange and correlation[8] calculations. The fact that Euwema's HF result for total energy is much better than ours is mostly due to the poor description of the core functions that is achieved using the STO-3G basis set.[1,3] In fact, just employing a 6G standard[3] 1s orbital was sufficient to lower the total energy to 79.03 a.u./cell. The local density energy of Ref. 8, including a correlation contribution obtained with a large numerical basis set, is higher than the HF one of Ref. 7. This probably reflects the inadequacy of the local approach in evaluating the exchange contribution to energy, especially for inner shells.

As far as the binding energy is concerned, that is, the difference with respect to atomic calculations performed in the same approximation, the situation is quite different. The local density result is in excellent agreement with experiment. Of the two HF data the present one seems to be more reasonable in spite of the poorer basis set. It has already been observed[1,4,5] that Euwema's technique encounters some difficulties in the treatment of charge imbalances orginating from their truncation criteria, which can affect total-energy data. We estimated the correlation energy *a posteriori* using the Hartree-Fock charge distribution in the local density correlation functional of Gunnarsson and Lundqvist.[9] Subtracting the atomic correlation energy evaluated in the same way, a contribution to the binding energy of 2.4 eV/cell was obtained, giving a total of 12.2 eV/cell.

TABLE I. Total energy of hexagonal boron nitride as a function of M, the radius defining the "quantum" zone as distinguished from the "classical" zone. n_M is the number of stars of direct lattice cells with radius less than M; E^1 is the total energy calculated disregarding the "classical" contribution $E^{\mathrm{Mad}}(M)$; E^2 is the corrected total energy. Energies are in eV, M is in Å.

n_M	M	E^1	$E^{\mathrm{Mad}}(M)$	E^2
6	7.64	−2129.528	−0.114	−2129.642
12	12.60	−2129.629	−0.035	−2129.664
18	15.8	−2129.683	+0.005	−2129.678
24	19.7	−2129.705	+0.016	−2129.689

TABLE II. Calculated total and binding energies of cubic boron nitride.

	Hartree-Fock minimal basis[a]	Hartree-Fock extended basis[b]	Local-exchange and correlation extended basis[c]
Total energy (a.u./cell)	−78.291	−79.250	−78.980
Binding energy (eV/cell)	9.83	8.34	12.8

[a] This work.
[b] Reference 7.
[c] Reference 8.

Table III compares the calculated data of binding energy, equilibrium lattice parameter, and force constant of the four isoelectronic compounds with the corresponding experimental data, when available. The binding energy for HBN is slightly different from the one previously reported,[1] due to the more severe tolerances adopted here. The HF treatment of the two hexagonal compounds has been reduced, as usual, to a single layer. In the case of boron nitride we calculated *a posteriori* the Coulomb interaction energy between layers by assigning to each nuclear position the net atomic charge as calculated according to a Mulliken population analysis: This contribution turned out to be negligibly small (0.0085 eV/cell).

The calculated binding energies represent a fraction between 70% and 75% of the experimental ones, the difference being mainly due to the correlation error. While the binding energy of the two boron nitride crystals is practically the same, as expected, diamond appears slightly more stable than graphite against experimental evidence. The experimental difference in stability between carbon and boron nitride compounds is semiquantitatively reproduced.

Experimental lattice parameters are satisfactorily reproduced by the calculated data. The results are better for the three-dimensional with respect to the two-dimensional systems, and for the two carbon compounds with respect to boron nitrides. A semiquantitative agreement is also observed between the

TABLE III. Calculated and experimental binding energies, lattice parameters, and force constants.

System	Binding energy (eV) Calc.	Binding energy (eV) Expt.	Binding energy (eV) Calc./Expt.	Lattice parameter (Å) Calc.	Lattice parameter (Å) Expt.	Force constant (mdyn/Å) Calc.	Force constant (mdyn/Å) Expt.
Cubic BN	9.83	13.0	0.75	3.59	3.62	7.31	
Diamond	11.38	15.2	0.75	3.59	3.57	6.40	4.79
Hexagonal BN	9.80	13.0	0.75	2.60	2.51	7.99	
Graphite	10.68	15.2	0.70	2.51	2.46	7.90	8.40

calculated and the available experimental force constants. Much of the residual discrepancy from experiment of both lattice parameters and elastic constants would undoubtedly be eliminated using better basis sets within the HF approximation. Since the wave function at the calculated conformational minima is not appreciably different from the one corresponding to the experimental lattice spacing, all the following results are calculated for the latter configuration.

Concerning the electron charge distribution, a first indication is provided by a Mulliken population analysis which shows that cubic boron nitride is much less ionic than the corresponding hexagonal compound; the positive net charges on boron are in fact 0.21 and 0.50 electrons, respectively. These figures must be taken with care because the factorization of the charge distribution into atomic contributions is rather artificial. A better description of the modification in the charge distribution induced by the formation of the chemical bond is provided in Fig. 1, where the two atomic electron densities and their superposition are compared with the calculated density for cubic boron nitride. The partially covalent character of the bond is apparent from the buildup of charge between nearest neighbors, which is appreciable though not as high as in diamond or graphite (the Mulliken bond populations are 0.74 and 0.86 for the latter compounds, while they are 0.64 and 0.77 for cubic and hexagonal boron nitride, respectively). The charge transfer from boron to nitrogen is recognizable in Fig. 1 as a slight decrease in the anisotropy of the electron density of the solid with respect to the atomic superposition; the corresponding curves for HBN are qualitatively the same.

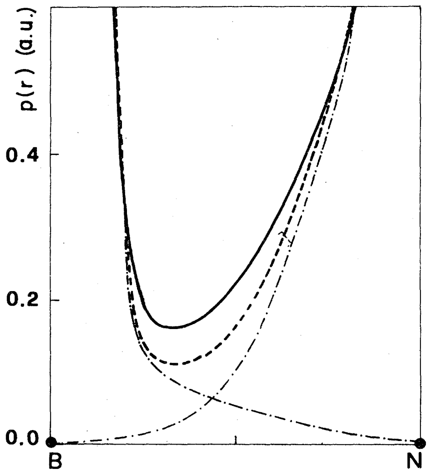

FIG. 1. Charge density in cubic boron nitride along the boron-nitrogen bond(—) as compared with superposition data (-----) obtained by summing the free-atom contributions (—·—·—·).

Figure 2 represents the differences between the densities of the two boron nitride compounds with respect to the corresponding carbon compounds. The bond lengths have been scaled so as to make the end atoms coincide. The two curves are nearly identical although HBN exhibits a slightly higher anisotropy, thereby confirming the indication provided by the net charges. Near the nuclei the differences are obviously dictated by the different size of the core orbitals.

Another way of looking at electron charge distributions, which provides a relatively easy comparison with experimental data, is through their Fourier transform. We report in Table IV the experimental[10] and calculated x-ray factors for CBN. While for some reflexes ($F_{111}, F_{331}, F_{511}, F_{333}$) our results are very similar to the experimental ones, for many of them our method gives worse values than not only the ones calculated with the other *ab initio* methods, but also the ones obtained with a simple superposition of atomic charge distributions. The last two rows supply the agreement factors, defined as

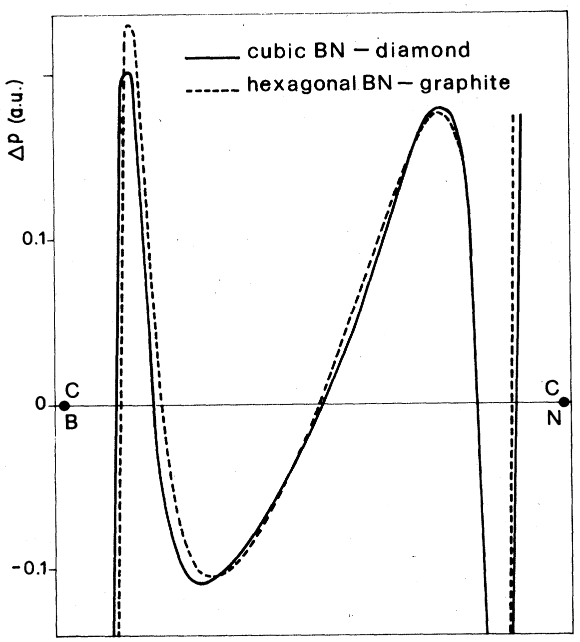

FIG. 2. Differential charge densities along the bond between boron nitride compounds and the isostructural carbon compounds. All densities are in atomic units.

$$R=\sum_i |F_i^{\mathrm{expt}}-F_i^{\mathrm{calc}}| \Big/ \sum_i |F_i^{\mathrm{expt}}|$$

for cubic boron nitride (R_{CBN}) and, for comparison, the ones reported in Ref. 2 for diamond (R_D). Going from diamond to CBN our R rises by a factor 1.5 and all others reduce. In particular the atomic superposition model (that for diamond gave an R more than twice ours) performs here as well as our method does.

While it is known[3] that for ionic or partially ionic compounds the $3G$ set performs worse than for covalent systems, the present disagreement is rather surprising and larger than the one expected from the results reported in the previous section. Anyway, further experimental data would be welcome in order to allow a detailed discussion on a firmer basis. Even for such a well studied system as silicon, the agreement factor between different experimental sets can be as bad as 0.015 or worse.[11]

Table V lists the calculated Compton profiles for CBN, HBN, and graphite in three directions; the results for diamond have been previously reported.[2] The experimental x-ray results of Weiss and coworkers[10,12] are shown in the same table. The reported experimental error amounts to 4% at $q=0$ for HBN, but it can be even larger than that. In fact, the impressive refinement of Compton scattering techniques that has taken place in the last years has shown that in early measurements such effects as multiple scattering have been largely underestimated. For this reason, we think that Weiss's data can just be used for the purpose of qualitative comparison (at $q=0$, $J_{\mathrm{graphite}} > J_{\mathrm{HBN}} > J_{\mathrm{CBN}} \approx J_{\mathrm{diamond}}$). A more detailed discussion is possible by comparing theoretical data

TABLE IV. Experimental and calculated x-ray factors for cubic boron nitride. R is the agreement factor.

hkl	Expt.[a]	Hartree-Fock[b]	Hartree-Fock[c]	Local exchange and correlation[d]	Atomic superposition[a]
111	4.92±0.15	4.93	5.05	4.97	4.62
200	1.56±0.05	1.34	1.56	1.58	1.40
220	4.17±0.10	4.05	4.10	4.17	4.21
311	2.59±0.10	2.46	2.52	2.64	2.69
222	0.50±0.02	0.37	0.44	0.57	0.48
400	3.22±0.10	3.11	3.20	3.20	3.30
331	2.17±0.05	2.16	2.22	2.16	2.17
420	0.32±0.01	0.22	0.28	0.32	0.29
511	1.96±0.06	1.94	1.97	1.95	1.90
333	1.96±0.06	1.94	1.97	1.97	1.90
R_{CBN}		0.037	0.020	0.010	0.036
R_D		0.023	0.024	0.015	0.051

[a] Reference 10.
[b] This work.
[c] Reference 7.
[d] Reference 8.

TABLE V. Experimental and calculated Compton profiles $J(q)$ for cubic boron nitride, hexagonal boron nitride, and graphite. J and q in atomic units.

	Cubic BN				Hexagonal BN				Graphite			
q	Expt.[a]	Calculated			Expt.[a]	Calculated			Expt.[a]	Calculated		
		100	110	111		$10\bar{1}1$	0001	$11\bar{2}0$		$10\bar{1}1$	0001	$11\bar{2}0$
0.0	4.08±0.08	4.33	4.30	4.19	4.28±0.18	4.39	4.44	4.37	4.32±0.04	4.41	4.52	4.47
0.1	4.05	4.31	4.28	4.17	4.23	4.37	4.41	4.36		4.38	4.49	4.45
0.2	4.00	4.27	4.22	4.14	4.16	4.31	4.32	4.32	4.24	4.33	4.41	4.40
0.3	3.98	4.19	4.11	4.05	4.06	4.21	4.18	4.23		4.26	4.26	4.31
0.4	3.91	4.06	3.96	3.94	3.94	4.06	3.98	4.07	3.98	4.16	4.07	4.16
0.5	3.70	3.88	3.77	3.80	3.71	3.86	3.73	3.84		4.01	3.82	3.92
0.6	3.50	3.64	3.54	3.62	3.50	3.61	3.45	3.55	3.52	3.76	3.53	3.61
0.7	3.24	3.37	3.30	3.40	3.24	3.32	3.15	3.25		3.43	3.22	3.27
0.8	2.93	3.06	3.07	3.16	2.93	3.00	2.84	2.97	2.88	3.05	2.89	2.95
0.9	2.64	2.73	2.84	2.88	2.59	2.69	2.54	2.72		2.67	2.57	2.67
1.0	2.39±0.05	2.39	2.59	2.57	2.28±0.05	2.38	2.25	2.47	2.20	2.34	2.26	2.43
1.1		2.07	2.30	2.24		2.09	1.99	2.21	1.90	2.04	1.97	2.18
1.2	1.86	1.77	1.97	1.92	1.76	1.82	1.75	1.92	1.64	1.77	1.71	1.90
1.3		1.50	1.63	1.63		1.57	1.54	1.61	1.42	1.53	1.49	1.61
1.4	1.45	1.28	1.32	1.38	1.37	1.34	1.36	1.32	1.22	1.30	1.30	1.32
1.5		1.10	1.06	1.15		1.15	1.20	1.08	1.08	1.11	1.14	1.07
1.6	1.13	0.96	0.89	0.96	1.06	0.98	1.07	0.91	0.94	0.94	1.01	0.87
1.7		0.84	0.77	0.81		0.85	0.96	0.78		0.81	0.90	0.74
1.8	0.86	0.76	0.70	0.70	0.86	0.75	0.86	0.70		0.71	0.81	0.66
1.9		0.69	0.64	0.63		0.67	0.78	0.65		0.63	0.73	0.60
2.0	0.68±0.02	0.61	0.59	0.58	0.68±0.02	0.60	0.71	0.60		0.58	0.66	0.56

[a] Reference 10.

[b] Reference 12.

along different directions for the four compounds among themselves. Figures 3 and 4 show the calculated anisotropies along the directions of maximum and minimum anisotropy for the cubic and carbon compounds, respectively. The anisotropy is increased when passing from hexagonal to cubic and from ionic to covalent systems. It is interesting to observe that in hexagonal compounds and especially in graphite, for $q=0$ the Compton profile is higher in the nonbonding [0001] direction with respect to the free-electron-like directions parallel to the basal-plane. This effect can be related to the presence of atomiclike tails of the wave function along the nonbonding direction. Euwema's[7,13] calculated anisotropies have also been reported in Fig. 3. While qualitatively similar to ours, they point to a much larger difference between the distribution of momenta in diamond along the two nonbonding [100] and [110] directions.

The band structure of CBN is shown in Fig. 5. The minimum of the conduction band occurs at $\vec{k}=X$, while in other calculations[7,8] it is along the $\Gamma-X$ line. The resulting gap is 11.3 eV, to be compared with the ones of HBN (12.7 eV) and of diamond (13.9 eV) calculated in the same approximation. The corresponding experimental data, as obtained from optical spectra, are 6.4–8,[8] 5.8, and 5.4, respectively. As expected, the differences between HF and experimental data are very large. In fact, HF can give good results only for ground-state properties, and their eigenvalues must be considered a byproduct or a starting point for more comprehensive approaches.[14]

Local-density-functional results for band structure are far better than the HF ones (for example the CBN gap of Ref. 8 is 8.8 eV). Nevertheless, when parametric adjustments are excluded, the discrepancies with the experimental data remain, in general, far from negligible.[8,15,16]

In conclusion, the quality of our results for the ground-state properties of the four compounds is generally satisfactory and comparable with that of computations using much larger basis sets. As far as the method is concerned, it has proven versatile in describing two- and three-dimensional, covalent

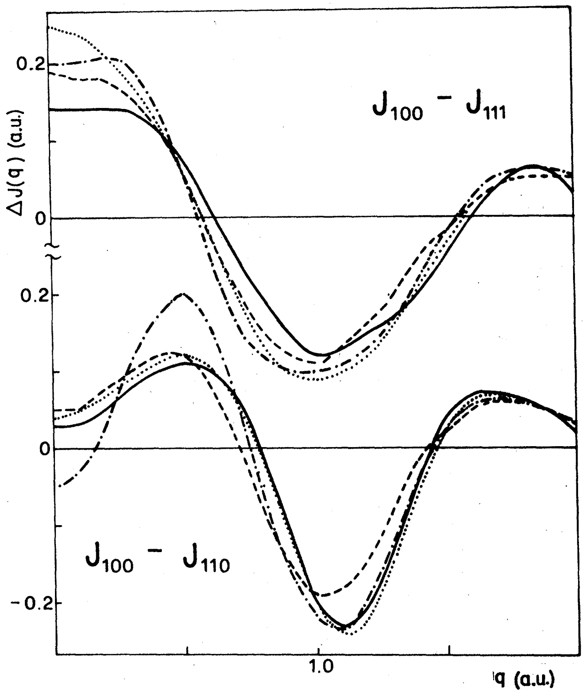

FIG. 3. Calculated anisotropies of the Compton profile for cubic boron nitride and diamond; J and q in atomic units. Cubic boron nitride: (—) present and (---) Euwema's (Ref. 7) results. Diamond: —·—·—· present and (······) Euwema's (Ref. 13) results.

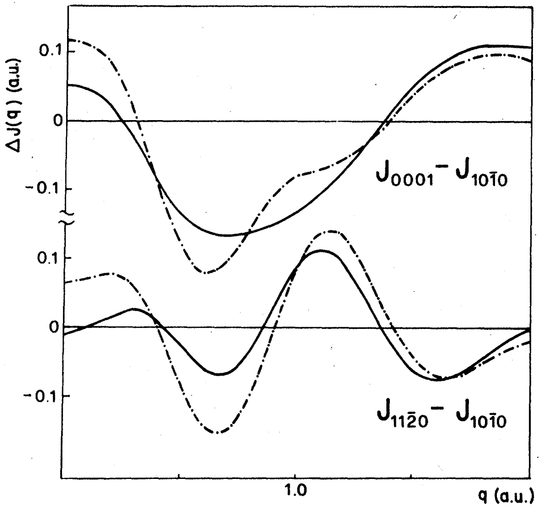

FIG. 4. Calculated anisotropies of the Compton profiles for hexagonal boron nitride (—) and graphite (—·—·—·).

or partially ionic compounds.

Work is in progress to improve the computational technique and especially to allow greater variational freedom which seems to be, at present, the principal reason for the shortcomings of the method. Of course, even when a near HF solution will be obtained, a large set of quantities of great interest in solid state physics, connected with the excited-state description, and more directly related to correlation effects will still be out of reach. Nonetheless, starting from a sound and well defined solution one can realistically plan to apply some simplified but effective many-body corrections to take into account the correlation effects.[14,17,18]

ACKNOWLEDGMENT

This work was partially supported by the Italian Council of Research (C.N.R.).

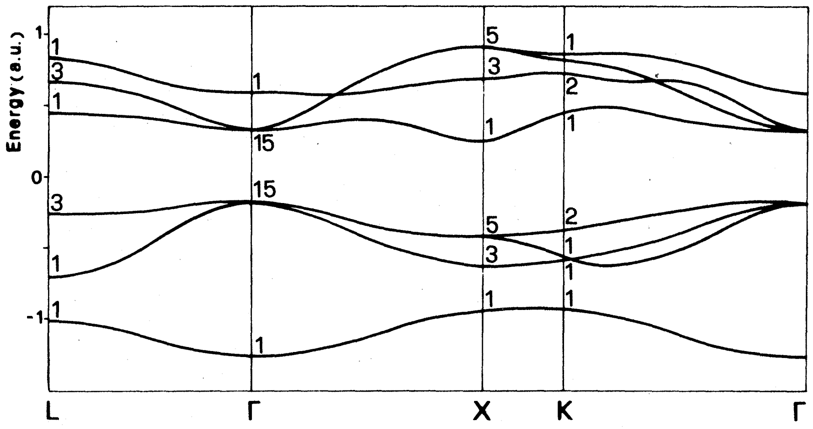

FIG. 5. Self-consistent HF band structure of cubic boron nitride.

[1] R. Dovesi, C. Pisani, and C. Roetti, Int. J. Quantum Chem. 17, 517 (1980).

[2] R. Dovesi, C. Pisani, F. Ricca, and C. Roetti, Phys. Rev. B 22, 5936 (1980).

[3] W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. 51, 2657 (1969); W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.* 52, 2769 (1970).

[4] C. Pisani and R. Dovesi, Int. J. Quantum Chem. 17, 501 (1980).

[5] T. H. Upton and W. A. Goddard, III, Phys. Rev. B 22, 1534 (1980).

[6] H. J. Monkhorst, Phys. Rev. B 20, 1504 (1979).

[7] R. N. Euwema, G. T. Surratt, D. L. Wilhite, and G. C. Wepfer, Philos. Mag. 29, 1033 (1974).

[8] A. Zunger and A. J. Freeman, Phys. Rev. B 17, 2030 (1978).

[9] O. Gunnarsson and B. J. Lundqvist, Phys. Rev. B 13, 4274 (1976).

[10] R. J. Weiss, Philos. Mag. 29, 1029 (1974).

[11] R. Dovesi, M. Causà, and G. Angonoa, following paper, Phys. Rev. B 24, 4177 (1981).

[12] R. J. Weiss and W. C. Phillips, Phys. Rev. 176, 900 (1968).

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

[14] N. E. Brener, J. L. Fry, and T. C. Collins, Int. J. Quantum Chem. S14, 455 (1980).

[15] A. Zunger, Phys. Rev. B 21, 4785 (1980).

[16] S. Antoci and L. Mihich, Phys. Rev. B 21, 799 (1980).

[17] N. E. Brener, Phys. Rev. B 11, 929 (1975); 11, 1600 (1975).

[18] S. T. Pantelides, D. J. Mickish, and A. B. Kunz, Phys. Rev. B 10, 2602 (1974).