Structure prediction based on \textit{ab initio} simulated annealing for boron nitride

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Possible crystalline modifications of chemical compounds at low temperatures correspond to local minima of the energy landscape. Determining these minima via simulated annealing is one method for the prediction of crystal structures, where the number of atoms per unit cell is the only information used. It is demonstrated that this method can be applied to covalent systems, at the example of boron nitride, using \textit{ab initio} energies in all stages of the optimization, i.e. both during the global search and the subsequent local optimization. Ten low lying structure candidates are presented, including both layered structures and 3d-network structures such as the wurtzite and zincblende types, as well as a structure corresponding to the $\beta$-BeO type.

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I. INTRODUCTION

The knowledge of the crystal structure of a solid compound is one of the basic questions in solid state theory\cite{1, 2, 3, 4, 5}. Since the early 1990’s, an effort has been made to develop methods to predict structures of solids without any experimental information about the structure. The starting point is the realization that any (meta)stable modification of a (solid) compound corresponds to a locally ergodic region on the energy landscape of the chemical system. For low temperatures, such regions are centered on local minima of the energy that are surrounded by sufficiently high energy barriers. Since both the thermodynamically stable and the multitude of kinetically stable modifications are of interest, the global search is not restricted to the determination of the global minimum, but also includes local minima\cite{6}.

The most common methods used for the structure prediction of solids are simulated annealing\cite{7, 8}, genetic algorithms\cite{9, 10, 11, 12}, basin hopping\cite{13, 14}, or the recently introduced metadynamics\cite{15}.

Structure prediction usually involves a huge amount of CPU time, and therefore efficient ways to keep the calculations tractable have to be found. Thus, the procedures were initially split in two steps: first, a global search on the potential surface was performed. The energy was evaluated with empirical potentials, e.g. Coulomb and Lennard-Jones potentials, or chemically/physically motivated cost functions. After the global search, e.g. using simulated annealing, possible structure candidates were locally optimized on the \textit{ab initio} level, usually with density functional theory.

Empirical potentials are very efficient, but also have various drawbacks: they work reasonably well for ionic systems, but less for covalent systems; and some knowledge of the expected bond type is required in advance to choose the potential. Recently\cite{16}, we demonstrated that a full \textit{ab initio} treatment is feasible in both stages, i.e. the global search and the subsequent local optimization can both be performed on the \textit{ab initio} level. The system considered (lithium fluoride) was chosen for several reasons: the small number of electrons leads to fast calculations, and the ionicity of the system makes convergence easy. Moreover, the system had earlier been studied with model potentials\cite{17, 18}, and it turned out that the relevant minima were the same when full \textit{ab initio} structure prediction was performed\cite{16} (for a brief summary see also\cite{19}).

In the present work, boron nitride (BN) was chosen as an example for a covalent system. This is a significant extension of the previous work, since a covalent system is much more difficult to study: covalent bonds between the atoms have to be formed, and convergence for random structures is much more difficult in this case. At zero pressure, BN has a hexagonal structure, with space group 194, see e.g.\cite{20}. Under pressure, it may transform to a zincblende\cite{21} or a wurtzite structure\cite{22}, and a corresponding phase diagram was obtained\cite{23}. There is, however, an ongoing discussion concerning the correct phase diagram, see e.g.\cite{24}. Also, a rhombohedral structure was found (a layered structure similar to the hexagonal structure)\cite{25}, and turbostratic boron nitride with a random arrangement of the layers has been reported\cite{26}. These structures are summarized in table\\ref{tab:1}.

For overviews, see also\cite{27, 28}. Early \textit{ab-initio} calculations were performed from the mid 1980’s onwards, e.g.\cite{29, 30, 31, 32, 33, 34, 35, 36, 37}.

The present task is for several reasons far from straightforward: first, the CPU time has to be reduced by a large factor. As we showed for the system LiF\cite{16}, simply performing simulated annealing with standard \textit{ab initio} calculations would lead to CPU times of the order of 2 years for a single run, and often hundreds of such runs need to be performed. Therefore, very subtle methods have to be employed to reduce the CPU time for the \textit{ab initio} calculations, without losing too much accuracy. In our earlier study of LiF, very careful tests were required in order to reduce the CPU time to a few days. Similarly, many tests have to be performed to reduce the required CPU time in the case of BN to reasonable values. Secondly, one needs a strategy to converge the system in all the global exploration: at the beginning of the search, the unit cell has a very large volume, and the atoms are at random positions within the cell, i.e. the
configuration is like in a gaseous state. The total energy calculation at such a geometry has to be converged, and it has to be converged for all the subsequent steps of the simulated annealing procedure. This has to be done in an automatic way, since thousands of calculations at successive geometries are performed. Finally, it is a very interesting and important question whether this procedure will find all the very different structure types: the layered structures, and the three-dimensional structures such as wurtzite and zincblende.

II. METHOD

The general method consists of several steps: first, a simulated annealing run with a subsequent stochastic quench is performed, to identify possible candidate structures. This is followed by a local optimization based on analytical gradients. Finally, the symmetry and space group are identified. This is repeated many times, in order to identify as large as possible a set of structure candidates, and to obtain some statistics about the structures found.

The details for the BN calculations are described in the following paragraphs. 4 boron and 4 nitrogen atoms were placed at random positions in a large unit cell which was initially cubic with the cell parameter a=6.23 Å. This initial volume is computed by first employing the atomic/ionic radii to estimate the total volume occupied by the atoms in the solid state and then multiplying this number by a sufficiently large factor (typically between 3 and 10), to allow the atoms enough freedom to reach any arrangement independent of the initial random placement in the simulation cell. This factor was varied in preliminary calculations, where it was found that choosing a larger volume than the one selected (6.23 Å³ = 242 Å³, which is already by a factor of ~5 larger than the volume of e.g. the zincblende structure) did not lead to significantly different results.

Each simulated annealing run had a length of 12500 steps, and the initial temperature of 1.00 eV (corresponding to 11604 Kelvin) was reduced to ~0.78 eV at the end of the run. The length is thus somewhat longer than in the case of LiF [10], because it is more difficult to approach possible candidate structures in a system with covalent bonds. The simulated annealing was followed by a quench with 5000 steps, i.e. a simulated annealing run with a temperature of 0 eV, which means that only downhill moves are allowed during the quench. The quench thus moves the geometry obtained after the simulated annealing further towards a local minimum. The moves were chosen as: moving individual atoms (70%), exchanging atoms (10%), changing the lattice parameters with fixed fractional coordinates (10%), changing the lattice parameters with fixed cartesian coordinates (5%), and changing the origin (5%, this move is important if subsequently the cell parameters change). No symmetry was prescribed during the simulated annealing and quench runs, i.e. the space group was always P1.

A minimum distance between two atoms (given by the sum of the radii of the atoms, multiplied with 0.7) was prescribed in order to avoid unrealistic geometries which may lead to numerical instabilities. The radii used were based on tabulated values for atomic and ionic radii, as a function of charge, and the Mulliken charge computed for the previous configuration. In those moves which change the lattice constant, the probability of reducing the lattice constant was enlarged to 60%, to speed up the reduction of the cell size.

The ab initio calculations were performed with the CRYSTAL06 code [38], which is based on local Gaussian type orbitals. Two basis sets were used during the simulated annealing runs, starting from a [3s2p] basis set for B and N, with the inner [2s1p] exponents as in [39]. In the case of basis set I, additional sp exponents of 0.4 for B and 0.3 for N were chosen, and the outermost exponent of the B 2sp contraction (0.4652) was removed. In the case of basis set II, the outer sp exponents were chosen as 0.25 for B and 0.297 for N. The basis sets are given in table III. In the stage of the local optimization, the basis sets used were the [3s2p1d] basis sets from [32] (basis set III in table III).

The basis sets during the simulated annealing are therefore chosen slightly different from the ones used in the local optimization (less diffuse functions, no polarization functions), to speed up the global search which is the time-consuming part of the procedure. To test these basis sets, as a preliminary step, the energies of the wurtzite and of the layered Bₖ structure were computed with various basis sets (table III). With basis set III, which is used during the local optimization, the Bₖ structure is more favorable by ~30 mₑ, i.e. ~0.8 eV (1Eₜₕ = 1 hartree = 27.2114 eV). The smallest basis set I gives preference to the wurtzite structure instead, by 33 mₑ (0.9 eV), and basis set II gives preference to the Bₖ structure, by 8 mₑ (0.2 eV). One might thus fear that
basis set I would not yield the layered structures during the global search; however, this is not the case, as will be shown in the results section; and there does not seem to be a strong bias due to the basis set. Basis set I is however advantageous because calculations are roughly twice as fast as with basis set II.

Concerning the choice of the *ab initio* method, it has to be taken into account that convergence at a random geometry is necessary during the global exploration stage. As mentioned earlier, the initial geometry has a cell volume ~5 times larger than the experimental volume, and the atoms are randomly arranged. A typical band structure of such a geometry is very localized due to the large interatomic distances, and completely different from the band structure of the experimental geometry in the solid state. Therefore, convergence is absolutely non-trivial. It turned out that convergence was best achieved with the Hartree-Fock approach, due to the fact that the band gaps are usually very large. Indeed, the band structure and corresponding densities of states display band gaps of ~6 eV (Hartree-Fock), ~0.5 eV (B3LYP), and ~0.1 eV (LDA) for this initial structure. Note that this gap corresponds to a random initial structure and is very different from the gap of the final structure; but it is necessary to converge a calculation for this random initial geometry, and for all the geometries subsequently generated, until the end of the simulated annealing and quench. For comparison, calculations with the hybrid functional B3LYP were found to be much more difficult to converge, and a large mixing ratio was required: 90%, in combination with the Anderson mixing scheme; 35% was sufficient in the case of Hartree-Fock (the mixing ratio is the ratio with which the previous Fock operator is added to the new one, in order to achieve convergence). This leads to many iterations and thus a large CPU time. The local density approximation (LDA) was very difficult to converge for random atom arrangements, and needed more $k$ points and level shifting.

Interestingly, even for the initial structure consisting of widely spaced, nearly isolated atoms, it was sufficient to use the restricted Hartree-Fock approach, i.e. it was not necessary to take into account spin-polarization which would be the case for a free atom.

The thresholds for integral selection were enlarged from $10^{-6}$, $10^{-6}$, $10^{-6}$, $10^{-12}$ to $10^{-4}$, $10^{-4}$, $10^{-8}$, respectively, and the self consistent field cycles were stopped when the difference between two subsequent cycles was below $10^{-4} E_h$. A mesh with $4 \times 4 \times 4$ $k$-points was used. The error associated with the $k$ mesh can be estimated by computing the energy difference when changing the lattice constant: e.g. changing the lattice constant of BN in the zincblende structure from 3.7 to 3.6 Å changes the energy by 0.01368 $E_h$ for four formula units with a $4 \times 4 \times 4$ mesh, and by 0.01436 $E_h$ with a $8 \times 8 \times 8$ mesh. The associated error with the mesh is thus 0.01436-0.01368 = 0.00068 $E_h$ and reasonably small.

The simulated annealing and subsequent quench are the time consuming parts, and a single run takes of the order of one week on a single CPU. The same approach would have been feasible with the B3LYP functional, but at a much higher cost, for the reasons discussed above (around a month instead of one week CPU time). It appeared therefore more reasonable to perform four times as many runs (here: around 329, see table IV) using the Hartree-Fock approach, as with the B3LYP approach where around 80 runs would have been feasible with a comparable total CPU time.

The local optimization is not very time consuming and was done with default parameters for the integral selection and the self consistent field cycles. The full geometry optimization can by now be routinely performed with analytical gradients [40-43, 44, 45, 46, 47, 48] as implemented in the CRystal06 release. The local optimization, starting from the structure after the quench, was done both at the HF level and at the LDA level; in nearly all the cases, the resulting final minimum structures turned out to be the same. In addition, for these final structures, also a B3LYP optimization was performed, in order to compare Hartree-Fock, B3LYP and LDA. The basis set used was basis set III in table III. In addition, in appendix A larger basis sets were tested, for comparison.

The symmetry was analyzed with the program KPlot [49] where algorithms to find the symmetry and space group [50, 51] are implemented. For the most important structures, the enthalpy was computed, in order to investigate the pressure dependence of the phases.

### III. RESULTS AND DISCUSSION

The most relevant structures found are displayed in figures [12, 15] and [18] visualized with XCRYsDen [48]. Optimized geometries are given in table V. First, the experimentally observed $B_h$ structure was obtained (so-called hexagonal boron nitride, space group 194). Closely re-

| structure | basis set I | total energy |
|-----------|-------------|--------------|
| $B_h$     | -316.6687   |              |
| II        | -316.7495   |              |
| III       | -316.8452   |              |

*TABLE II: The Hartree-Fock energies (in hartree, per four formula units) of the $B_h$ and wurtzite structures, computed with the small basis sets used during the global optimization (basis set I, II), in comparison with the energy obtained with the basis set used for the local optimization (basis set III). The geometry was fixed at the computed equilibrium geometry of basis set III (table V).*
lated are two additional layered structures, with space group 160 and 187, respectively. In the \( B_6 \) structure, sheets are made of edge-connected six-membered rings of 3 boron and 3 nitrogen atoms in alternating sequence (see figure 1). The neighboring sheets are stacked vertically below and above, with alternating atoms (i.e. N sits vertically above B, and vice versa; the stacking order is ABAB). In space group 160, the same sheets are formed, but only three atoms have neighbors in the layer above, and the other three atoms have neighbors in the layer below (the stacking order is ABCABC, i.e. like in rhombohedral BN [25]). The structure with space group 187 has stacking order ABAB, where again three atoms have neighbors vertically above and below in the next layer. These three layered structures have a very similar total energy, and also the enthalpy as a function of pressure looks very similar (see figure 5).

The wurtzite structure is displayed in figure 2 left. The zincblende structure is displayed in figure 2 middle, and has a similar energy as the wurtzite structure. At zero pressure, the energies of the wurtzite and zincblende structure are comparable to that of the layered structures in figure 1.

The structure with space group 136 has six-membered rings (3 B, 3 N, alternating), but also rings with 4 (2 B, 2 N) atoms. This leads to angles close to 90° and a less favorable energy (see figure 2 right). This structure corresponds to the \( \beta \)-BeO type [49], which demonstrates that the method presented gives reasonable low-lying structure candidates: as Be has one electron less than B, and O one more than N, it makes sense that such the \( \beta \)-BeO structures is found as a candidate structure also for BN. Under ambient conditions, BeO crystallizes in the wurtzite structure, and the \( \beta \)-BeO structure is found as a high temperature phase [49].

The structure with space group 62 has four-, six- and eight membered rings. The topology is similar to the one of the aluminum network in the SrAl\(_2\) structure under ambient pressure (space group 74, Imma): one has to replace one aluminum atom with boron, the neighboring one with nitrogen, and discard the strontium. This is reasonable, as the two aluminum atoms obtain two electrons from strontium and thus have 8 valence electrons together, i.e. the same number of valence electrons as one boron and one nitrogen atom together. The structure with space group 14 consists of layers - each of them consisting of rings with four or eight atoms. Finally, two structures with relatively large channels (i.e. large regions in the unit cell without atoms) were found, with space groups 8 and 9, respectively.

The geometries are in reasonable agreement with the available experimental data in table IV. The computed cell parameter \( a \) and the interlayer distance are approximately constant for the layered structures with only six-membered rings (with space groups 194, 160, 187); this is also observed in the experiment when comparing the \( B_6 \) and the rhombohedral structure.

Total energies and statistics are given in table IV. The five energetically lowest lying structures found were the layered structures (space group 194, 160, 187) and the wurtzite and zincblende structure. At zero pressure, LDA favors wurtzite and zincblende (by 0.05 \( E_h \) per four formula units), whereas B3LYP (by 0.01 \( E_h \)) and Hartree-Fock favor the layered structures. This is in reasonable agreement with other calculations, e.g. reference [30] and references therein gives the layered structure by about 0.06 eV/atom (0.02 \( E_h \) per four formula units) higher than the wurtzite and zincblende structures. Also, the zincblende and wurtzite structure are nearly degenerate, and similarly the hexagonal and rhombohedral structure. These results are stable with respect to the choice of the basis set, as calculations with larger basis sets show (see appendix A).

The statistics shows that the layered structures are frequently found, as well as the 3d-structures such as wurtzite or zincblende. The statistics includes all runs where Hartree-Fock energies were used during the simulated annealing. 10 runs were performed, where the B3LYP functional was used during the simulated annealing procedure. In two of these runs, a good structure candidate was found (wurtzite and the layered structure with space group 160). However, as was mentioned, the B3LYP runs require much more CPU time, and therefore the runs were mainly performed using the Hartree-Fock approach during the simulated annealing. In total, about 16 % of the runs gave one of the structure candidates in table IV. The other runs yielded either no good structure candidates (like "amorphous" structures) or only energetically very unfavorable structures.

When pressure is applied, the lower coordinated structures become less favorable, which is in agreement with the rule that the coordination number increases with pressure, see e. g. [50]. The enthalpies are displayed in figure 5 for LDA, and for B3LYP, respectively. Interestingly, in the case of B3LYP the layered structures are favorable at zero pressure, with wurtzite and zincblende becoming favorable at a pressure of \( \sim 3 \) GPa.
FIG. 1: (Color online) The layered structures found, with space group 194, 160 and 187. Green (light) spheres correspond to boron, blue (dark) spheres to nitrogen atoms, respectively. The lines indicate the unit cells.

FIG. 2: (Color online) The structures found, with space group 186, 216 and 136.

FIG. 3: (Color online) The structures found, with space group 62 and 8.
FIG. 4: (Color online) The structures found, with space group 14 and 9.

FIG. 5: (Color online) The enthalpy of the most relevant structures, at the LDA and B3LYP level. Structure candidates are labeled by their space group.
TABLE III: Basis sets used for the global search (I, II) and the local optimization (III)

| basis set I | basis set II | basis set III |
|-------------|-------------|---------------|
| exponent    | contraction | exponent      | contraction | exponent | contraction |
| B           |             |               |             |           |             |
| 2.082E+03   | 1.850E-03   | 2.082E+03     | 1.850E-03   | 2.082E+03 | 1.850E-03   |
| 3.123E+02   | 1.413E-02   | 3.123E+02     | 1.413E-02   | 3.123E+02 | 1.413E-02   |
| 7.089E+01   | 6.927E-02   | 7.089E+01     | 6.927E-02   | 7.089E+01 | 6.927E-02   |
| 1.985E+01   | 2.324E-01   | 1.985E+01     | 2.324E-01   | 1.985E+01 | 2.324E-01   |
| 6.292E+00   | 4.702E-01   | 6.292E+00     | 4.702E-01   | 6.292E+00 | 4.702E-01   |
| 2.129E+00   | 3.603E-01   | 2.129E+00     | 3.603E-01   | 2.129E+00 | 3.603E-01   |
| sp          |             |               |             |           |             |
| 2.282E+00   | -3.687E-01  | 2.312E-01     | 2.312E-01   | 2.282E+00 | -3.687E-01  |
| -           | 4.652E-01   | 1.199E+00     | 8.668E-01   | 4.652E-01 | 1.199E+00   |
| sp          |             |               |             |           |             |
| 0.4         | 1.0 1.0     | 0.25          | 1.0 1.0     | 0.197     | 1.0 1.0     |
| d           |             |               |             |           |             |
| -           | -           |               | 0.8         | 1.0       |             |
| N           |             |               |             |           |             |
| s           |             |               |             |           |             |
| 4150.0      | 0.001845    | 4150.0        | 0.001845    | 4150.0    | 0.001845    |
| 620.1       | 0.01416     | 620.1         | 0.01416     | 620.1     | 0.01416     |
| 141.7       | 0.06863     | 141.7         | 0.06863     | 141.7     | 0.06863     |
| 40.34       | 0.2286      | 40.34         | 0.2286      | 40.34     | 0.2286      |
| 13.03       | 0.4662      | 13.03         | 0.4662      | 13.03     | 0.4662      |
| 4.47        | 0.3657      | 4.47          | 0.3657      | 4.47      | 0.3657      |
| sp          |             |               |             |           |             |
| 5.425       | -0.4133 0.238 | 5.425      | -0.4133 0.238 | 5.425     | -0.4133 0.238 |
| 1.149       | 1.224 0.859 | 1.149         | 1.224 0.859 | 1.149     | 1.224 0.859 |
| sp          |             |               |             |           |             |
| 0.3         | 1.0 1.0     | 0.297         | 1.0 1.0     | 0.297     | 1.0 1.0     |
| d           |             |               |             |           |             |
| -           | -           |               | 0.8         | 1.0       |             |
TABLE IV: Total energies of the most relevant structures, and statistics. Energies are in hartree units ($1 \ E_h = 27.2114 \text{ eV}$), for 4 formula units. A run is considered successful, if one of the most relevant structures, as displayed in this table, was found.

| name of modification | space group | energy [$E_h$] | number of times found |
|----------------------|-------------|----------------|-----------------------|
|                      |             | LDA            | B3LYP                 | HF        | basis I | basis II |
| hexagonal BN         | 194         | -315.9121      | -318.5115             | -316.8753 | 1       | 2        |
|                      | 160         | -315.9125      | -318.5110             | -316.8740 | 11      | 4        |
| I-BN                 | 187         | -315.9123      | -318.5109             | -316.8739 | 0       | 2        |
|                      | 186         | -315.9629      | -318.4988             | -316.8452 | 8       | 2        |
| wurtzite             | 216         | -315.9619      | -318.4991             | -316.8459 | 4       | 2        |
|                      | 136         | -315.9347      | -318.4753             | -316.8147 | 2       | 1        |
| II-BN                | 62          | -315.8958      | -318.4437             | -316.7821 | 4       | 2        |
|                      | 8           | -315.8958      | -318.4437             | -316.7821 | 4       | 2        |
| III-BN               | 9           | -315.8075      | -318.4085             | -316.7594 | 0       | 1        |
|                      | 14          | -315.8075      | -318.4085             | -316.7594 | 0       | 1        |

number of successful runs 36 (18.9 %) 16 (11.5 %)

number of runs in total 190 139
| space group and modification | LDA      | B3LYP    | HF        |
|-----------------------------|----------|----------|-----------|
| hexagonal BN                | \( \text{a}=2.50 \ \text{Å}, \text{c}=5.88 \ \text{Å} \) | \( \text{a}=2.51 \ \text{Å}, \text{c}=6.40 \ \text{Å} \) | \( \text{a}=2.50 \ \text{Å}, \text{c}=6.43 \ \text{Å} \) |
| \( B_h \)                   | \( \text{B (1/3, 2/3, 1/4)} \) | \( \text{B (1/3, 2/3, 1/4)} \) | \( \text{B (1/3, 2/3, 1/4)} \) |
| \( \text{I-BN} \)           | \( \text{N (1/3, 2/3, 3/4)} \) | \( \text{N (1/3, 2/3, 3/4)} \) | \( \text{N (1/3, 2/3, 3/4)} \) |
| \( \text{II-BN} \)          | \( \text{B (0, 0, 0)} \) | \( \text{B (0, 0, 0)} \) | \( \text{B (0, 0, 0)} \) |
| wurtzite                    | \( \text{N (1/3, 2/3, 3/4)} \) | \( \text{N (1/3, 2/3, 3/4)} \) | \( \text{N (1/3, 2/3, 3/4)} \) |
| \( \text{zincblende} \)     | \( \text{B (0, 0, 0)} \) | \( \text{B (0, 0, 0)} \) | \( \text{B (0, 0, 0)} \) |
| \( \beta\text{-BeO} \)      | \( \text{N (0.0001, 0.0011)} \) | \( \text{B (0.0002, 0.0008)} \) | \( \text{B (0.0003, 0.0026)} \) |
| \( \text{III-BN} \)         | \( \text{B (0.0004, 0.0016)} \) | \( \text{B (0.0005, 0.0022)} \) | \( \text{B (0.0006, 0.0027)} \) |
| \( \text{IV-BN} \)          | \( \text{N (0.0006, 0.0023)} \) | \( \text{N (0.0007, 0.0029)} \) | \( \text{N (0.0008, 0.0035)} \) |
| \( \text{V-BN} \)           | \( \text{B (0.0008, 0.0036)} \) | \( \text{B (0.0009, 0.0042)} \) | \( \text{B (0.0010, 0.0048)} \) |
| \( \text{VI-BN} \)          | \( \text{N (0.0010, 0.0050)} \) | \( \text{N (0.0011, 0.0056)} \) | \( \text{N (0.0012, 0.0062)} \) |
IV. CONCLUSION

It was shown that structure prediction based on simulated annealing and using \textit{ab-initio} energies during both the global and local optimization is feasible for a covalent system such as boron nitride. This is a significant extension of the previous work \cite{10} where this approach was shown to be feasible for an ionic system. Covalent systems are more difficult to study as covalent bonds need to be established between the neighbors, and convergence problems are more severe in this case. Three layered structures, the wurtzite and zincblende structure, a structure of the \(\beta\)-BeO type, and four other favorable structures were found. Applying pressure leads to a preference of the higher coordinated structures.

APPENDIX A: LARGER BASIS SETS TO EXTRAPOLATE THE BASIS SET LIMIT

In the present work, a main task is to compute the energy differences between various structures. Besides the functional, the choice of the basis set has an influence on these results. In order to investigate this in more detail, the basis set used for the local optimization was further enlarged, and the total energies were computed for the most important structures. Here, enlarging the basis set means to include more diffuse functions. It turned out that this was only possible for the nitrogen atom, whereas more diffuse functions on boron led to linear dependence problems. Therefore, in a first step, one \(sp\) shell with exponent 0.15 was added to the nitrogen basis set III in table III, which resulted in a \([4s3p1d]\) basis set for nitrogen (basis set IV). In a second step, two \(sp\) shells (with exponents 0.15 and 0.6) were added to the nitrogen basis, i.e. a \([5s4p1d]\) basis set was obtained (basis set V). Note that these basis sets work reasonably well at zero pressure, but numerical instability sets in with compression, i.e. enthalpies (as in figure V) could only be obtained up to a relatively small pressure.

A geometry optimization was performed with these basis sets. The results are displayed in table [VI]. It becomes obvious, that the energy differences between the various structures remain essentially constant; the total energy becomes lower with increasing basis set. This is visualized in figure [6].

The geometry slightly changes when enlarging the basis set. Most prominent is the change of the \(c\)-axis for the layered structures when the basis set is enlarged. This is due to the weak bonding between the individual layers. However, as a whole, the basis set does not change the relative energies between the structures.
TABLE VI: A comparison of three basis sets for the energetically most favorable structures found.

| space group | basis set | cell parameters, in Å (LDA) | energy, in $E_h$ |
|-------------|-----------|-----------------------------|-----------------|
| 194         | III       | a=2.50 c=5.88              | -315.9121       |
| hexagonal BN| IV        | a=2.51 c=6.24              | -315.9556       |
|             | V         | a=2.51 c=6.18              | -315.9659       |
| 160         | III       | a=2.50 c=8.72              | -315.9125       |
| I-BN        | IV        | a=2.51 c=9.27              | -315.9562       |
|             | V         | a=2.50 c=9.19              | -315.9668       |
| 187         | III       | a=2.50 c=5.83              | -315.9123       |
| II-BN       | IV        | a=2.51 c=6.18              | -315.9564       |
|             | V         | a=2.50 c=6.12              | -315.9672       |
| 186         | III       | a=2.54 c=4.19              | -315.9629       |
| wurtzite    | IV        | a=2.54 c=4.19              | -315.9884       |
|             | V         | a=2.54 c=4.18              | -316.0035       |
| 216         | III       | a=3.60                     | -315.9619       |
| zincblende  | IV        | a=3.60                     | -315.9873       |
|             | V         | a=3.60                     | -316.0014       |
| 136         | III       | a=4.38 c=2.54              | -315.9347       |
| III-BN      | IV        | a=4.39 c=2.54              | -315.9591       |
|             | V         | a=4.37 c=2.54              | -315.9749       |
| 62          | III       | a=4.76 b=2.58 c=4.29       | -315.8958       |
| IV-BN       | IV        | a=4.79 b=2.58 c=4.29       | -315.9216       |
|             | V         | a=4.76 b=2.57 c=4.29       | -315.9366       |
FIG. 6: Total energies for the various structures, in hartree per four formula units, for basis sets III, IV and V, at the geometry optimized for each basis set. Structure candidates are labeled by the space group.
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