

## Electronic correlations of cubic boron nitride

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We have calculated total and binding energies of zinc-blende-structure boron nitride. Starting from a self-consistent-field ground-state calculation within a finite basis of Gaussian orbitals centered at the different atoms, the electron correlations were treated by applying the local ansatz. The electronic correlations are predominantly short ranged, as was also found for its isostructural compound, diamond. Of specific importance are correlations on the atomic scale. Electrons correlate strongly at the nitrogen atoms. The correlation strength within the B—N bonds and the reduction of the total-atomic-charge fluctuations is discussed in detail. For an agreement between calculated and experimental binding energies, additional basis functions on interstitial sites turned out to be necessary. Without them, correlations in the interstitial regions are too poorly covered. Such an effect should be relevant for all future calculations on open-structure materials. The final results for the binding energy compare well with calculations made within the local-density approximation.

### I. INTRODUCTION

There is considerable interest in the properties of the zinc-blende-structure compound boron nitride (BN). It has been studied in detail from an experimental point of view<sup>1</sup> as well as by theoretical investigations. Like carbon, BN crystallizes in two forms, a cubic zinc-blende and a hexagonal (graphitelike) structure. This makes a comparative study of these isostructural compounds particularly interesting from a more basic perspective.

As far as ground-state properties are concerned, *ab initio* calculations have been performed in the Hartree-Fock (HF) approximation<sup>2,3</sup> as well as in the local-density approximation<sup>4-7</sup> (LDA).

We reported here on ground-state correlation calculations for cubic boron nitride that were performed using the local ansatz.<sup>8-10</sup> This scheme uses a HF calculation as the starting point and includes correlations with the help of a variational ansatz for the correlated ground state. It has been tested on calculations for small molecules<sup>10,11</sup> and has been applied for several solids, ranging from three-dimensional semiconductors like diamond<sup>12,13</sup> and silicon<sup>14</sup> to two-dimensional graphite<sup>13</sup> and one-dimensional polyenes.<sup>15,16</sup>

These calculations are performed within a well-specified subspace spanned by a finite number of basis orbitals for each atom. In this respect, the method compares with standard quantum-chemistry schemes. Due to that restriction, the real-space integrations inherent in the HF and correlation calculations are performed analytically. While within the HF approximation, such a restriction does not lead to problems, it shows shortcomings when performing correlation computations. These are mainly connected with the convergency of the correlation energy with increasing basis size. It was tried rather successfully before to obtain reliable estimates for finite-basis-size corrections to the energy.<sup>11,12,14,15</sup>

Contrary to quantum-chemistry methods, the scheme

is restricted to correlation operators with a well-defined local meaning. This is the reason why correlation calculations for solids can be performed.

In this study, we extend our investigations to BN in an attempt both to understand in detail how electrons correlate in this partially ionic compound and to test further how well the local ansatz applies for quantitative calculations of the correlation energy contributions to cohesion in covalent structures. Besides, the finite-basis-size corrections are critically investigated.

In addition, we hope to obtain insight into the electronic properties of these compounds that cannot be gained from the LDA, and try to improve the quantitative understanding by using the local ansatz.

The paper is organized as follows. In Sec. II the equations are summarized which are required for *ab initio* calculations of the correlation energy. In Sec. III, we report on details of the calculations and discuss the results. Correlation contributions to the binding energies are also given and compared with calculations within the LDA and with experimental information, as well as with previous work on diamond and graphite. Section IV contains a discussion of the charge distribution and the strength of electron correlations in these compounds. Conclusions are given in the last section and a comparison is made with an alternative method that has been recently developed for correlation calculations in solids.<sup>17,18</sup> This is a Monte Carlo computation scheme for a Jastrow ansatz<sup>19</sup> with a minimal number of variational parameters, applied to inhomogeneous systems.

### II. FORMALISM

The *ab initio* calculations are done within a finite basis set  $\{f_i(\mathbf{r})\}$  of Gauss-type orbitals (GTO's) centered at different atoms. In terms of them the Hamiltonian is written as

$$H = H_0 + H_{\text{int}}$$

$$= \sum_{i,j,\sigma} T_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{i,j,k,l} V_{ijkl} a_{i\sigma}^\dagger a_{k\sigma'}^\dagger a_{l\sigma} a_{j\sigma} + V_K, \quad (1)$$

where

$$T_{ij} = \int d^3r f_i^*(\mathbf{r}) \left[ -\frac{1}{2}\Delta + V(\mathbf{r}) \right] f_j(\mathbf{r}) \quad (2)$$

and

$$V_{ijkl} = \int d^3r \int d^3r' f_i^*(\mathbf{r}) f_j(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} f_k^*(\mathbf{r}') f_l(\mathbf{r}'). \quad (3)$$

The term  $V_K$  represents the interaction energy of the nuclei. Atomic units (a.u.) are used.  $V(\mathbf{r})$  is the single-electron potential due to the nuclei. Electrons in states  $f_i(\mathbf{r})$  with spin  $\sigma$  are created or annihilated by operators  $\hat{a}_{i\sigma}^\dagger, \hat{a}_{i\sigma}$ . The fermion operators  $a_{i\sigma}^\dagger, a_{i\sigma}$  in the above equations are defined by the following anticommutation relations:

$$\begin{aligned} \{a_{i\sigma}, \hat{a}_{j\sigma'}^\dagger\} &= \delta_{ij} \delta_{\sigma\sigma'}, \\ \{a_{i\sigma}, a_{j\sigma'}^\dagger\} &= S_{ij}^{-1} \delta_{\sigma\sigma'}, \\ \{\hat{a}_{i\sigma}, \hat{a}_{j\sigma'}^\dagger\} &= S_{ij} \delta_{\sigma\sigma'}, \end{aligned} \quad (4)$$

where  $S_{ij} = \int d^3r f_i^*(\mathbf{r}) f_j(\mathbf{r})$  defines the overlap matrix between the basis functions.

A prerequisite for the correlation energy calculation is the knowledge of the self-consistent-field (SCF) ground-state wave function  $|\psi_{\text{SCF}}\rangle$  and its energy. It is determined by the one-particle eigenstates of the effective one-particle Hamiltonian

$$H_{\text{SCF}} = \sum_{i,j,\sigma} F_{ij} a_{i\sigma}^\dagger a_{j\sigma}, \quad (5)$$

where

$$\begin{aligned} F_{ij} &= T_{ij} + \sum_{k,l,\sigma} (V_{ijkl} - \frac{1}{2} V_{ilkj}) \langle a_{k\sigma}^\dagger a_{l\sigma} \rangle \\ &= T_{ij} + V_{ij}^{\text{SCF}} \end{aligned} \quad (6)$$

defines the Fock matrix. The expectation value  $\langle \rangle$  is defined as the one within the SCF ground state  $|\psi_{\text{SCF}}\rangle$ .

The Hamiltonian (1) is separated into a SCF part and a residual interaction part  $H_{\text{res}}$ , i.e.,

$$H = E_{\text{SCF}} + H'_{\text{SCF}} + H_{\text{res}}, \quad (7)$$

with

$$E_{\text{SCF}} = \langle H \rangle, \quad (8)$$

$$H'_{\text{SCF}} = H_{\text{SCF}} - \langle H_{\text{SCF}} \rangle, \quad (9)$$

and

$$H_{\text{res}} = H_{\text{int}} - \sum_{i,j,\sigma} V_{ij}^{\text{SCF}} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{i,j,\sigma} V_{ij}^{\text{SCF}} \langle a_{i\sigma}^\dagger a_{j\sigma} \rangle. \quad (10)$$

For the treatment of electron correlations, the local ansatz is used.<sup>8-10</sup> This variational ansatz is written as

$$|\psi_0\rangle = e^S |\psi_{\text{SCF}}\rangle, \quad (11)$$

with

$$S = - \sum_n \eta_n O_n. \quad (12)$$

The operators  $O_n$  are of the following three forms:

$$O_n = \begin{cases} n_{i\uparrow} n_{i\downarrow} \\ n_i n_j = \sum_{\sigma,\sigma'} n_{i\sigma} n_{j\sigma'} \\ \mathbf{s}_i \cdot \mathbf{s}_j. \end{cases} \quad (13)$$

The  $n_{i\sigma}$  are occupation-number operators and  $\mathbf{s}_i$  are spin operators for electrons in local region  $i$  with spin  $\sigma$ . The different regions are described by localized functions in terms of the basis orbitals

$$g_i(\mathbf{r}) = \sum_j \gamma_{ij} f_j(\mathbf{r}). \quad (14)$$

A proper choice of these functions is essential for the method and has been described in detail before. Here, we will follow the procedure used for silicon.<sup>14</sup>

The operators  $O_n$  are local operators which generate a correlation hole around each electron. The operator  $n_{i\uparrow} n_{i\downarrow}$ , for example, when applied to  $|\psi_{\text{SCF}}\rangle$  select that part in which electrons are simultaneously present in the local region  $g_i(\mathbf{r})$ . When added by means of the exponential prefactor, this part obtains less weight ( $\eta > 0$ ) than it had in  $|\psi_{\text{SCF}}\rangle$ . Similarly, the operators  $n_i n_j$  ( $\mathbf{s}_i \cdot \mathbf{s}_j$ ) introduce density (spin) correlations between electrons in local orbitals  $g_i(\mathbf{r})$  and  $g_j(\mathbf{r})$ . This wave function without the spin operators, when chosen for the homogeneous electron gas, is the Jastrow function.<sup>19</sup>

The operators  $O_n$  (13) when applied to  $|\psi_{\text{SCF}}\rangle$  create one- and two-particle excitations out of the SCF ground state. The states generated by them are not orthogonal to  $|\psi_{\text{SCF}}\rangle$ , either. In the following only those contributions of the operators orthogonal to  $|\psi_{\text{SCF}}\rangle$  and to all one-particle excitations are kept. These modified operators allow one to reduce charge fluctuations around the charges found for the SCF ground state. The inclusion of the one-particle excitations would allow the charge distribution of the correlated ground state to be modified as compared with the SCF ground state. This readjustment is expected to be reasonably small in covalent semiconductors, however.

The variational parameters  $\eta$  are determined by minimizing the energy

$$E = \frac{\langle \psi_0 | H | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}. \quad (15)$$

According to a linked-cluster theorem<sup>20</sup> one can also write  $E = \langle \psi_0 | H | \psi_0 \rangle_c$ , where the subscript  $c$  implies that only connected contractions must be taken when the expectation value is evaluated. Since this expression cannot be computed exactly, a variational expansion in terms of the  $\eta_n$  parameters up to second order is made. This results in

$$E_{\text{corr}} = E - E_{\text{SCF}} \\ = -2 \sum_n \eta_n \langle O_n \tilde{H} \rangle_c + \sum_{n,m} \eta_n \eta_m \langle O_n \tilde{H} O_m \rangle_c, \quad (16)$$

where  $\tilde{H} = H - E_{\text{SCF}}$ . The individual expectation values are computed by using Wick's theorem. There, the restriction to fluctuations for the operators  $O_n$  simply means that no contractions within the operators are allowed.

Owing to this expansion, one no longer obtains an upper bound for the exact energy when minimizing Eq. (16). This approximation works only if the correlations are sufficiently weak. It corresponds in quantum chemistry (QC) to a specific coupled-cluster calculation and is there called CEPA-0.<sup>21</sup> The local ansatz compares with standard QC schemes in quality but it reduces drastically the number of two-particle excitations out of the SCF ground state that are considered. As a result, it is possible to calculate correlations for larger systems than with conventional QC schemes. Such a reduction in correlation space costs a price, though. Typically 5% of the correlation energy obtainable by a complete coverage of these excitations for a given one-particle basis are lost.<sup>10,11</sup>

The actual computation of the correlation energy for a solid separates into independent sets of calculations. The starting point is a SCF calculation within a sufficiently good basis set (here a double- $\zeta$  plus polarization function set is used; this means two sets of GTO's for each occupied orbital and one set of  $d$  orbitals for each atom).

The second step is the coverage of interatomic correlations for the whole solid. The corresponding operators describe mostly correlations which arise due to bonding. In the case of BN, the natural choice for the localized functions  $g_i(\mathbf{r})$  forming these operators is the one of atomic hybrids, i.e., hybridized  $s$  and  $p$  atomic orbitals, which point into the bond directions. They are obtained from the occupied orbitals of the SCF ground state (see Ref. 14). All these atomic orbitals are orthogonalized to the core states and to each other. These correlations are quite strong and for them, Eq. (16) is computed without further approximations. The most important contributions come from operators where the orbitals  $i$  and  $j$  are on the same atom [see Eq. (13)]. Operators built from pairs of orbitals on neighboring atoms are considered too, and longer-range correlations are estimated. Details will be given below.

The final step is the inclusion of the intra-atomic correlations. They describe the short-range part of the correlation hole. In order to treat them properly, the atomic volume of the different atoms needs to be subdivided as finely as possible. It is separated into different shells, each of which is segmented into different angular regions. This subdivision depends on the number of basis functions available on a given atom. The segmentation of the atomic volume becomes finer the higher the angular functions used. Here, we used two shells for each atom, one with a 12-fold and the other with a 4-fold segmentation. The optimization of the intra-atomic regions was performed by minimizing a partial contribution to the total correlation energy making a number of simplifying ap-

proximations. This step was explained in Ref. 14 in detail. The dominant part of the total intra-atomic correlation energy is obtained by adding these contributions from all atoms independently. Small corrections need then to be computed. They come from overlap effects of different atomic volumes and from short-range correlations of electrons on neighbor atoms and will be discussed in connection with the actual calculation.

### III. NUMERICAL APPLICATION TO BORON NITRIDE

#### A. SCF calculation

The SCF calculation was performed with the Hartree-Fock self-consistent-field (HF SCF) computational scheme CRYSTAL.<sup>22,23</sup> This program has been adapted to the aims of the local ansatz and has been used for correlation calculations on diamond and graphite before.<sup>13</sup> For boron nitride, the SCF calculation was done within a finite basis set by using for each atom a ( $7s3p/4s2p$ ) contracted GTO basis set which was optimized by Roos and Siegbahn<sup>24</sup> for the individual atoms. An additional set of polarization functions was also included. Since the electronic charge redistributes in the crystal as compared to the atoms, for each atom the outermost exponents of the  $s$  and  $p$  functions were replaced by a common exponent and were reoptimized on the SCF ground-state energy. Due to a large change for the outer exponents on the B atom, the third  $s$  and the first set of  $p$  functions on it needed to be rescaled too in order to avoid linear-dependency problems in the SCF computations. The basis functions are represented in Table I.

The total energy per unit cell of this SCF ground state is  $E_{\text{SCF}} = -79.209$  a.u./unit cell. Within the original basis set, the SCF ground-state energies for the single atoms are  $E_B = -24.513$  a.u. and  $E_N = -54.335$  a.u.,<sup>24</sup> respectively. This implies an electronic binding energy of  $\epsilon_{\text{SCF}} = -0.361$  a.u./unit cell. The additional sets of  $d$  functions contribute to it with an energy of  $-0.025$  a.u./unit cell. In order to estimate the Hartree-Fock limit we analyzed the results of calculations for small molecules such as  $\text{BH}_3$  and  $\text{NH}_3$  within a more complete basis set.<sup>25</sup> There it was found that an additional set of  $d$  and  $f$  functions leads to a gain in energy that is one order of magnitude smaller than with the first set of polarization functions. We assume that the corrections are of the same order for BN. The final results are listed in Table II together with the estimated uncertainties. A previous calculation within a different basis had given a SCF binding energy of  $\epsilon_{\text{SCF}} = -0.354$  a.u./unit cell,<sup>3</sup> in very good agreement with our result. There, the basis set was of comparable quality for the valence orbitals but had only one orbital each for the core states, thus keeping them frozen in the form for the neutral atoms.

#### B. Interatomic correlations

The first part of the correlation procedure consists in performing the interatomic correlation calculations. For this purpose, the functions  $g_i(\mathbf{r})$  for the interatomic

TABLE I. Exponents and coefficients for the basis orbitals and the core and valence atomic orbitals for the B atom and N atom in BN.

|   |       | Exponents | Coefficients | Core orbitals | Valence orbitals |
|---|-------|-----------|--------------|---------------|------------------|
| B | $s_1$ | 992.49    | 0.0075       | 0.6203        | -0.0437          |
|   |       | 147.33    | 0.0583       |               |                  |
|   |       | 31.735 9  | 0.2801       |               |                  |
|   |       | 8.389 4   | 0.7484       |               |                  |
|   | $s_2$ | 2.486 51  | 1.0          | 0.4470        | -0.0631          |
|   | $s_3$ | 0.508 6   | 1.0          | 0.0395        | 0.0548           |
|   | $s_4$ | 0.2       | 1.0          | -0.0096       | 0.1421           |
|   | $p_1$ | 4.233 4   | 0.1983       | 0.0           | 0.0967           |
|   |       | 0.832 55  | 0.8908       |               |                  |
|   | $p_2$ | 0.2       | 1.0          | 0.0           | 0.1071           |
|   | $d_1$ | 0.5       | 1.0          | 0.0           | 0.0              |
| N | $s_1$ | 2038.41   | 0.0074       | 0.6022        | -0.0463          |
|   |       | 301.689   | 0.0574       |               |                  |
|   |       | 66.463    | 0.2729       |               |                  |
|   |       | 17.808 1  | 0.7540       |               |                  |
|   | $s_2$ | 5.304 5   | 1.0          | 0.4663        | -0.0645          |
|   | $s_3$ | 0.765 0   | 1.0          | 0.0576        | 0.1229           |
|   | $s_4$ | 0.31      | 1.0          | -0.0044       | 0.2076           |
|   | $p_1$ | 5.954 6   | 0.2201       | 0.0           | -0.2042          |
|   |       | 1.232 9   | 0.8729       |               |                  |
|   | $p_2$ | 0.31      | 1.0          | 0.0           | -0.2582          |
|   | $d_1$ | 0.7       | 1.0          | 0.0           | 0.0              |

correlations of the valence electrons were calculated together with the atomic core functions to which all these functions need to be orthogonalized. This way, the correlations restrict to the valence shell only. We assumed that the core orbitals are sufficiently well described in terms of the basis functions on the individual atoms. The corresponding coefficients were obtained after a Wannier transformation of the Bloch states which described the lowest occupied bands and by neglecting contributions from other sites. The core orbitals in terms of the basis orbitals are given in Table I.

With these core states known, the density matrix is reduced to the density matrix of the valence electrons. From the latter, the functions  $g_i(\mathbf{r})$  for the valence electrons, i.e., orthogonalized atomic hybrids, were generated.<sup>14</sup> First the two different atomic hybrids, which point into the bond direction, were constructed from a bond orbital. The latter one was generated by localizing the occupied eigenfunctions of the density matrix.

The last column of Table I contains the basis orbital

coefficients of a bond orbital from which the two respective hybrids were generated. Here, the N atom joined by the bond is assumed to be in the (1,1,1) direction of the B atom. In the table, the coefficients for the  $p$  orbitals represent the values to be taken for each of the  $x, y, z$  orbitals.  $d$ -orbital contributions were omitted.

The other functions were generated by applying the operations of the space group. In a next step they were orthogonalized among each other and to the core states of different atoms. Such an orthogonalization is performed within a cluster of finite size. More than 99% of the total electronic charge is covered by these states so that they are well suited for a charge distribution analysis (see Sec. IV).

The interatomic correlations separate into three parts. First the contributions from operators defined on single atoms were calculated. Due to crystal symmetry, this problem reduces to six different  $\eta$  parameters, one for each kind of operator defined for the two different atoms [see Eq. (16)]. The calculation of the expectation values  $\langle O_n \tilde{H} \rangle_c$  and  $\langle O_n \tilde{H} O_m \rangle_c$  converges well within a small cluster. In a first step, clusters which contain one of the central atoms and its four nearest neighbors were considered (cluster I). These clusters were then systematically increased. Convergency was reached when all next-nearest-neighbor effects were covered. There is no need for a cluster that contains all next-nearest neighbors of a given atom at once. Rather, it is sufficient to include a subset of next-nearest neighbors only. This leads to a cluster with eight atoms that when properly chosen serves the calculations on nitrogen as well as boron at the

TABLE II. SCF binding energy and HF limit (a.u.).

|                          | $\epsilon_{\text{SCF}}$    |
|--------------------------|----------------------------|
| (4s2p1d)                 | -0.361 <sup>a</sup>        |
| finite basis corrections | -0.003 <sup>b</sup> ±0.002 |
| HF limit                 | -0.364 <sup>b</sup> ±0.002 |

<sup>a</sup>Present work.

<sup>b</sup>Estimated.

TABLE III. Expectation values  $\langle O_n \tilde{H} \rangle$ ,  $\langle O_m \tilde{H} O_n \rangle$  for interatomic operators on the B atom and the N atom each for different cluster sizes.

|                                                                                             | Cluster I | Corrections cluster II |                      | Final result |
|---------------------------------------------------------------------------------------------|-----------|------------------------|----------------------|--------------|
|                                                                                             |           | Binding direction      | No-binding direction |              |
| B atom                                                                                      |           |                        |                      |              |
| $\langle n_{i\uparrow} n_{i\downarrow} \tilde{H} \rangle$                                   | 0.026 14  | +0.000 58              | -0.000 16            | 0.026 26     |
| $\langle n_i n_j \tilde{H} \rangle$                                                         | 0.028 86  | -0.003 38              | -0.000 69            | 0.020 74     |
| $\langle \mathbf{s}_i \cdot \mathbf{s}_j \tilde{H} \rangle$                                 | -0.003 51 | +0.000 30              | +0.000 06            | -0.002 79    |
| $\langle n_{i\uparrow} n_{i\downarrow} \tilde{H} n_{i\uparrow} n_{i\downarrow} \rangle$     | 0.099 11  | +0.000 69              | +0.000 06            | 0.099 97     |
| $\langle n_i n_j \tilde{H} n_i n_j \rangle$                                                 | 0.418 70  | +0.003 18              | -0.000 07            | 0.424 93     |
| $\langle \mathbf{s}_i \cdot \mathbf{s}_j \tilde{H} \mathbf{s}_i \cdot \mathbf{s}_j \rangle$ | 0.064 98  | +0.000 33              | +0.000 05            | 0.065 74     |
| N atom                                                                                      |           |                        |                      |              |
| $\langle n_{i\uparrow} n_{i\downarrow} \tilde{H} \rangle$                                   | 0.031 09  | -0.001 30              | -0.000 03            | 0.029 71     |
| $\langle n_i n_j \tilde{H} \rangle$                                                         | 0.040 61  | +0.001 04              | +0.000 12            | 0.042 91     |
| $\langle \mathbf{s}_i \cdot \mathbf{s}_j \tilde{H} \rangle$                                 | -0.004 06 | -0.000 09              | -0.000 03            | -0.004 28    |
| $\langle n_{i\uparrow} n_{i\downarrow} \tilde{H} n_{i\uparrow} n_{i\downarrow} \rangle$     | 0.084 84  | +0.003 46              | +0.000 24            | 0.088 22     |
| $\langle n_i n_j \tilde{H} n_i n_j \rangle$                                                 | 0.371 52  | +0.006 97              | +0.001 02            | 0.387 49     |
| $\langle \mathbf{s}_i \cdot \mathbf{s}_j \tilde{H} \mathbf{s}_i \cdot \mathbf{s}_j \rangle$ | 0.052 63  | +0.001 72              | +0.000 19            | 0.056 45     |

same time. Table III shows that for both atoms the largest cluster to be computed contains eight atoms. These are the two central atoms and all their nearest neighbors (cluster II). The dominant corrections come from expectation values where the local orbital in the direction toward the additional atoms is involved.

Correlations between neighbor atoms were included and longer-range contributions estimated. They describe van der Waals polarization effects, i.e., they behave like  $1/R^6$  with increasing distance. The final results are presented in Table IV.

The calculation of the interaction matrix elements  $V_{ijkl}$

needed for these computations was performed within the Karlsruhe version of the Columbus program package.<sup>26</sup>

### C. Intra-atomic correlations

The next part of the correlation calculations consists in computing the intra-atomic correlations. To determine the intra-atomic orbitals  $g_i(\mathbf{r})$  for boron and nitrogen, we used the same method as for Si before.<sup>14</sup> As done there, the cutoff parameters and weight factors by which these states were generated from the atomic orbitals were optimized by a set of calculations within a small five-atom

TABLE IV. Contributions to the correlation and binding energies.

|                                  | Boron nitride<br>(a.u./unit cell) |               | B atom<br>(a.u.) | N atom<br>(a.u.) | Binding energy<br>(a.u./unit cell) |             |
|----------------------------------|-----------------------------------|---------------|------------------|------------------|------------------------------------|-------------|
| Interatomic correlations         |                                   |               |                  |                  |                                    |             |
| Single-site operators            | -0.065 92                         |               |                  |                  |                                    |             |
| Neighbor-atom operators          | -0.003 1                          |               |                  |                  |                                    |             |
| Longer-range correlations        | -0.001 0                          | $\pm 0.000 5$ |                  |                  |                                    |             |
| Total interatomic contributions  | -0.070 1                          | $\pm 0.000 5$ | -0.021           |                  |                                    |             |
| Intra-atomic correlations        |                                   |               |                  |                  |                                    |             |
| Single-site operators            | -0.117 1                          |               |                  |                  |                                    |             |
| Overlap corrections              | +0.002 3                          |               |                  |                  |                                    |             |
| Neighbor-atom operators          | -0.016 8                          |               |                  |                  |                                    |             |
| Total intra-atomic contributions | -0.131 6                          |               | -0.037           | -0.086           |                                    |             |
| Total correlation energies       |                                   |               |                  |                  |                                    |             |
| Result LA                        | -0.201 7                          | $\pm 0.000 5$ | -0.058           | -0.086           | -0.058                             | $\pm 0.001$ |
| Correction LA                    | -0.010                            | $\pm 0.001$   | -0.003           | -0.005           | -0.002                             | $\pm 0.001$ |
| Correction finite basis          | -0.084                            | $\pm 0.006$   | -0.011           | -0.036           | -0.037                             | $\pm 0.006$ |
| Final result                     | -0.296                            | $\pm 0.007$   | -0.072           | -0.127           | -0.097                             | $\pm 0.007$ |

cluster each, including the atom involved and its nearest neighbors. For these optimizations, the calculations were restricted to second-order perturbation expansion, i.e., the values  $\langle OHO \rangle_c$  were replaced by  $\langle OH_{SCF}O \rangle_c$ .

Since interatomic and intra-atomic operators are nonorthogonal, both types of correlations have to be taken into account simultaneously in order to determine the intra-atomic contributions. Intra-atomic contributions are defined in the following as modifications due to the newly added intra-atomic operators.

First the single-site contributions were computed. In evaluating the matrix elements only those basis functions were included which are centered either at one of the central atoms or at one of its nearest neighbors. Going to an eight-atom cluster increases the single-site intra-atomic contributions on boron by roughly 5% leading to a total correction of 20%. Here, the more delocalized character of the electrons on boron shows up since corresponding calculations for nitrogen converge better. In order to obtain a well-converged result for boron, an additional computation was performed for a cluster that includes three specific third-nearest neighbors in one direction. The inclusion of these additional local states did not change sizably the results anymore, guaranteeing that convergence was reached by the calculation within the smaller cluster.

The total intra-atomic correlation energy is not just a superposition of single-site contributions. As has been found out before, the only relevant corrections to such a superposition arise from neighbor sites. They are split into two different contributions. The first is an overlap effect. It arises because neither the local regions around individual atoms are well separated from each other nor are the intra-atomic correlation operators on different sites orthogonal. Such an overlap effect is computed by performing a calculation with intra-atomic correlations on a boron and a nitrogen site at the same time and comparing the result with the individual boron and nitrogen contributions. When summed up, the overlap corrections are one order of magnitude smaller than the single-site contributions.

The second contribution arises from short-range correlations between neighboring atoms. They are covered by operators built from pairs of intra-atomic states, one from boron and the other from nitrogen. The individual contributions and the final results are presented in Table IV.

This fast convergence of the intra-atomic correlation contributions is not astonishing because the dominant longer-range parts are covered by the interatomic contributions.

As mentioned above, for these computations the largest cluster from which all information may be gained to obtain well-converged results for the single-site intra-atomic contributions contained 11 atoms. Most computations were performed for clusters containing eight atoms only. In previous calculations,<sup>12,14,15</sup> only for the two central atoms of such an eight-atom cluster the basis set needed to be extended by  $d$  functions. The reason for this restriction was that these calculations were based on a SCF computation within a basis of double- $\zeta$  quality and only for correlation purposes one set of  $d$  functions on

each of the central atoms was added.

Here, polarization functions were already used on the SCF level. Within the present calculation,  $d$  orbitals were therefore included on all the atoms of the clusters. Leaving them completely out would cause on the interatomic level an increase in interatomic correlation energy of 9%. For intra-atomic calculations, the effect of the  $d$  orbitals could not be well estimated from results with  $d$  orbitals on the two central atoms only. It turned out that the effect of the  $d$  functions on two nearest-neighbor atoms is not additive. For nitrogen a complete set of nearest-neighbor B atoms including  $d$  functions was needed. These functions, although not used for the local states in this calculation, changed the total intra-atomic correlation energy on nitrogen by 13%. A set of additional  $d$  functions on one of these nearest neighbors alone already changed this energy by 11%. A guess of the effect of nearest-neighbor  $d$  functions based on the latter value alone would have led to a correction of 44% and caused an error of 31%. Convergence for the intra-atomic correlation energy on boron with respect to neighbor  $d$  functions was better. There the final result could be predicted from a cluster calculation with  $d$  orbitals on two sites only with an accuracy of 0.3%. An explanation for this difference is certainly that the  $d$  orbitals on the B atom are considerably more delocalized than those on the N atom.

#### D. Binding energy

Knowing the corresponding value for the free atoms<sup>27</sup> and the solid within the related finite basis sets, it is easy to calculate the individual contributions to the binding energy. So-called interatomic correlations on a B atom refer to excitations within the valence shell, i.e., from the  $2s$  occupied orbital into  $2p$  unoccupied ones. Such an excitation does not exist for the N atom. In Sec. III A, the calculated binding energy in the SCF approximation and the estimated HF limit were discussed. Correlation energy contributions to the binding energy are listed in the last column of Table IV.

The calculations done so far have two shortcomings. The first is due to the specific selection of operators from the total space of two-particle excitations within the restricted basis set. From molecular calculations, it is known that the local ansatz misses roughly 5% of the total correlation energy due to this restriction.<sup>10,11</sup> We assume that the same shortcoming applies for solids as well.

The second and most important correction is connected with the finite basis used here. It is known that such a basis set underestimates the correlation energies for the independent free atoms by  $-0.011$  a.u. for boron and  $-0.036$  a.u. for nitrogen, respectively. The correlation energies of the atoms when calculated within the same basis set as used in the solid computation (but without contractions of the outer exponents) were determined by a standard quantum-chemical calculation.<sup>27</sup> The corresponding correlation limits were taken from the literature.<sup>25,39</sup> It is further known how these corrections change when the atoms are part of a small molecule like  $BH_3$  and  $NH_3$  (for a detailed discussion, see the Appen-

TABLE V. Binding energy contributions of boron nitride (a.u./unit cell).

|                           |                     |        |
|---------------------------|---------------------|--------|
| SCF result                | -0.361              |        |
| Finite-basis corrections  | -0.003              | ±0.002 |
| HF limit (estimated)      | -0.364              | ±0.002 |
| Correlation contributions |                     |        |
| Result local ansatz       | -0.058              | ±0.001 |
| Corrections LA            | -0.002              | ±0.001 |
| Finite-basis corrections  | -0.037              | ±0.006 |
| Final result              |                     |        |
| Zero-point motion         | +0.012              |        |
|                           | -0.449              | ±0.007 |
| Experimental value        | -0.485 <sup>a</sup> |        |

<sup>a</sup>Reference 5.

dix). A first guess for the basis size defects is to transfer these values to the solid calculation. That is for the total correlation energy roughly the correction for a free B atom multiplied by a factor of 1.6 and that for a free nitrogen atom by a factor of 1.9. From similar comparisons on C molecules it is known that such factors usually vary by 10% for different bonding.

Adding these finite-basis-size corrections to the final result, an estimated total correlation energy per unit cell is obtained, together with an error bar representing the uncertainties for estimates on small molecules. These values as well as the final values for the correlation contributions to the binding energy are listed in Table IV, too. The final result for the binding energy is presented in Table V. In order to compare with experimental values, corrections due to zero-point vibrations of the atoms were subtracted.<sup>7</sup> The outcoming binding energy is underestimated by 0.036 a.u. as compared with the experimental value. The defect is one order of magnitude larger than the error bar due to uncertainties in the estimates of the finite-basis-size corrections.

#### E. Inclusion of new basis functions on empty sites

The deviation of the binding energy computed so far from the experiment can only be explained by a poor estimate of finite-basis-size corrections. As was explained above, the basis size defects were guessed by transferring the corresponding values found for small molecules to the solid calculation. Table VI present a few results obtained by the same method as in the present calculation.

As can be seen, the defects occur only for both three-dimensional solids diamond<sup>12,13</sup> and BN but not for graphite<sup>13</sup> and polyethylene.<sup>15</sup> There is an important difference between these systems. While the outer environment in all low-dimensional systems looks like that of small molecules, the situation in a three-dimensional solid is very different. There is no outer-atom-like part of the electronic charge around the atoms. Besides, in the cases considered here, the three-dimensional structure contains large open areas. These areas contain a non-negligible

TABLE VI. Electronic binding energy of BN, diamond, graphite, and polyethylene (a.u./unit cell).

| Binding energy | Estimated value | Experimental value |
|----------------|-----------------|--------------------|
| Boron nitride  | -0.449±0.007    | -0.485             |
| Diamond        | -0.541±0.007    | -0.555             |
| Graphite       | -0.556±0.007    | -0.555             |
| Polyethylene   | -0.470±0.005    | -0.468             |

part of the electronic charge that might be seen as being condensed from the outside charge of the individual atoms. It is plausible to assume that correlations within these areas are very different from correlations in the outer parts of a molecule or atom. Although the charge distribution within these areas is apparently well described by the basis orbitals centered on the individual atoms, these basis orbitals contain no degree of freedom for a finer short-range correlation within these domains. Therefore all changes in correlation energy due to such a charge redistribution were left out so far. When comparing diamond with BN, then we expect larger corrections for those domains for BN because the charges around B atoms, although smaller than those around C atoms, are significantly more delocalized. This argument would allow one to understand the increase in deviations for BN.

In order to test this idea, we have repeated the correlation calculation including an *s*-like function on each of the interstitial positions. As the exponent, we have chosen  $\alpha=0.4$  a.u. These interstitial positions can easily be imagined when describing the BN crystal structure within a cubic supercell with length *a*. There, the B atoms have a fcc-like order with one atom fixed at  $\mathbf{r}=(a/4)(0,0,0)$  in the unit cell and the N atoms the same order with one atom fixed to  $\mathbf{r}=(a/4)(1,1,1)$ . One set of empty sites is used to add four new neighbors around each B atom to the existing four N atoms. We call these sites pseudo-N-sites. They are represented by the position  $\mathbf{r}=(a/4)(1,1,-1)$ . Corresponding, pseudo-B-sites are generated at the position  $\mathbf{r}=(a/4)(0,0,2)$  and its fcc lattice. The change in the SCF energy is  $1.010^{-3}$  a.u., indicating that there is no need for such functions on the SCF level.

For the correlation calculation these interstitial orbitals were used as additional intra-atomic regions on the interstitial sites. These positions were treated like normal atoms. This leads first to a single intra-atomic correlation contribution on each of them and next to overlap and pair correlation corrections with neighbor B and N atoms each. As was already explained in Sec. III C, for the evaluation of matrix elements only basis functions on a small cluster were used. When these intra-atomic correlation calculations for the pseudo-atom-sites were performed, a complete neighborhood of each of the two different pseudoatoms was included. This led to a cluster of 16 atoms. To make such a computation feasible, *d* functions were added only on B atoms and on the central N atom.

From the positions of the pseudoatoms in the unit cell, it follows that each pseudo-N-site has four nearest-

neighbor B atoms, four nearest-neighbor pseudo-B-sites, and six next-nearest-neighbor N atoms. A similar relation holds for each pseudo-B-site.

Table VII gives the additional contributions to the correlation energy. When added up, a sizable increase of the total correlation energy is found. For the binding energy, the effect of these additional basis functions for the individual atom calculations needs to be considered. It was found that four additional *s* orbitals in the pseudo-N positions around a B atom lead to an increase in correlation energy of 0.0015 a.u., the corresponding pseudo-B functions for a N atom to 0.0017 a.u.<sup>27</sup> As can be seen, these functions are roughly a factor of 4 more relevant for the solid leading to a sizable contribution to the binding energy that amounts to  $-0.010$  a.u./unit cell. The rescaling factors 1.6 and 1.9 found from molecules would only have given a contribution to the binding energy that amounts to  $-0.002$  a.u./unit cell. Therefore one-quarter of the original defect in the binding energy estimate is removed by adding only a single *s* orbital on each of the interstitial positions. The outcoming value is  $-0.457$  a.u./unit cell. Adding a larger basis set on these places would allow one to improve this result even more.

When returning to the empirical rescaling of finite-basis-size defects, one sees that values halfway in between the rescaling functions as found from the molecules and as found from the interstitial contributions would bring the binding energy close to the experimental value.

Our results indicate that the calculations done so far have covered correlations in the interstitial regions poorly. An important task for the future will be to cover these contributions better and to develop a way to derive an empirical correction for the finite-basis-size defect that includes these contributions as well.

Our present guess for the binding energy is still 0.028 a.u. above experiment. It is of interest to compare this value with results obtained within the LDA.<sup>5,6</sup> There, calculations using plane waves as basis functions obtain values that overestimate the binding energy by 0.041 a.u. A different LDA calculation in a GTO basis set of double- $\zeta$  quality led to a binding energy of  $-0.496$

a.u./unit cell.<sup>7</sup> Its deviation from the first result of 0.030 a.u./unit cell originates from the lack of polarization functions which contribute significantly as seen in our SCF calculations. There, the difference between a double- $\zeta$  result and our guess of the HF limit amounted to  $0.028 \pm 0.002$  a.u./unit cell.

#### IV. CHARGE DISTRIBUTION AND CORRELATION STRENGTH

It is very easy to deduce the ionic charge distribution in BN from our calculation, since for correlation purposes orthogonalized atomic orbitals (hybrids) were generated. For the SCF ground state, we obtain a valence electron charge  $\langle n_{i\sigma} \rangle$  for atomic orbitals *i* on B sites of 0.3146 and for hybrids on N sites 0.6841. This leads to a total charge of  $n_B = 2.517$  and  $n_N = 5.473$ . The approximations made when the atomic hybrids were determined cause a total loss in charge of roughly 0.1%. This ionic charge on boron of  $+0.48$  is much larger than values found by a Mulliken population analysis within a calculation using a minimal basis before.<sup>2</sup> We did not attempt to find out whether this discrepancy originates from artefacts of the small basis in this calculation or whether it is connected with principal shortcomings of a Mulliken analysis for solids. Our interpretation of the charge distribution with the help of orthogonalized atomic orbitals leads to an ionizity in fair agreement with a value needed to explain the pion capture at the boron nucleus.<sup>28</sup> There, interesting differences arise for the different structures of BN.

When correlations are included, this charge distribution changes only very little. Therefore BN comes out rather ionic with half an electron transferred from the rather delocalized atomic orbitals on boron into the localized ones on nitrogen.

Of interest is furthermore the strength of the correlations  $\Sigma$ . It is defined as the reduction of charge fluctuations within an atomic hybrid *i* around the average charge distribution due to correlations ( $\Delta^2 n_{i_{\text{corr}}} - \Delta^2 n_{i_{\text{SCF}}}$ ), compared with the maximal reduction ( $\Delta^2 n_{i_0} - \Delta^2 n_{i_{\text{SCF}}}$ ), present in the completely correlated state, i.e.,

$$\Sigma = \frac{\Delta^2 n_{i_{\text{corr}}} - \Delta^2 n_{i_{\text{SCF}}}}{\Delta^2 n_{i_0} - \Delta^2 n_{i_{\text{SCF}}}}. \quad (17)$$

Charge fluctuations are largest in the SCF ground state:

$$\Delta^2 n_{i_{\text{SCF}}} = 2 \langle n_{i\sigma} \rangle (1 - \langle n_{i\sigma} \rangle), \quad (18)$$

where  $\Delta^2 n_i$  is defined as  $\Delta^2 n_i = \langle n_i^2 \rangle - \langle n_i \rangle^2$ .

Within a perfectly correlated limit but with a charge distribution  $\bar{n}_i$  that is not an integer number, there is a residual charge fluctuation that amounts to

$$\Delta^2 n_{i_0} = \begin{cases} \bar{n}_i (1 - \bar{n}_i), & 0 \leq \bar{n}_i \leq 1 \\ (2 - \bar{n}_i)(\bar{n}_i - 1), & 1 \leq \bar{n}_i \leq 2 \end{cases}. \quad (19)$$

TABLE VII. New contributions to the correlation energy (a.u./unit cell).

|                                |         |
|--------------------------------|---------|
| pseudo-N correlations          |         |
| Single-site operator           | -0.0030 |
| pseudo-N-B operators           | -0.0039 |
| pseudo-N-N operators           | -0.0026 |
| pseudo-B correlations          |         |
| Single-site operator           | -0.0010 |
| pseudo-B-B operators           | -0.0006 |
| pseudo-B-N operators           | -0.0018 |
| pseudo-N pseudo-B correlations |         |
|                                | -0.0001 |
| Final result                   | -0.0130 |



TABLE VIII. Relative and absolute reduction of charge fluctuations within the atomic hybrids and of the total charge fluctuations.

|                                                              | Boron nitride |        | Diamond |
|--------------------------------------------------------------|---------------|--------|---------|
|                                                              | B atom        | N atom |         |
| $\Sigma$                                                     | 23%           | 30%    | 16%     |
| $\Delta^2 n_{i_{\text{corr}}} - \Delta^2 n_{i_{\text{SCF}}}$ | 0.024         | 0.031  | 0.040   |
| $\Delta$                                                     | 28%           | 40%    | 32%     |
| $\Delta^2 n_{\text{corr}} - \Delta^2 n_{\text{SCF}}$         | 0.42          | 0.60   | 0.64    |

The actual charge fluctuations in the correlated ground state are roughly given as

$$\Delta^2 n_{i_{\text{corr}}} \cong \Delta^2 n_{i_{\text{SCF}}} - 2 \sum_n \eta_n \langle O_n n_{i\uparrow} n_{i\downarrow} \rangle_c. \quad (20)$$

Table VIII contains the correlation strength as well as the absolute reductions of the charge fluctuations in an atomic orbital for boron and nitrogen and compares it to the values on a C atom in diamond. It can be seen that the electrons in nitrogen are rather strongly correlated.

Another value of interest is that of the total charge fluctuations. In the SCF approximation, this value  $\Delta^2 n_{\text{SCF}}$  is given as the sum over the individual charge fluctuations in each atomic hybrid while correlated reductions of charge fluctuations  $\Delta^2 n_{\text{corr}}$  arise from correlations in the individual hybrids but between them as well. Table VIII gives the values  $\Delta^2 n_{\text{corr}} - \Delta^2 n_{\text{SCF}}$  and

$$\Delta = \frac{\Delta^2 n_{\text{corr}} - \Delta^2 n_{\text{SCF}}}{\Delta^2 n_{\text{SCF}}}. \quad (21)$$

Here, it can be seen from the values for B, C, and N that the relative reduction  $\Delta$  rises almost linearly with the occupation. These values demonstrate once more that electrons in inhomogeneous systems correlate sizably on an atomic scale. Atomic charge fluctuations are always reduced to values almost halfway in between the uncorrelated and the strongly correlated limits. The results for these correlations are very little influenced by short-range correlations. Therefore the restriction to a finite basis set per atom does not matter for them.

## V. CONCLUSIONS

We have given results of a detailed correlation calculation for the ground state of boron nitride. As in all cases handled before, correlations on the atomic scale, i.e., correlations described by interatomic operators, play a dominant role. Charge fluctuations that come in due to bonding are reduced by almost 50% as compared with the SCF ground state. It is due to these corrections that many-body effects influence ground-state properties mostly. This is seen by the answer to the quest for the origin of dimerization in polyacetylene<sup>16</sup> as well as by an explanation for a lot of smaller or larger defects of the description of transition metals within the LDA.<sup>29-31</sup> In the latter case, these conclusions could not yet be made

from *ab initio* calculations but were based on a careful treatment of a reasonable model Hamiltonian. Even for high-temperature superconducting compounds, these many-body effects could be analyzed—this time by *ab initio* calculations but for finite clusters only, not yet for the solid.<sup>32,33</sup>

The largest shortcomings within our correlation calculations arose for the correlation energy and its contributions to binding. The reason for this defect is well known from molecular calculations. Within a given one-particle basis, the very short-range cusp of the correlation hole around the individual electrons is poorly described. It is averaged over the partial atomic volume spanned by the typical hybrids that can be formed from the given basis. Within the actual basis set used, the valence electron correlation energy is underestimated by 30%. A finite-basis-size correction was introduced before that splits the basis defect into a set of contributions on the individual atoms. These contributions were taken from results on small molecules. While this empirical correction has worked rather well so far, a deficiency of 10% was found for the compound BN. It was demonstrated that this defect originated from a poor coverage of correlations in the interstitial positions within the given basis set. For the future, the basis sets used need to be extended by functions on interstitial positions, as was done here.

It is of interest to make a comparison with another scheme with which correlations in inhomogeneous systems can be handled.<sup>17,18</sup> It is a Monte Carlo integration of a specific Jastrow ansatz. Starting from an SCF ground state, correlations are added by an exponential operator. In its exponent, a two-particle density operator is written that simulates the correct correlation cusp for a homogeneous electron gas with the average density of the solid or alternatively contains a single variational parameter determining this cusp. This way, the short-range part of the correlation hole is much better covered than within a calculation limited to a finite one-particle basis set. However, no special attention is given to correlations described by atomic operators and the long-range correlations may well be described completely wrong. Covering these correlations by additional operators would require one to optimize too many variational parameters within such a Monte Carlo calculation. It was a remarkable success that within this scheme the correlation of the valence electrons of diamond could be computed.<sup>17</sup> It turned out there that within such a single parameter treatment almost 90% of the correlation energy could be obtained.<sup>12,13,17</sup> For diamond, interatomic correlations contribute with 25% to the correlation energy,<sup>12,13</sup> indicating that more than half of the energy gain due to these correlations is covered by the single parameter ansatz. For the binding energy contribution, the deficiency of this ansatz is somewhat larger. This shortcoming is hidden by a too large estimate for the HF binding energy. Within a Monte Carlo calculation, one is restricted to systems of finite size. Therefore, on the level of the one-particle calculations, a finite size correction needed to be estimated. This correction was apparently overestimated, as can be seen when comparing the resulting HF binding energy with previous estimates.<sup>12,13,17</sup> A detailed com-

parison will be given elsewhere.<sup>13</sup>

There are different alternatives to improve beyond the present state of our correlation calculations. The first is to stay in finite but more extended basis sets. A set extended to two  $d$ -function sets and one  $f$ -function set per B or N atom can be handled within the correlation treatment without problems. When some basis functions on the interstitials are added too, then such a basis should decrease the actual basis size defect to less than half of its present size and should allow one to obtain a more precise estimate of the contributions still lacking.

An alternative is to introduce two-particle wave functions so that the correlation cusp is better described but to stay within an analytic treatment. Such schemes have been recently worked out for atoms and small molecules.<sup>34-37</sup> When extending the local ansatz, these functions would come in for intra-atomic correlations only. Due to the experience gained for intra-atomic correlations, they would, even for a solid calculation, enter only for single sites and pairs of neighbor atoms; furthermore, they were to be included only in second-order perturbation expansion, restrictions that make such an extension feasible.

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#### APPENDIX: ESTIMATE OF FINITE-BASIS-SIZE CORRECTIONS FOR THE MOLECULES BH<sub>3</sub> AND NH<sub>3</sub>

In order to be able to estimate the basis size defects for solid calculations, it is necessary to obtain them for small molecules. Here, we have selected BH<sub>3</sub> and NH<sub>3</sub> as representatives for the solid BN. The experimental values for the binding energy of these molecules  $\epsilon_{\text{expt}}$  has been deduced from standard heat of formation data.<sup>38</sup>

TABLE IX. Contributions to the binding energy (a.u.).

|                              | BH <sub>3</sub>        | NH <sub>3</sub>     |
|------------------------------|------------------------|---------------------|
| $\epsilon_{\text{elec}}$     | -0.443 32              | -0.473 82           |
| HF limit                     | -0.371 57 <sup>a</sup> | -0.325 <sup>b</sup> |
| $\epsilon_{\text{corr}}$     | -0.071 75              | -0.149              |
| $\epsilon_{\text{corr}}(fb)$ | -0.059 60 <sup>c</sup> | -0.112 <sup>c</sup> |
| $\Delta\epsilon_{XH_3}$      | -0.012 15              | -0.037              |

<sup>a</sup>Reference 25.

<sup>b</sup>Reference 39.

<sup>c</sup>Reference 27.

Those were corrected by the zero-point vibration energy,  $E_{\text{vib}}(0 \text{ K})$ ,<sup>38</sup> i.e., the electronic contribution to the binding energy is defined as

$$\epsilon_{\text{elec}} = \epsilon_{\text{expt}} - E_{\text{vib}}(0 \text{ K}). \quad (22)$$

When subtracting from  $\epsilon_{\text{elec}}$  the HF limit of the binding energies, an estimate for the correlation energy contribution to the binding energy ( $\epsilon_{\text{corr}}$ ) is obtained. This value is compared in Table IX with the corresponding contribution obtained within the finite basis  $\epsilon_{\text{corr}}(fb)$ .

The resulting defect  $\Delta\epsilon_{XH_3}$  ( $X=B,N$ ), is roughly separated into  $X$  and  $H$  atomic contributions. The corrections for the  $X$  atom within the molecule  $XH_3$ , i.e.,  $\Delta_X(XH_3)$ , turn out to be

$$\begin{aligned} \Delta_X(XH_3) &= -3\Delta_H(XH_3) + \Delta\epsilon_{XH_3} \\ &= \begin{cases} -0.006 15 \text{ a.u.}, & X=B \\ -0.030 86 \text{ a.u.}, & X=N \end{cases} \end{aligned} \quad (23)$$

The same basis set underestimates the correlation energies for the independent free atoms by  $-0.011$  a.u. for boron and  $-0.036$  a.u. for nitrogen, respectively. For the molecules, the deficit in total correlation energy is represented by the one for a free B atom multiplied by a factor of 1.6 and that for a free N atom, multiplied by a factor of 1.9.

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