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LCAO-LDA calculation of Compton profiles in hexagonal BN; comparison with experiments

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Abstract. The linear-combination-of-atomic-orbitals self-consistent-field process is used with either Hartree–Fock or Kohn–Sham equations in order to calculate average and directional Compton profiles of hexagonal boron nitride. Basis sets and electron correlation effects are discussed and the results are compared with very recent theoretical and experimental data. The reciprocal form factor along the *c*-axis is also calculated and analysed.

1. Introduction

Structure factors and directional Compton profiles are the main sources of information about the electronic structure of solids. It is well known that they are complementary. In fact, while the values of the structure factors are very dependent on core electrons, the Compton profile is very sensitive to the valence electron distribution and gives better information about the chemical bond. This is due to the high density of these electrons at low momenta. The substantial progress as regards the experimental accuracy of electron momentum distributions obtained from directional Compton scattering data is coming to provide one of the most important and reliable tests of the quality of calculations at different levels of sophistication. At this stage, hexagonal boron nitride is seen as a very good example compound.

In recent work [1, 2], accurately measured directional Compton profiles have been reported and compared with those calculated from two theoretical models:

- (i) the self-consistent-field (SCF) energy band structure obtained using the pseudo-potential plane-wave technique and the local density approximation (LDA);
- (ii) the linear-combination-of-atomic-orbitals (LCAO) Hartree–Fock (HF) model.

A very satisfactory agreement between the calculations obtained using the LDA model and experiment is obtained, but the LCAO-HF method [3] leads to a significant discrepancy at small values of the electron momentum. It is likely that this discrepancy is attributable both to the use of a minimal basis set and to the HF level of approximation.

In this study, the same LCAO-HF method as was used in [3] and implemented in the CRYSTAL program [4] is chosen again. However, important improvements have been carried out during these last few years. They allow a better stability to be achieved in the calculations, and the use of large basis sets with polarization functions leading to more

accurate results. Moreover, the present calculations are performed at the HF level but also taking into account the electronic correlation by solving the Kohn–Sham (KS) equations after each cycle of the SCF process according to the method recently introduced in CRYSTAL by Causà and Zupan [5]. The HF and KS wave functions are built up from two all-electron basis sets including d-like polarization functions, already used in the study of cubic boron nitride (cBN) [6]. The directional and average Compton profiles are deduced and compared accurately with the most recent experimental data.

The plan of this paper is as follows. In section 2, the main features of the LDA applied to the LCAO method are briefly reviewed and the basis sets associated with each atom are described. Section 3 is devoted to the comparison of the results obtained at the HF and LDA levels. Finally, comparisons with experiment are made and the quality of the wave functions used in this work is discussed in section 4.

2. The method and basis sets

The high-energy inelastic scattering of photons by electrons allows us to have access to the electron momentum distribution (EMD) $\rho(\mathbf{p})$. Within the impulse approximation [7] in which the energy transfer to the recoil electrons must greatly exceed their binding energy, the Compton profile $J(q)$ is defined as the projection of $\rho(\mathbf{p})$ along the scattering z -vector for a given value of the momentum ($p_z = q$):

$$J(q) = \int_{p_x, p_y} \rho(\mathbf{p}) \, dp_x \, dp_y = \int_{p_x, p_y} \Psi(\mathbf{p}) \Psi^*(\mathbf{p}) \, dp_x \, dp_y. \quad (1)$$

$\Psi(\mathbf{p})$ is the wave function in the momentum space and the Compton profile is subject to the normalization rule $\int_{-\infty}^{+\infty} J(q) \, dq = Z$ where Z is the number of electrons.

In this work, the ground state described by the wave function $\Psi(\mathbf{r})$ and the electron density $\rho(\mathbf{r})$ are obtained by a SCF process with the HF equations or by the density functional theory (DFT) in the local density approximation (LDA) where HF equations are replaced by Kohn–Sham (KS) equations.

In both cases, the electron density is

$$\rho_{HF/KS}(\mathbf{r}) = \int_{\text{Brillouin zone}} d\mathbf{k} \sum_{i_{occ.}} |\phi_{i,HF/KS}^k(\mathbf{r})|^2$$

where the crystalline orbitals $\phi_{i,HF/KS}^k(\mathbf{r})$ are solutions of the one-particle equations

$$\hat{h}_{HF/KS} \phi_{i,HF/KS}^k(\mathbf{r}) = \epsilon_{i,HF/KS}^k \phi_{i,HF/KS}^k(\mathbf{r}).$$

The Hartree–Fock mono-electron operator is defined as follows:

$$\hat{h}_{HF} = \hat{t} + \hat{v} + \hat{J}[\rho(\mathbf{r})] + \hat{K}[\rho(\mathbf{r}, \mathbf{r}')]]$$

where \hat{t} , \hat{v} , \hat{J} and \hat{K} are, respectively, the kinetic, the external potential, the Coulomb and the exchange operators, while the Kohn–Sham mono-electron operator is

$$\hat{h}_{KS} = \hat{t} + \hat{v} + \hat{J}[\rho(\mathbf{r})] + \hat{v}^{X-C}(\mathbf{r})$$

where the exchange–correlation potential \hat{v}^{X-C} is the functional derivative of the exchange–correlation density functional energy:

$$\hat{v}^{X-C}(\mathbf{r}) = \frac{\delta E^{X-C}[\rho]}{\delta \rho(\mathbf{r})} \quad \text{with} \quad E^{X-C} = \int_{\text{unit cell}} d\mathbf{r} \, \epsilon^{X-C}[\rho](\mathbf{r}).$$

Details of numerical calculations are given in [5].

Then $\rho(\mathbf{r})$ can be written as follows:

$$\rho_{HF/KS}(\mathbf{r}) = \sum_{\mu, \nu, g} P_{HF/KS}^{\mu, \nu, g} \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r})$$

where χ_{μ} and χ_{ν} are atomic orbitals respectively associated to the $\mathbf{0}$ th and g th cells of the LCAO periodic HF or KS methods, and $P_{HF/KS}^{\mu, \nu, g}$ are the corresponding density matrix elements.

In the momentum space we have also

$$\rho_{HF/KS}(\mathbf{p}) = \sum_{\mu, \nu, g} P_{HF/KS}^{\mu, \nu, g} \chi_{\mu}(\mathbf{p}) \chi_{\nu}(\mathbf{p})$$

where $\chi_{\mu}(\mathbf{p})$ (and $\chi_{\nu}(\mathbf{p})$) are Fourier transforms of $\chi_{\mu}(\mathbf{r})$ (and $\chi_{\nu}(\mathbf{r})$):

$$\chi(\mathbf{p}) = \int \chi(\mathbf{r}) e^{-i\mathbf{p}\cdot\mathbf{r}} d\mathbf{r}.$$

And, finally, the directional Compton profile expression becomes

$$J_{HF/KS}(q) = \sum_{\mu, \nu, g} P_{HF/KS}^{\mu, \nu, g} \int_{p_x, p_y} \chi_{\mu}(\mathbf{p}) \chi_{\nu}(\mathbf{p}) dp_x dp_y$$

where the integrals can be calculated analytically as described in appendix A of reference [8].

As in a preceding study of the charge density of cBN, two basis sets are used [6]. They are denoted as B_1^* and B_2^* where the star indicates the presence of a d-like polarization function on each atom with the same exponent (0.8). B_1^* is built with 6–21G basis sets centred on B and N atoms while B_2^* includes a 6–21G set for B and a 7–311G set for N. The gaussian exponent associated with the valence shells is reoptimized for the hexagonal phase with its experimental geometry ($a = 2.504 \text{ \AA}$, $c = 6.66 \text{ \AA}$). In B_1^* , the optimization of the exponent of the outer gaussian function associated with each 3sp valence shell leads to the values $\alpha(\text{B}) = 0.130$ and $\alpha(\text{N}) = 0.302$. In B_2^* , it is necessary to optimize the exponents of the two last gaussian functions corresponding to the 3sp and 4sp valence shells of nitrogen. The values obtained are $\alpha_{3sp}(\text{N}) = 0.460$ and $\alpha_{4sp}(\text{N}) = 0.250$ while the optimized exponent of the outer gaussian function of the boron basis set becomes $\alpha(\text{B}) = 0.170$.

3. The electronic structure and Compton scattering

In the previous study of cBN, it was shown that the B_1^* and B_2^* basis sets lead to calculations of structure factors in very satisfactory agreement with experiment. Before calculating the Compton profiles of hBN with these same reoptimized basis sets, we make sure of their quality as regards obtaining experimental physical properties like the binding energy.

3.1. The binding energy and Mulliken population analysis

The binding energy is defined as the difference between the total energy of the hBN unit cell and the sum of the energies of the free atoms. To take into account the electron correlation, the HF energies are corrected ‘*a posteriori*’ according to Perdew’s non-local DFT formula [9] recently introduced in the CRYSTAL code [10]. The values of the binding energy are found to be 0.486 and 0.473 au when they are calculated with the use of B_1^* and B_2^* , respectively. They are slightly smaller than those corresponding to cBN: 0.496 and 0.479 au respectively, and remain in very good agreement with experiment: 0.485 au [11, 12]. It should be noted that the ‘*a posteriori*’ correlation correction obtained using the LDA

formula of Ceperley and Alder [13] leads to values smaller by 0.03 au (0.455 and 0.442 au) when both B_1^* and B_2^* are used. Finally, the comparison of the bulk energies shows that cBN is less stable than hBN by 0.35 and 0.30 eV with the use of B_1^* and B_2^* respectively and that B_2^* stabilizes hBN by 1.05 eV with respect to B_1^* .

Table 1. Atomic total charges (in e^-), valence orbital charges projected onto the p valence band of nitrogen, and overlap populations according to a Mulliken population analysis and calculated at the HF and LDA levels with the use of B_1^* , B_2 and B_2^* basis sets.

	B_1^* HF	B_1^* LDA	B_2 LDA	B_2^* HF	B_2^* LDA
N					
Total charge	7.85	7.44	7.40	7.55	7.22
s	0.06	0.10	0.07	0.07	0.11
p_{xy}	2.61	2.40	3.39	2.47	2.39
p_z	1.54	1.37	2.18	1.60	1.46
d	0.01	0.01	—	0.01	0.01
B					
Total charge	4.15	4.56	4.60	4.45	4.78
s	0.41	0.45	0.18	0.45	0.48
p_{xy}	0.87	1.01	0.77	0.96	0.99
p_z	0.42	0.59	0.40	0.37	0.51
d	0.07	0.06	-	0.06	0.05
B–N	0.79	0.80	0.64	0.70	0.72
B–B	–0.03	–0.03	0.03	0.01	0.03
N–N	–0.02	–0.02	–0.04	–0.03	–0.03

It is well known that the Mulliken population analysis gives only an approximation of the electronic structure: the charges on the atoms and the overlap populations are not accurate and must be considered only as an indication, since the assignment of overlap populations is arbitrary. However, it is convenient to use it within a given method, in order to roughly analyse the changes of the atomic charge versus different factors such as choice of basis set. Table 1 reports the total charges on atoms, the overlap populations between first and second neighbours and also the orbital charges of the valence shells projected onto the valence band of the band structure. These values are calculated when B_1^* , B_2 and B_2^* are used: the B_2 basis set is similar to the B_2^* set without the d-like polarization function for B and N atoms.

The following comments can be made on the basis of an examination of table 1. Generally speaking, hBN has a semi-covalent character since charge transfer from boron towards nitrogen is obvious and the overlap population between the nearest neighbours B and N is about $0.75 e^-$. The comparison with cBN [6] shows that hBN has a more highly covalent character. The significant participation of boron p orbitals in the p valence band of nitrogen confirms the large degree of covalent character of the BN bond. More precisely, when the electron correlation is taken into account at the LDA level the degree of covalent character of the BN bond is significantly increased whatever the basis set is. This result is readily explained by the decrease of the net charge on the nitrogen atom and by the increase of the participation of the p orbitals of boron in the p valence band of nitrogen. The addition of a d-like polarization function to the B and N atomic orbital basis sets also produces a similar effect. Finally, the semi-covalent character of hBN is modified by these basis set and electron correlation effects. The charge transfer from boron towards nitrogen

can vary from $0.8 e^-$ (as in cBN) to $0.2 e^-$ when polarization functions are used and when the electronic correlation is taken into account. This result should be kept in mind when one is studying Compton profiles.

3.2. Compton profiles

Within the impulse approximation, total average Compton profiles $\bar{J}(q)$, valence directional Compton profiles along the [001], [110] and $[1\bar{1}0]$ directions, and the reciprocal form factor $B(\mathbf{r})$ along the [001] direction have been calculated with the four combinations of methods and basis sets (the LDA level with the use of B_1^* , B_2 and B_2^* basis sets and the HF level with the use of only the B_2^* set). All of the values are convoluted with the experimental resolution FWHM (0.16 au) [1].

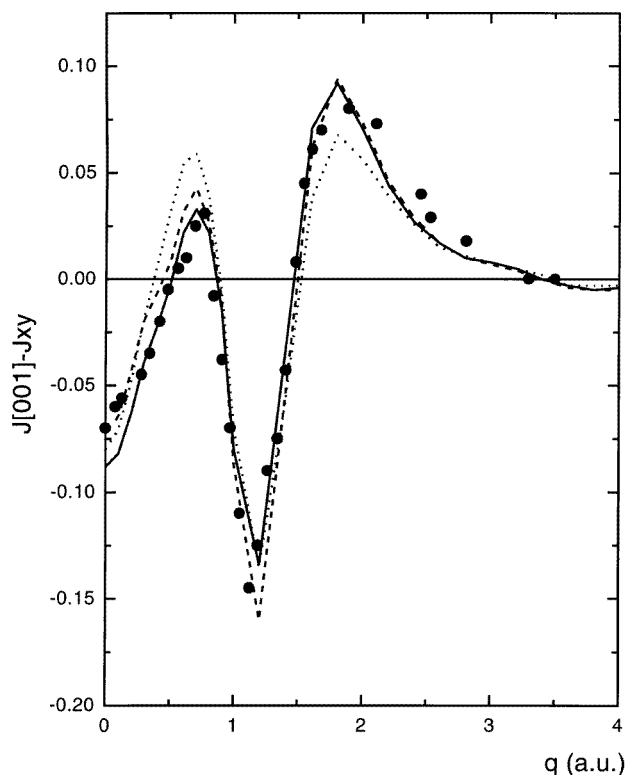


Figure 1. The valence Compton profile anisotropy $J_{[001]} - J_{xy}$ versus q . J_{xy} is the basal-plane Compton profile defined by $\frac{1}{2}(J_{[110]} + J_{[1\bar{1}0]})$. The experimental data are as given in [1] and [2]. Full, dashed and dotted lines correspond to the calculations done at the LDA level with the use of B_2^* and B_1^* and at the HF level with the use of B_2^* respectively.

Table 2 and figure 1 report the values of the total average Compton profiles and the valence profile anisotropy, respectively. The more recent experimental results are also given for comparison.

3.2.1. The basis set and electron correlation effects. To complete the information deduced from table 2 and figure 1, differences of Compton profiles, $A = J(B_2^*) - J(B_1^*)$ and

Table 2. Total average Compton profiles of hBN calculated at the HF and LDA levels with the use of B_1^* , B_2 and B_2^* basis sets. The experimental data are as given by Ahuja *et al* [15]

q	B_1^*	B_2	B_2^*	B_2^*	Experiment
	LDA	LDA	HF	LDA	
0.0	4.404	4.380	4.354	4.384	4.378
0.1	4.383	4.359	4.333	4.363	4.361
0.2	4.317	4.294	4.271	4.298	4.294
0.3	4.208	4.185	4.165	4.189	4.179
0.4	4.053	4.031	4.017	4.036	4.018
0.5	3.854	3.834	3.827	3.838	3.812
0.6	3.611	3.594	3.593	3.598	3.566
0.7	3.328	3.315	3.322	3.319	3.286
0.8	3.014	3.007	3.021	3.010	2.984
0.9	2.683	2.682	2.700	2.684	2.668
1.0	2.353	2.357	2.382	2.358	2.353
1.2	1.753	1.759	1.786	1.760	1.765
1.4	1.286	1.290	1.311	1.291	1.291
1.6	0.962	0.962	0.975	0.963	0.958
1.8	0.755	0.753	0.758	0.754	0.747
2.0	0.620	0.619	0.619	0.620	0.615
2.5	0.433	0.435	0.431	0.434	0.432
3.0	0.322	0.326	0.323	0.325	0.328
3.5	0.243	0.246	0.246	0.247	0.256
4.0	0.184	0.187	0.186	0.187	0.197

$B = J(B_2^*) - J(B_2)$ in the LDA method and $C = J(\text{LDA}) - J(\text{HF})$ with the use of B_2^* , are calculated either along the [001] direction or in the basal plane (xy) and represented versus q in figure 2.

At small values of q ($q < 0.7$ au) Compton profiles calculated with the use of B_2^* are smaller than those obtained with B_1^* . This observation is quite general since it is valid for both the average and directional Compton profiles. The largest differences remain rather small and are observed along the [001] direction. Comparison of the Compton profile values obtained with B_2 and B_2^* in the LDA method shows that the presence of a d-like polarization function in each AO basis set does not in practice affect the values of the Compton profiles. The average Compton profile is always very slightly greater with B_2^* (table 2), while the largest difference is still obtained along the [001] direction where the value obtained with B_2^* is smaller by only 0.009 au than that calculated with B_2 (curves B of figure 2).

When the electron correlation is taken into account, the values of the Compton profiles corresponding to the small values of q slightly increase with respect to the HF values, as the comparison of columns 4 and 5 of table 2 and the examination of curves C of figure 2 show. This increase is rather small. The maximum corresponds to $q = 0$, and represents only 0.6% of the J -value. This result is general since it in practice affects the average, directional and basal-plane Compton profiles in the same way. However, it is interesting to note that the electron correlation effect is the most sensitive for the basal-plane profiles, which are more dependent on the nature of the chemical bond. The electron momentum density obtained at small momentum values is therefore higher when calculated at the LDA level. This result agrees well with the increase of the degree of covalent character of the BN bond since the charge transfer from boron towards nitrogen is two times smaller at the LDA level than at the HF one (table 1).

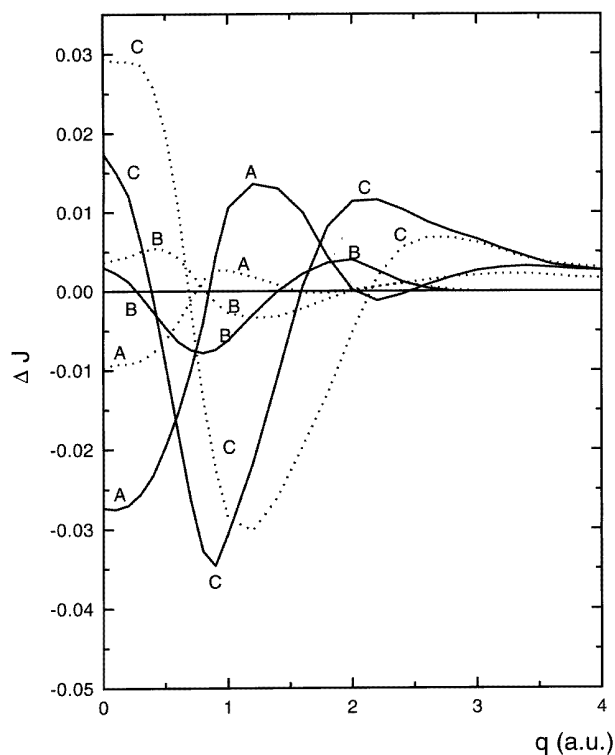


Figure 2. Variations of the differences $A(\text{LDA}) = J(B_2^*) - J(B_1^*)$, $B(\text{LDA}) = J(B_2^*) - J(B_2)$ and $C(B_2^*) = J(\text{LDA}) - J(\text{HF})$ versus q along the [001] direction (full lines) and in the basal plane xy (dotted lines).

3.2.2. Comparison with experiments. Two kinds of experimental data are available in the literature—according to whether they are derived from the study of pellet powder samples or from that of crystals. In the first kind, average Compton profiles are measured [14, 15] or obtained [15] by calculating a 1:2 weighted average of the J_{\parallel} and J_{\perp} values [16]. For simplification, only the more recent data [15] are given in table 2 for comparison with our calculated values. Examination of table 2 shows that at small q -values the Compton profiles calculated at the LDA level are higher than the experimental ones while the reverse is observed when calculations are done at the HF level. The best conditions of calculation (the LDA level and use of the B_2^* basis set) lead to an excellent agreement with experiment [15]. It must be underlined that the highest difference between experimental and calculated values corresponds only to a relative difference of 1% at $q = 0.7$ au. Taking into account the rather large experimental error of the Weiss's data [14], the agreement with our values can be also considered as satisfactory, contrary to that obtained by comparison with the values of Tyk *et al* [16] which are too small.

When experiments are performed on crystals, Compton profiles are determined along characteristic directions to represent the differences of the electron momentum distributions and to give information about the chemical bond. For hBN, Loupiau *et al* [1] presents the $J_{[001]} - J_{xy}$ profile anisotropy, where J_{xy} is an average Compton profile in the layer where the crystallites are randomly oriented. To obtain results which can be compared with the best accuracy with experiment, directional in-plane $J_{[1\bar{1}0]}$ and $J_{[110]}$ Compton profiles are

calculated along these two directions perpendicular and parallel to the BN bond, respectively. An average in-plane J_{xy} Compton profile is defined as $J_{xy} = \frac{1}{2}(J_{[1\bar{1}0]} + J_{[110]})$. Figure 1 compares the $J_{[001]} - J_{xy}$ anisotropy calculated at both the LDA and HF levels with the use of B_1^* and B_2^* sets with experiment [1, 2]. All of the calculated anisotropies, even those at the HF level, are in agreement with experiment, thus showing that the discrepancy of the LCAO-HF calculations of Dovesi *et al* [3] is attributable to a very great extent to the use of a minimal basis set (STO-3G). With the use of more extended basis sets, the basis set effect becomes small and the contribution of valence electrons is satisfactorily taken into account in the calculation of Compton profiles. The electron correlation effect is significant and contributes to an improvement of the calculated values towards the experimental data (see table 2 and figure 1). Finally, the agreement between our optimal (the LDA level and the B_2^* basis set) calculated profile anisotropy and experiment is excellent, and of even better quality than that calculated by Louprias *et al* [1] with a LDA pseudopotential plane-wave method.

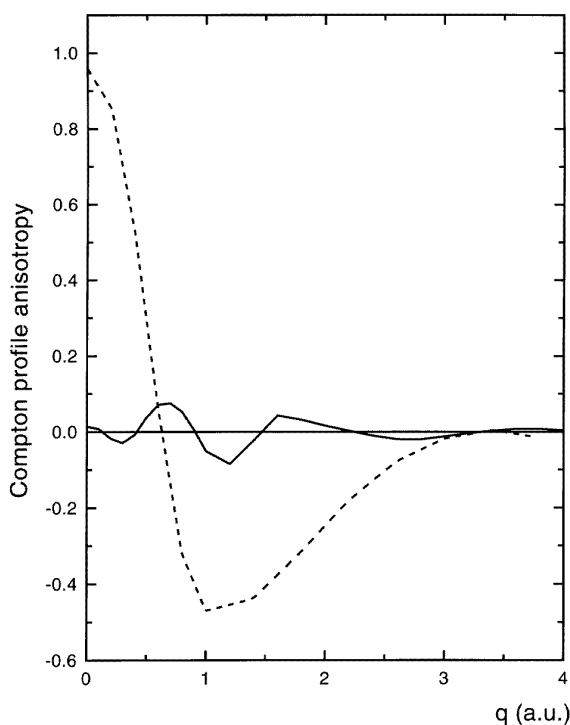


Figure 3. The Compton profile anisotropy in the basal plane of hBN. The full line represents $\Delta J = J_{[1\bar{1}0]} - J_{[110]}$ where the directions $[1\bar{1}0]$ and $[110]$ are parallel and perpendicular to the BN bond. The dashed line corresponds to the difference $J_{\parallel} - J_{\perp}$ calculated in the molecular system, for comparison [8].

4. Discussion and conclusions

New LCAO-LDA calculations including electron correlation have been made for the triperiodic hBN system in order to obtain its average and directional Compton profiles.

They lead to an excellent agreement with experiments when rather sophisticated all-electron basis sets are used. The electron correlation effect is small (less than 1%) but significant. It contributes to a better quality of the Compton profiles when compared with experiment contrary to what is obtained in the case of graphite [17]. As already mentioned by Loupiau *et al* [1], Compton profile anisotropies are rather low, especially between the basal-plane directions parallel and perpendicular to the bond (figure 3). This result justifies the assumption according to which it is possible to consider identical values of in-plane J_{xy} and directional $J_{[1\bar{1}0]}$ and $J_{[110]}$ Compton profiles.

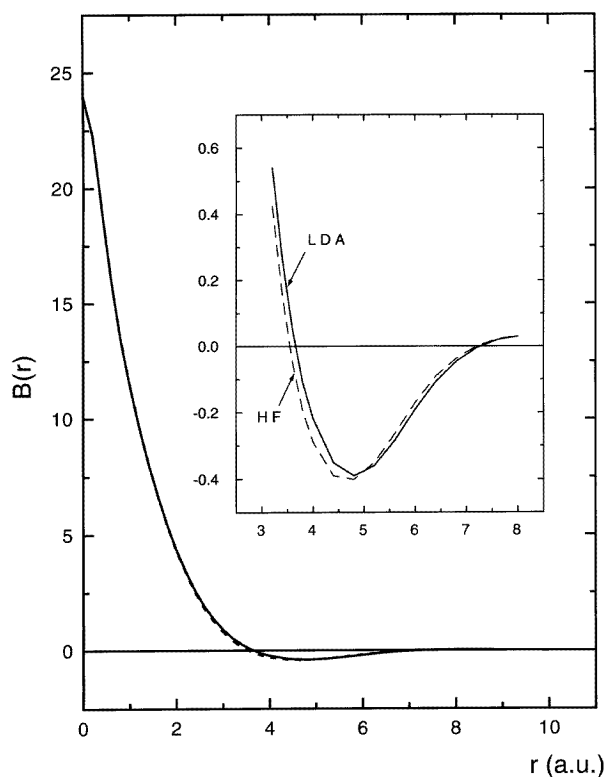


Figure 4. Variations of the reciprocal form factor $B(r)$ along the $[001]$ direction calculated with B_2^* at the LDA and HF levels.

Finally, by Fourier transforming the directional Compton profile $J_{[001]}$, the reciprocal form factor $B(r)$ is calculated along the c -axis of the hexagonal structure and figure 4 represents its variations obtained at the LDA and HF levels with the use of B_2^* . The negative part of the curves which is found in the range 3.5–7.5 au is attributable to the anti-bonding character of the nitrogen p-orbital interactions and to a lower extent to the interactions between B and N second neighbours. On the other hand, the zero-crossing points of the $B(r)$ function obtained at the LDA level correspond to the distances 6.90 and 13.70 Å, which represent with a very satisfactory accuracy the value of the lattice parameter c and that of $2c$, respectively. However, it should be noted that the values obtained within the HF approximation (6.71 and 13.61 Å) are in better agreement with the experimental value (6.66 Å). This result can be explained on the basis of the more highly insulating

character when hBN is calculated at the HF level with respect to that observed at the LDA level. In fact, the ionicity is larger (see table 1), the gap is overestimated, and therefore the zero-crossing points of $B(r)$ are more accurate [7]. These results also show the good quality of the wave functions from which the Compton profiles and reciprocal form factors are calculated.

In a very recent study [8], Compton profiles and reciprocal form factors have been reported for a BN molecule described with the same interatomic distance as in hBN and the same basis set B_2^* . A comparison between the results of the molecular and periodic systems shows that the electron correlation effect is opposite in these two cases since it causes an increase of the Compton profile in the periodic system and a decrease in the molecular one. A similar conclusion to that given above for the different $B(r)$ shapes obtained according to whether the calculation is at the HF or LDA level is deduced. The different sorts of anti-bonding orbital in the molecule and the periodic hBN are responsible for this result. Finally the Compton profile anisotropies ($J_{\parallel} - J_{\perp}$) for the molecular and periodic structures are compared in figure 3. The amplitude of the anisotropy variation for hBN is much smaller than that for the molecule at small impulse values.

In summary, the recent improvements introduced in the CRYSTAL program allow much more stable computations to be made with sophisticated all-electron basis sets, so leading to accurate Compton profile values. Our results are in excellent agreement with experiments. They show that the triperiodic LCAO-LDA wave functions are perfectly adapted for the calculation of Compton profiles.

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