Computational study of boron nitride nanotube synthesis: how catalyst morphology stabilizes the boron nitride bond.

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In an attempt to understand why catalytic methods for the growth of boron nitride nanotubes work much worse than for their carbon counterparts, we use first-principles calculations to study the energetics of elemental reactions forming N2, B2 and BN molecules on an iron catalyst. We observe that in the case of these small molecules, the catalytic activity is hindered by the formation of B2 on the iron surface. We also observe that the local morphology of a step edge present in our nanoparticle model stabilizes the boron nitride molecule with respect to B2 due to the ability of the step edge to offer sites with different coordination simultaneously for nitrogen and boron. Our results emphasize the importance of atomic steps for a high yield chemical vapor deposition growth of BN nanotubes and may outline new directions for improving the efficiency of the method.

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I. INTRODUCTION

Boron nitride nanotubes (BNNT) consist of hexagonal graphitic-like sheet of alternating boron and nitrogen atoms rolled into a tube. The structure of BNNTs is analogous to the well-known (monatomic) carbon nanotubes (CNT), but their physical properties are quite different from those of their carbon counterpart. The mechanical and wear-resistant properties of both materials are of the same impressive order (for example, the Young’s modulus is in the terapascal range), while the electronic properties of BNNTs can be more attractive. CNTs are either metals or semiconductors depending on their chirality, while BNNTs are always semiconductors with the gap (~ 5.5 eV) practically independent of the nanotube chirality and its diameter.

As hexagonal boron nitride (h-BN) is very resistant to oxidation, BNNTs which inherit these properties, are suitable for shielding and coating at the nanoscale. Despite these prospects, BNNTs have received very little attention compared to CNTs due to various difficulties in their reproducible and efficient synthesis.

The fact that the BNNT consists of two different atomic species implies that the synthesis of BNNTs is more complicated than the synthesis of monatomic CNTs, as additional chemical reactions are possible. CNTs are typically synthesized from hydrocarbon precursors and according to current theoretical understanding of the CNT formation process, individual carbon atoms diffuse in or on a metal nanoparticle, forming graphitic networks that eventually gives rise to the appearance of a CNT (see e.g. Refs. [12-14]).

Assuming that these ideas are relevant to the growth of BNNTs, it becomes important to understand the factors that determine whether individual nitrogen and boron atoms diffusing on a catalytic surface result in the formation of BN structures, or N2 molecules and B clusters.

In this paper, in an attempt to understand why catalytic methods for the growth of BNNTs work much worse than for their carbon counterparts, we use first-principles calculations to study the behavior of N2, B2 and BN molecules on an iron catalyst. Such molecules are the simplest systems involved, and the complete understanding of their behavior on the catalyst surface is a prerequisite to understanding the whole process. We assume an ideal situation, where the precursors used for producing BNNTs (and similar structures), are decomposed into individual boron and nitrogen atoms and deposited on the catalyst. We chose iron as the typical catalyst used in chemical vapor deposition (CVD) growth. We then investigate under which situations the BN formation becomes energetically favorable. We show that on a (110) close-packed surface of BCC iron, B2 formation will dominate while at step edge regions, BN formation will be the most favorable reaction.

This paper is organized as follows: In Sec.[II] we first give a brief review of the synthesis methods of BNNTs and similar structures. In Sec.[II F] we explain the approximations and the computational approach we have chosen and how they can be justified. In Sec.[III] we discuss in detail the computational methods. In Sec.[IV] we present our results and demonstrate how specific catalyst morphologies stabilize the BN bond. To better understand the underlying chemistry, in Sec.[IV C] we analyze the electronic structure of the adsorbed molecules. Finally in (Sec.[V]), we discuss how BN catalytic synthesis on iron might be spoiled and how the situation could be improved.

II. SYNTHESIS OF BNNTS AND RELATED STRUCTURES

BNNTs have been synthesized with various methods and in a wide range of temperatures. Nearly all the methods show traces of metal particles, but their role as a catalyst is far from clear. In this section, we give a
brief overview of BNNT synthesis, with the emphasis on the role of catalysts if present in the synthesis method.

A. Arc-discharge

BNNTs were synthesized for the first time with the arc-discharge method, using BN-packed tungsten anode and copper cathode. Successively various anode and cathode materials, including hafnium diboride, tantalum press-filled with boron nitride and a mixture of boron, nickel and cobalt have been used. Typically, amorphous particles have been observed at the BNNT tip or encapsulated in BN cages. These particles could be metallic (borides), implying a metal catalyzed synthesis, while the encapsulated material could also be BN and the synthesis would be non-catalytic. A non-catalytic open-ended growth (involving no nanoparticles) has also been proposed.

Keeping in mind that temperatures in the arc-discharge method reach beyond 3000 °C, it is probably not well-suited for mass production of BNNTs.

B. Laser-ablation

The laser ablation method is based on the Vapour-Liquid-Solid (VLS) mode, in which the target material is evaporated and precipitated from the vapour-phase, eventually forming nanoparticles and solid, wire-like nanostructures. These are then carried by a gas flow to a collector.

Yu, Zhou, et al. used BN powder as the target (T ∼1200 °C) and observed that adding small amounts of catalyst Ni and Co into the target, resulted in longer nanotubes of better quality that were more often single-walled. Metal particles were observed to encapsulate inside BN material and they were thought to play an important role in the synthesis.

In other studies featuring higher temperatures (2400°C-3000°C), pure BN targets were used and BNNT growth from pure boron nanoparticles was observed.

In other laser-based techniques used for synthesizing BNNTs, the resulting product is typically collected directly from the target itself: Laude et al. achieved BN dissociation by laser heating in low pressure nitrogen atmosphere. This resulted in BNNTs and BN polyhedra that grew out of liquid boron. Golberg et. al. heated cubic BN by laser in diamond anvil cell at high temperature and pressure, producing BNNTs directly from the liquid phase. Ablation of BN by high-frequency laser in low-pressure nitrogen atmosphere produced BNNTs and BN "nanohorns".

C. Ball-milling and Annealing

Annealing methods have been used to produce BN nanowires, "nanobamboos" and BNNTs. These methods produce tubular BN structures by first milling the boron containing starting material into a fine powder during long times (typically ∼ 24h) and then annealing it at temperatures of ∼ 1000-1200°C in an inert or nitrogen containing atmosphere. The starting material, h-BN or pure boron powder, have been used. During the milling, the starting material can be activated by performing the milling in reactive atmospheres. Pressurized N₂ or ammonia gas have been used for this purpose. Nanosized metal particles observed frequently in the samples come from the metal balls used in the milling process.

There seems to be no generally accepted scheme how nanotubules form in this synthesis method. Metallic nanoparticles were observed frequently in the samples, and it was argued that they facilitate the growth of nanotubules while it was concluded in other works that they are not important. Some authors simply state that their role is not clear.

In general, the nanotubes synthesized by these methods are of poor quality and the yields are very small, so the methods are not, at least at the present stage, very suitable for mass-production of BNNTs.

Related to these methods is the work of Koi, Oku and co-workers, in which either hematite or Fe₂N powder together with boron powder was annealed in nitrogen atmosphere at ∼ 1000 °C. Iron particles coated in BN layers, BN nanowires, "nanobamboo" structures, nanotubes and "cup-stacked" nanotubules were synthesized. In these works, the formation of BN layers in the reactions involving Fe₄N has been described in two different ways: Either Fe₄N and Fe₂B become liquid, boron segregates on the nanoparticle surface and reacts with the N₂ atmosphere, or an amorphous boron layer on the Fe₄N is converted to BN as the Fe₄N is reduced from nitrogen.

D. Chemical Vapour Deposition

In a Chemical Vapour Deposition (CVD) method, one or more volatile precursors react and decompose on the catalyst to form the desired compound. CVD methods for producing BN filaments and BNNTs have been utilized in several works.

Gleize et al. used diborane and ammonia or N₂ gases as the boron and nitrogen containing precursors. These were deposited on various boride surfaces (including Zr,Hf,Ti,V,Nb and Ta borides) at a temperature of 1100°C. It was observed that diborane did not play any role in the tubule growth (diborane and ammonia formed amorphous BN only), but the boron in the reaction came from the boride catalyst itself.
both as a catalyst and as a reactant for the tubules. Successive studies using similar temperatures have made the same observation.

Louie et al. deposited borazine on cobalt, nickel, and nickel boride catalyst particles and concluded that the boride catalyst gave the best results. Huo, Fu, et al. used for the nitrogen containing precursor a mixture of ammonia and nitrogen gas. The boron source was again the catalyst itself which consisted of iron boride nanoparticles.

In another study, nickel boride nanoparticles supported on alumina (in order to avoid nanoparticle agglomeration) with ammonia and nitrogen were used. BNNTs were observed to grow out of the nickel boride nanoparticles at T=1100-1300 °C, while no “nanobamboo” structures were observed (agglomeration was avoided).

Ma et al. emphasized that CVD using metal catalysts must be difficult due to the poor wetting property of BN with metals. For this reason they used melamine diborate to create a metal-free B-N-O precursor. This precursor then reacted with N2 at 1200-1700 °C. Tip-growth of multi-walled BNNTs from amorphous B-N-O clusters was observed. The synthesis was explained by condensation of BN from the vapor-phase into the B-N-O particles, or either by reduction of B2O3 vapor.

Borazine and similar molecules have been used in CVD to produce BN nanotubes. Shelimov and Moskovits created BN nanotubes by depositing 2,4,6-trichloroborazine on aluminum oxide at a temperature of 750 °C. These kinds of methods are based on the thermal decomposition (pyrolysis) of borazine and similar molecules on surfaces and there is a direct connection to the CVD synthesis of h-BN thin films, a theme that has been reviewed by Paine and Narula.

E. Other

Other methods include the substitution of carbon atoms in CNTs by boron and nitrogen, reduction-nitridation reactions and boric acid reacting with activated carbon. Finally, the most successful method up to date for synthesising BNNTs is by Tang and co-workers.

In the method of Tang et al., boric oxide vapour was created in situ and reacted with ammonia at temperatures T ≥ 1100 °C. Boric oxide was created from magnesium oxide and boron powder. Magnesium was also thought to act as a catalyst in the reduction of boric oxide into boron nitride. This method seems to be related to the “classical high-temperature” methods to produce bulk h-BN, where the formation of h-BN is attributed to the gas forming property of the undesired elements (oxygen) and the thermodynamical stability of h-BN.

By this method, boron and nitrogen could be converted into BNNTs by an efficiency of 40% and hundreds of milligrams of BNNTs were produced. Most of the nanotubes were open-ended, although some encapsulated material was found in the sample. Liquid-phase magnesium drops could have catalyzed the reaction, but in this case they were evaporated in the final process. The quantity and quality of BNNTs depended strongly on the temperature: below 1100 °C, quality was better, but yield was small. Increasing the temperature, increased the yield, but tube diameter started to grow and BN flakes were formed when temperature was beyond 1250 °C. Adding FeO to the initial MgO powder, solved this problem and BNNTs could be produced up to 1700 °C. The growth then seemed to be catalytic.

F. Common features and the role of catalyst as the simulation challenge

As evident from this brief review, BNNT nanotubes can be synthesized by various methods, and in nearly all of them, metal particles which may have catalytic activity, are present. However, the role of metal catalysts in BNNT growth is not well understood.

In the CVD methods and when metal catalysts are involved, it seems to be important to use borides instead of pure metals. Borides are able to dissolve boron and nitrogen at the same time, while the solubility of boron for example in iron, is known to be very small. On the other hand, borides likely provide boron atoms during the BNNT growth, so they act both as the catalyst and the reactant itself, which is conceptually very different from the case of CNT synthesis.

In methods using borazine and similar molecules, we must keep in mind that these molecules already contain the desired boron nitride bonds. We can then imagine that the pyrolysis of these molecules in temperatures of T~800°C is used rather to remove the hydrogen atoms, than breaking the boron nitride bonds. This synthesis can then be conceptually quite different from the other synthesis methods. Finally, in the state of the art method (Tang, Golberg, Zhi and others), the catalytic role of iron and magnesium used in the process is not fully understood.

All these synthesis methods pose interesting challenges for theoretical calculations. However, to our knowledge only a single ab initio study on BNNT synthesis has been published. In that study, the non-catalytic growth of BNNTs was considered and it was shown that open-ended growth of single-walled armchair BNNTs is in principle possible.

Modelling a catalytic process is a very challenging problem. Many of the ab initio studies in this field concentrate in studying situations where the catalyst is reactive enough to dissociate a precursor, while not being too reactive to block the synthesis. A typical example of a thoroughly studied catalytic synthesis process is the ammonia synthesis and its rate limiting step, the N2 dissociation.

In this work, we study the adsorption energies, reac-
tion energies and some reaction barriers for simple boron and nitrogen containing molecules on a catalyst. We are trying to find reasons why BNNT synthesis on transition metals has proven to be so difficult and if the boron nitride formation could be made energetically favorable. We do this by studying the stability of the boron nitride bond on iron. This can be seen as a natural first step before addressing more complicated issues and catalysts (such as borides).

Our computational set up mimicks the CVD synthesis. We assume that the precursors (not defining them) have dissociated and donated B and N atoms on the catalyst. In the simulations, we then adsorb individual B and N atoms on the surface and calculate the reaction energetics when these adsorbed atoms (X$^*$ and Y$^*$) form adsorbed molecular species (XY$^*$).

Thinking in terms of this simplified model of CVD synthesis it is easy to understand why boron nitride structures can be much more difficult to form than pure carbon structures; in the carbon case and looking at the reaction energies and some reaction barriers for simple boron molecules, i.e. XY$^* = N_2^*$, B$_2^*$, or BN$^*$. As the adsorbed boron and nitrogen atoms react on the catalyst surface, complicated surface species might form, for example, boron clusters, boron-iron clusters, BN molecules and chains and clusters consisting of both boron and nitrogen, etc. If our goal is to understand the problems in BNNT synthesis in such a complex situation, a good first step is to study the most simple surface species, i.e. the adsorbed diatomic molecules that can be formed with adsorbed B and N. If, by studying these simple diatomic molecules, we find situations where the catalyst “promotes” the formation of BN$^*$ molecule instead of N$_2^*$ and B$_2^*$ molecules, this should have consequences in more realistic situations as well.

Finally, we emphasize that in this work we are interested in the theoretical aspect of the boron nitride bond stabilization. Modelling realistic reaction conditions is out of the scope of the present work. This would typically call for the calculation of several adsorption and coadsorption configurations, coverages and reaction paths. We also concentrate in the small molecular species B$_x$N$_y$, where x,y={0,1}. Considering bigger molecules at the DFT level becomes computationally very difficult as the number of the possible molecules increases as $2^n$ (n=x+y).

The slab usually contains a step edge in order to model a realistic nanoparticle with active sites.

In the following, we assume that two adsorbates, X$^*$ and Y$^*$, are far away from each other on the surface and we bring them together to form a new adsorbate species XY$^*$. The energy for this reaction X$^*$ + Y$^*$ → XY$^*$ can be calculated as follows:

$$\Delta E = (E(XY^*) + E_0) - (E(X^*) + E(Y^*))$$

where $E(X^*)$ is the energy of the adsorbed surface species X$^*$ and $E_0$ is the energy of a surface unit cell without adsorbates. We manipulate Eq. (1) as follows:

$$\Delta E = (E(XY^*) - E_0) - ((E(X^*) - E_0) + (E(Y^*) - E_0))$$

$$= E_a(XY^*) - (E_a(X^*) + E_a(Y^*))$$

(2)

In the last line of the equation, we have used energy values $E_a$ defined as:

$$E_a(X^*) = E(X^*) - E_0.$$  

(3)

We observe from Eq. (2), that using “shifted” energy values $E_a$ defined in Eq. (3), we can calculate the reaction energy for a reaction X$^*$ + Y$^*$ → XY$^*$ on the surface with the simple formula

$$\Delta E = E_a(XY^*) - (E_a(X^*) + E_a(Y^*)).$$

(4)

In the Results section, we tabulate values of $E_a$ in different parts of the catalyst surface (terrace, edge) and then use these tabulated values to calculate reaction energetics using Eq. (4).

Using the same notation, the adsorption energy can be written as follows:

$$E_{ads} = E(X^*) - E(X) - E_0 = E_a(X^*) - E(X),$$

(5)

and the dissociative adsorption energy, i.e. energy for reaction XY(g) → X$^*$ + Y$^*$ as:

$$E_{dis} = E_a(X^*) + E_a(Y^*) - E(XY).$$

(6)

where E(X) is the energy of the molecular species in the gas phase.

**B. Computational methods**

The calculations were performed with programs in the framework of the density functional theory (DFT), as implemented in two different codes, SIESTA and VASP. The SIESTA code uses pseudo-atomic orbitals as its basis set, while VASP is based on plane waves. SIESTA relies on the pseudopotential method to describe the core electrons, while projected augmented waves (PAWs) can be used in VASP. All calculations
were done with periodic boundary conditions, collinear spin and using the Perdew-Burke-Ernzerhof (PBE) general gradient approximation (GGA). We use the Monkhorst-Pack (MP) sampling\cite{58} of the Brillouin zone in calculations involving the slab. As we are using different k-point samplings, we will indicate the fineness of the M×N brillouin zone sampling also with the area of the reciprocal space per one sampled k-point (A\textsubscript{BZ}). In this work, preliminary calculations were typically done with SIESTA, while the final energies were always calculated with VASP. Due to the more systematic control of accuracy in the VASP code, we use it as a benchmark for the more computationally efficient SIESTA code. Nudged Elastic Band (NEB) calculations\cite{67,68} for reaction barriers were performed entirely with VASP.

1. SIESTA

In SIESTA calculations, Troullier-Martins\cite{59,69,70} scalar-relativistic pseudopotentials, with non-linear core-corrections were used. The density of the real space grid was defined by a corresponding plane wave cutoff of \(\sim \) 350 Ry and the effective density of the grid was further increased using a grid cell sampling of 12 points. The basis set used by SIESTA consists of numerical pseudo-atomic orbitals.\cite{59,69,70} These orbitals are obtained from the same atomic calculation that is used to generate the pseudopotentials (thus the name “pseudo-atomic”). The cutoff radii and the amount of confinement of these orbitals can be defined either by the cutoff radii (\(r_c\)) or by the “energy shift” parameter (\(E_{\text{shift}}\)). Larger energy shift corresponding to increasingly confined orbitals and smaller cutoff radii.\cite{68} In SIESTA, a typical basis set is the double-\(\zeta\) polarized (DZP), that consists of doubled atomic orbitals and an extra set of polarization orbitals created using perturbation theory. A typical value for the \(E_{\text{shift}}\) parameter in solids is \(\sim 200\) meV.

For the molecular species in this study, we used the DZP basis set and \(E_{\text{shift}}=150\) meV. In the case of boron this leads to a basis set with doubled 2s and 2p-orbitals, plus an additional set of 3d-orbitals. The total amount of orbitals is then 13 for one boron atom. The cutoff radii defined using the energy shift for boron are 2.7 Å (2s), 3.3 Å (2p) and 3.3 Å (3d). For nitrogen the cutoff radii from the energy shift are 2.0 Å (2s), 2.5 Å (2p) and 2.5 Å (3d).

SIESTA has earlier been used to simulate iron nanoparticles\cite{59,69,70} using both the SZSP and DZSP basis sets. The SZSP consist of 3d, 4s and 4p orbitals while in DZSP 3d and 4s orbitals are doubled. In ref.\cite{59,69,70} an explicit confinement radius of \(r_c=2.3\) Å for both SZSP and DZSP basis sets was used and it was demonstrated that these basis sets with \(r_c=2.3\) Å produced very well the properties of iron, including the magnetism.\cite{59,69,70} However, in the present case and while studying chemisorption of molecules on iron surface, we prefer longer cutoff radii and thus use a SZSP basis with \(E_{\text{shift}}=150\) meV to define the cutoff radii of the orbitals. This way, the cutoff radii for the iron orbitals are 2.41 Å (3d), 3.9 Å (4s) and 3.9 (4p). In our basis set, all atoms have then basis orbitals that extend at least up to 2.5 Å and some of them up to 3.9 Å.

We represent the surface by a 3-layer iron slab, with the vacuum between neighboring slabs being always \(\sim 14\) Å. When placing a molecule on top of this slab, only the molecule and the top iron layer are allowed to move during the conjugent gradient (CG) geometry optimization. In order to speed up the calculation, the parameter adjusting the convergence of the self-consistency cycle is increased to \(10^{-3}\). This will affect the accuracy of the forces, so we simultaneously increase the force tolerance criterion for stopping the CG relaxation to 0.1 eV/Å. MP sampling is chosen to be 1×2, corresponding to \(A_{BZ}=0.15\) Å\(^{-2}\). The idea of this approximative calculation is to get a sound initial guess for the next stage, in which we use the VASP code.

2. VASP

In VASP, PAWs were used. The cutoff energy of the plane wave basis set was always 420 eV. We represent the surface by a 4-layer iron slab, with the vacuum between neighboring slabs always \(\sim 14\) Å. Only the bottom layer is fixed to the bulk positions during the CG relaxation. Mixing scheme in the electronic relaxation is the Methfessel-Paxton method\cite{71} of order 1. In a first stage, the system is relaxed using a 1×2 MP sampling, which corresponds to \(A_{BZ}=0.16\) Å\(^{-2}\). When needed, the CG relaxation is automatically started again or until the forces have converged to a minimum value of 0.01 eV/Å. After this, the relaxation is continued with MP sampling of 3×5, corresponding to \(A_{BZ}=0.02\) Å\(^{-2}\) and CG relaxation is restarted if needed. This way we are able to reach a maximum force residual of \(\approx 0.02\) eV/Å. In all calculations special Davidson block iteration scheme was used and symmetries of the adsorption geometries were not utilized. The standard “normal” accuracy was used.

In the case of NEB calculations, and due to the large number of atoms we are considering, only three image points (plus the two fixed points) were used. In general, we observed that NEB calculations with large surface slabs can be tedious; some configurations at the lowest energy path could bring down their total energies by shifting the iron layers in a collective movement and this way change the relative position of the adsorbant molecule to energetically more favorable site. To avoid this unphysical situation, we fixed the lowermost layers and relaxed only the topmost iron layer and the adsorbed molecule during the NEB calculations. This must exaggerate the reaction barriers, but we believe that this approximation should be valid for comparative estimations of the order of magnitude of the reaction barriers and for the observation of rate-limiting steps.
Figure 1: BCC iron (110) surface with a step. The unit cell which was used in our calculations is indicated by atoms with black color. Unit cell in this figure shows a three layer slab. Lengths of the unit cell sides are 9.8 and 15.6 Å.

C. Adsorption sites

The unit cell used in our calculations is depicted in Fig. (1). The coordinates of the iron surface atoms were always scaled to the computational lattice constant, which for SIESTA and VASP were 2.89 Å and 2.83 Å, respectively (the experimental value of the lattice constant for BCC iron being 2.87 Å[75]). The unit cell of Fig. (1) has either 68 (3-layer slab) or 92 (4-layer slab) atoms. Using a large enough unit cell, including both flat and stepped region, allows us to perform a comparative study of the adsorption energetics near and far away from the step. A large unit cell should also allow for more realistic relaxation of the topmost iron atoms. We will now explain our strategy for searching the optimal geometries of adsorbed molecules on the surface.

In Fig. (2a) we are considering nine different sites. Sites (1-3) are in a close-packed region of the iron surface. The remaining sites are either on top or in the vicinity of the step edge. In Fig. (2b) different positions of a diatomic molecule have been considered. For each position, a set of numbers has been associated. This nomenclature corresponds to the site numbering of Fig. (2a). The positions together with the associated site numbers constitute the systematic search for the adsorption site. This procedure is more clearly understood with the example of the BN molecule: At the beginning, we will assign the labels x and y used in Fig. (2b) as (x=B,y=N). After this, the BN molecule would be positioned according to each rotation in Fig. (2b) and for each rotation, the atom (x=B) is placed on the sites, indicated by the numbers for the x label in Fig. (2b). As BN has two different atomic species, we must repeat the procedure with (x=N,y=B). For a diatomic molecule with two different species, this accounts for 66 trial configurations and for a molecule consisting of one species only, half of that.

We perform the systematic search described above for each atom (N, B) and for each molecule (N₂, B₂, BN), using the approximative SIESTA calculations. During this first stage, quite many of the different trial configurations relax into the same energy minimum. Some 5-10 of the most favorable adsorption geometries are then recalculated with VASP for final results.

IV. RESULTS

A. Iron slab properties

Magnetism is known to play an important role in iron nanoparticles. Typically, the magnetic moment in the nanoparticle surface is increased, and deeper inside the nanoparticle, the magnetic moment approaches that of bulk iron. The central atom of small nanoparticles might even obtain a minority spin[73].

To test for this gradual change of magnetism when approaching the nanoparticle surface, we have plotted the magnetic profiles of the slabs used in this work in Fig. (3). In the case of SIESTA and VASP we have used the approximations described in Sec. (III B). For SIESTA, we obtain a bulk magnetic moment of 2.3 μB . Going from the center of the slab towards surface, the magnetic moment varies from 2.5 up to 3.0 μB . For VASP, the bulk magnetic moment is 2.18 μB and in the slab it varies from 2.3 to 2.8 μB . The experimental value for iron bulk magnetic moment is 2.2 μB[75]. In both cases, the atoms at the step edge obtain the highest magnetic moment. In Fig. (3), the magnetic profiles start from d ≈ -30Å with the high magnetic moment of the step edge atom. The magnetic moment is lowered by ≈ 0.2μB for atoms residing at the terrace. As we move under the terrace, magnetic moment is lowered again approximately by the same amount. SIESTA, with the SZSP basis set and the approximations described in Sec. (III B), gives slightly exaggerated magnetic moments (by ≈ 0.2μB when compared to VASP), but the overall behaviour is consistent with VASP.

In general, the magnetic moment at the top surface layer is enhanced by 20%-30% when compared to the bulk values. This is consistent with the behaviour of magnetism in iron nanoparticles[23] and on transition-metal surfaces[24].

B. Reactions of molecules on the catalyst

As we explained in Sec. (II F) where we motivated our computational approach, we concentrate on the most simple molecules that can be formed from N* and B* that
are adsorbed on the catalyst surface and look directly at the energetic balance of the reactions $X^*+Y^*\rightarrow XY^*$ that form $BN^*$, $N_2^*$ and $B_2^*$. When calculating the reaction energies, we use Eq. (4) and tabulated values of $E_s$.

The optimal positions for adsorbed N, B, N$_2$, B$_2$ and BN molecules have been found using the approach described in Sec. (III C) and they are illustrated in Fig. (4). The indices given to these molecular geometries (B$_2$-1, B$_2$-2 etc.) are the same as used in Tabs. (I) and (III) and in the density of state plots in Fig. (6). The main results of the adsorption energetics on the iron slab have been collected in Tab. (III). There the energetics have been categorized according to different regions of the iron slab of Fig. (2): The “terrace” corresponds to sites (1-3), “edge” region to sites (4-9) and the “terrace and edge” to all sites in Fig. (2). In each class the energetically most favorable surface geometry has been considered. In the “terrace and edge” column, the atoms are free to choose either terrace or edge sites (whichever is favorable), leading to different values than in “edge” and “terrace” rows.

From the results of Tabs. (III), we can conclude the
following: (1) The reaction $N^+ + N^* \rightarrow N_2^*$ is unfavorable in every region of the surface, (2) in the terrace, the reaction $B^* + B^* \rightarrow B_2^*$ is the most favorable, (3) in the edge region, $B^* + N^* \rightarrow BN^*$ is the most favorable reaction and (4) in a situation where both terrace and edges are available, BN formation is still slightly more favorable than $B_2$ formation. (5) All the atoms and molecules (with the exception of the nitrogen atom) prefer to populate the step edge.

Energy barriers have been calculated along a few reaction paths for reactions $X^* + Y^* \rightarrow XY^*$ involving boron and nitrogen both at the terrace and at the step edge. The reaction barriers and some atomic configurations along the lowest energy path have been illustrated in Fig. (5). From Fig. (5) we can see that the energy barriers for competing reactions $B^* + B^* \rightarrow B_2^*$ and $B^* + N^* \rightarrow BN^*$ have the same order of magnitude in both at the terrace and at the step edge. No rate-limiting steps are observed.

Next we will take a detailed look at the geometries, compare some of them to earlier computational results and finally, based on the detailed analysis of the geometries we give a simple explanation why BN formations is so favorable at the step edge. We start by looking at the adsorption geometries of individual nitrogen and boron atoms.

### 1. Adsorption of $N$

In the adsorption geometry N-1 of Fig. (4), changes in the positions of surface iron atoms surrounding the adsorbed nitrogen are observed. In order to quantify these changes, we have labeled some of the atoms with letters a, b, c and d. The distance from the adsorbed N atom to the neighboring iron atoms a and c (b and d) is 1.79 (1.96) Å. Iron atoms have moved in order to create a 4-fold site for the N atom by contracting the distance b-d by ~5% and expanding distance a-c by ~20%. The N atom is now almost completely incorporated in the first iron layer and its distance from the plane formed by atoms a,b,c and d is only 0.5 Å while its distance to the iron atom lying directly below is 2.47 Å. The rather big unit cell we are using in our calculations has made it possible for the iron atoms to “give way” for the nitrogen atom and to adsorb deeply into the adsorbant at approximately 4-fold symmetric site. In geometry N-2, the nitrogen atom has very similar coordination to N-1. Now nitrogen has found a 4-fold site by taking advantage of the iron atoms at the step edge. Three of the neighbour iron atoms (a,b,c) reside in the terrace, while one of them (d) sits in the step edge. The distance of nitrogen to the nearest neighbour iron atoms are 1.87 (a), 1.90 (b), 1.86 (c) and 1.91 (d) Å. Breaking the trend a bit, geometry N-3 prefers a 3-fold site. This must be related to the fact that it is in contact with two step edge atoms and so the chemical environment and charge transfer must be different at this site.

Based on the geometries N-1, N-2 and N-3 we can conclude that, within the unit cell used in this study, nitrogen prefers 3- or 4-fold sites with iron. Near the step edge there is no need to adsorb deeply into the iron layer in order to gain this desired coordination with iron. This is particularly true for geometry N-2 as it can easily have a 4-fold coordination with iron due to the step edge morphology. The energy differences between different nitrogen atom sites are not that big. From Tab. (I), they are of the order of ~0.2 eV. From the point of view of catalytic synthesis involving nitrogen atoms, we could argue that having more step edges than flat terrace areas on the surface is beneficial, as the adsorption of nitrogen very deeply into the iron layer can be avoided.

In Ref.[27] nitrogen adsorption on Fe(111), (100) and (110) has been studied using DFT calculations. It was found that on Fe(100), nitrogen prefers a 4-fold symmetric site. In the case of Fe(110), nitrogen was found to prefer a 3-fold site, but the unit cell used in that case was very small and only the first-layer of iron atoms was allowed to relax. It was also reported that calculated adsorption energies for Fe(111) and Fe(110) were smaller than for Fe(100), probably due to the lack of available 4-fold symmetric sites. In our case, an approximately 4-fold symmetric site is created in the Fe(110) surface by movement of iron atoms and the site created this way starts to resemble the one that exists in the Fe(100) surface. It is also noted in Ref.[27] that the reconstruction of iron surfaces due to nitrogen adsorption most likely consist of geometries very similar to the one observed in Fe(100).

We also calculated a configuration where the N atom is adsorbed into a 3-fold site on the terrace (not shown in the figures). The adsorption of nitrogen into the 3-fold terrace site was achieved by fixing all the iron atoms in the surface slab, this way avoiding the relaxation of N into the 4-fold site (i.e. at N-1). In this case we obtained $E_{ads} = -6.3$ eV and $E_r = -9.4$ eV.

Using a larger unit cell in our calculations would allow for stronger relaxations in the first iron layer. In this case, nitrogen in geometry N-1 could adsorb deeper into the adsorbant, and the situation would resemble even

| Adsorbate | $E_{ads}(t)$ | $E_{ads}(e)$ | $E_{ads}(t+e)$ | $E_{ads}(e)$ - $E_{ads}(t)$ |
|-----------|--------------|--------------|----------------|-----------------------------|
| N$^*$     | -6.6         | -6.4         | -6.6           | 0.2                         |
| B$^*$     | -6.3         | -6.7         | -6.7           | -0.5                        |
| N$_2^*$   | -1.1         | -1.2         | -1.2           | -0.1                        |
| NB$^*$    | -7.3         | -8.1         | -8.1           | -0.8                        |
| B$_2^*$   | -9.3         | -9.9         | -9.9           | -0.7                        |

Table II: Adsorption energies $E_{ads}$ for $N_2$, BN and $B_2$ molecules and N and B atoms in different parts of the iron surface. Terrace region (t) corresponds to sites (1-3), edge region (e) to sites (4-9) and the whole surface (t+e) to all sites in Fig.(2). The energy difference when moving the atom from the optimal site at the terrace (t) to the optimal site in the edge (e) is calculated in the last column. All energies listed are in the units of eV.
Table III: Reaction energies (eV) of some reactions on the iron surface in different regions. Terrace corresponds to sites (1-3), edge to sites (4-9) and the whole surface to all sites in Fig. (2). The adsorbate geometries that are used to calculate the energy for reaction $X^* + Y^* \rightarrow XY^*$ are indicated in parenthesis. Geometries are tagged with the same labels (N-1, N-2, etc.) as in Tab. (I) and Fig. (4). Reaction energies are calculated by taking the corresponding energies $E_s$ from Tab. (I) and using Eq. (4). (note: high cost for the reaction in the 4.th row is due to forcing the very unfavorable $N_2$ formation).

Figure 4: Some of the most stable geometries for $B_2$, $BN$ and $N_2$ molecules and the $B$ and $N$ atoms on the iron surface. Different geometries are tagged with the same labels as in Tab. (I). In the case of $BN$, magenta (blue) corresponds to boron (nitrogen).

more the adsorption of nitrogen into Fe(100), where the coordination of N is actually 5 (nitrogen is also bonded to the atom directly below). However, we did not pursue this possibility, as the computation with unit cells having > 100 iron atoms is extremely heavy.

2. Adsorption of $B$

In the geometry $B-1$ in Fig. (4), the boron atom has quite a high coordination. Again, we have labelled the neighboring atoms with letters. The distance to the nearest neighbor iron atoms are 2.03 (a), 2.48 (b), 1.93 (c), 2.1 (d) and 2.13 (e) Å. Distances to the iron atoms are
now longer than in the case of nitrogen, but the coordination is clearly higher. The bigger distance comes as no surprise, due to the higher orbital radius of boron atom when compared to nitrogen. In general, boron is also known to prefer high coordination. The higher coordination preference of boron is more clearly observed in the adsorption geometry B-2. The iron step edge atoms are not as tightly bound as the terrace atoms and for this reason the strong reconstruction of iron atoms seen in B-2 is possible. There are now altogether six iron atoms surrounding the boron atom (one of them directly below the boron atom), all within a distance of 2.0 - 2.24 Å.

In the adsorption geometry B-3 the preference for high coordination of boron is again obvious, but it is frustrated due to the lack of suitable sites. No strong reconstruction, like the one seen in geometry B-2, is observed, because arranging the iron atoms in the close-packed region would be energetically very unfavorable. Boron cannot push itself very deeply into the iron layer either, the trick employed by nitrogen in N-1, as it has more extended orbital radii. The “frustration” of B-3 when compared to B-1 and B-2 is obvious in the energetics of Tab. I, as B-1 and B-2 are practically degenerate and B-3 resides 0.3 eV higher in energy.

3. Adsorption of N₂

Looking at the N-N bond length of geometry N₂-1 in Tab. I, we can see that it has been expanded by ~ 20 %, which implies we are approaching dissociation. In Fig. 4 some of the neighboring iron atoms of the nitrogen atoms have been labelled with letters. The distances of the nitrogen atoms to their nearest iron neighbours are 1.93 (a), 1.94 (b), 2.04 (e) Å and 1.9 (d), 1.95 (c), 2.12 (e) Å. Similar to the case of an isolated nitrogen atom, nitrogen prefers a total coordination of four (i.e. surrounded by one nitrogen atom and three iron atoms). It is then not surprising that N₂ prefers the step edge; due to the morphology of the step edge, there are sites offering 3-fold coordination with iron for each one of the nitrogen atoms, while maintaining a reasonable N-N bond length.

The adsorption geometry N₂-2 is very similar to N₂-1 and it has N-N bond length expanded by ~ 14 %. Now the neighboring iron atoms move, but very slightly; the distances a-c and b-d expand both only by ~ 4 %. Each nitrogen atom is seen to have three iron neighbours. The nitrogen-iron nearest neighbor distances for each nitrogen atom are 2.09 (a), 1.89 (b), 2.07 (c) Å and 2.09 (a), 2.1 (c) Å. Again, the nitrogen atom coordination is four (three iron atoms and one nitrogen atom). The geometry N₂-3 is very similar to N₂-1 and N₂-2 and the total energies for all adsorption geometries of N₂ molecule from Tab. I are almost degenerate. The step edge geometry N₂-1 is slightly more favorable than the others, as the nitrogen atoms can obtain their preferred coordination without significant rearrangement of the iron atoms.

Earlier calculations of N₂ adsorption on iron surface include Refs. [79][80]. In Ref. [79], N₂ and N adsorption on the low-coordinated Fe(111) have been studied using DFT. In that reference, bigger N₂ concentrations (and smaller unit cells) were studied. In Ref. [80] the N₂ and N adsorption on Fe(110) were studied, using a 2×2 unit cell, but in this study, the atoms of the iron slab were fixed. These earlier computational studies are therefore not directly comparable to the present work.
In both Refs. [79,80] the N$_2$ molecule was found to prefer the “top” site (i.e. site (1) in Fig. (2)) and a geometry where the N-N bond projects into the vacuum (i.e. it is “standing” on the surface). We also find this same adsorption geometry (not shown in Fig. (4)) to be a local minimum, but its total energy is ≈ 0.6 eV higher than that of N$_2$-2 in Fig. (4). Keeping in mind that Ref. [79] emphasizes that N$_2$ adsorption geometries where both N-atoms are in contact with the iron adsorbant are very dependent on the coverage and that the coverage in our case is quite low, the result we have obtained is not surprising.

4. Adsorption of B$_2$

At first sight, the adsorption geometries of Fig. (4) for individual boron atoms and the B$_2$ molecule are very similar. The five nearest neighbour iron atoms for a single boron atom in B$_2$-1 are within the range of 2.2 - 2.47 Å. The coordination of a single boron atom in B$_2$-1 is therefore between 4 and 5, which is very similar to the case of B-1. The bond length of B$_2$-1 has been expanded by 10%. The tendency for high coordination is more clear in geometry B$_2$-2 where a strong reconstruction of the iron layer, similar to the case of B-1, occurs. For one boron atom in B$_2$-2 the four nearest neighbour iron atoms are within a range of 1.94-2.32 Å and the total coordination of a boron atom is then ~ 5 (i.e., four iron atoms and another boron atom).

In geometry B$_2$-3, one boron atom resides near a step edge and has a high coordination, while the other boron is in the terrace region and cannot get high coordination. The boron atoms in B$_2$-4 have obtained high coordination through the reconstruction of the iron layer (the situation looks very similar to B$_2$-2), but on the other hand, there must be a high energy cost for moving the iron layer atoms in the close-packed region. This can be seen in Tab. (1), where B$_2$-4 lies 0.3 eV higher in energy than B$_2$-2.

5. Adsorption of BN

As we have discussed in previous sections, nitrogen and boron atoms prefer different coordination numbers. They maintain their preferences even when forming a molecule. In particular, nitrogen was seen to prefer 3 to 4-fold coordination, while boron prefers 5 to 6-fold coordination. In the case of boron nitride molecule, we should then find a suitable surface morphology that would allow simultaneously these different coordinations for boron and nitrogen. It is obvious that the step edge offers the best possibility for this.

Looking at Fig. (4) and Tab. (1) we observe that the most favorable adsorption sites for the boron nitride molecule are indeed at the step edge. Looking first at BN-1, we see that the bond length is almost equal to the free molecule, expanded only by ~ 4%. The nearest neighbour iron atoms for nitrogen are 1.89 (c), 1.90 (d) and 2.25 (e) Å, while for boron they are 1.97 (a), 2.1 (e) and 2.31 (f) and 2.43 (d) Å. Geometries BN-2 and BN-3 exhibit a very similar trend, i.e. the boron atom is higher coordinated than the nitrogen atom. The geometries BN-4 and BN-5 are almost degenerate in energy and “frustrated” because the molecule is not able to obtain coordination of 3-4 for nitrogen and 5-6 for boron due to the flat morphology of the terrace region.

C. Electronic structure of molecules on the catalyst

In this section we take a look at the electronic structure and bonding of molecules on the iron adsorbant. In particular, we are interested why B$_2$ and BN are stabilized on the surface, while N$_2$ is so unstable. We do this by looking at the electronic states of the molecules in vacuum and at their density of states on the adsorbant.

A classical example of this kind of analysis is the Blyholder model for the CO molecule (see Ref. [81] and references therein), where the low-lying Molecular Orbitals (MO) stay relatively inert, while the MOs energetically near to the adsorbant d-states or overlapping with them (most notably the HOMO and LUMO states) dominate the chemisorption energies. Very related to our case is also the Norskov d-band model [82,83,84,85,86], where the metal sp-states broaden and shift the adsorbate states and these “renormalized” states are then hybridized with the metal d-states. In our case, we will take a very “rough” look only into the density of states without looking at the exact details of the orbital mixing, which might be very complicated due to the strong atomic reconstruction of the topmost iron layer (see for example geometries N-1 and B-2 in Fig. (4)). In particular, we are interested in which type of orbitals of the adsorbate (bonding or antibonding) interact most strongly with the metal d-states.

The iron atoms near the adsorbate are known to lower their magnetic moments, while the adsorbate itself might be demagnetized or even obtain a minority spin[79]. This demagnetization can also be seen in the density of states of the adsorbates in Fig. (8).

1. Adsorption of N$_2$

The energy levels of N$_2$ are plotted in Fig. (7) and they are similar to earlier published ones[52]. We observe that N$_2$ is closed-shell and that the energy difference between $\sigma_{p_z}$ (HOMO) and $\pi^*_p$ (LUMO) is ~ 8 eV. The bond order of N$_2$ is 3, and there is no net spin magnetic moment. When N$_2$ is put in contact with an adsorbant, the bonding is likely dominated by the $\sigma_{p_z}$ and $\pi^*_p$ states. From the electronegativity of nitrogen and iron, we could argue that N$_2$ is likely to receive electrons and thus bond through the antibonding state $\pi^*_p$ (LUMO). To be more
Figure 6: Density of states, projected into atom-centered iron d-orbitals (thick red line) and into B and N atom-centered s- and p-orbitals (blue line). The states have been interpreted using the same notation as in Figs. (7-8). Peaks with significant s-orbital character only when projected to atom-centered B and N orbitals are most easily identified ($\sigma_{pz}$, $\sigma^*_{pz}$). Majority (positive values) and minority spin (negative values) are indicated.

precise, this should depend on the relative position of the iron d-states with respect to the renormalized N$_2$ energy levels, as mentioned earlier.

Comparing the PDOS graphs of N$_2$-1 and N$_2$-2 in Fig. (6) to the energy diagram of Fig. (7), we can easily relate different peaks to the energy levels of the isolated N$_2$ molecule. In Fig. (6) the situation is most clear in the case of N$_2$-2, where we find altogether five N$_2$ peaks below the iron d-states. Two of these peaks (almost degenerate) must correspond to $\pi_p$ and one to $\sigma_{pz}$. There is no sign of a $\pi^*_p$ peak, so it has likely hybridized with the iron d-states. We can then conclude that N$_2$ is destabilized on the iron surface through adsorption using the antibonding $\pi_p$ orbitals.

2. Adsorption of B$_2$

In Fig. (8) we have plotted the energy levels of a single boron atom and the energy levels of the B$_2$ molecule. We observe that B$_2$ has an open shell structure. The energy difference between $\pi_p$ (HOMO) and $\sigma_{pz}$ (LUMO) is $\sim$ 160 meV. The bond order is 1 and B$_2$ has a net magnetic moment of 2 $\mu_B$. When the calculation includes spin-polarization, an exchange splitting of the energy levels is observed and the degeneracy of $\pi_p$ orbital is removed. Including spin-polarization in the calculation, lowers the energy of the B$_2$ molecule by 0.84 eV.

The adsorption of B$_2$ is likely to happen through $\pi_p$ and $\sigma_{pz}$ orbitals, as the gap between them is very small. Both of these orbitals are of bonding-type and this implies that B$_2$ will be stabilized upon adsorption. Looking at PDOS of B$_2$, when it has been placed on the iron surface (B$_2$-1 in Fig. (6)), we see that both the $\pi_p$ and $\sigma_{pz}$ MOs overlap with the iron d-states and the peaks corresponding to these MOs have hybridized with the iron d-states. The stabilization of B$_2$ on iron then looks natural in the light of the electronic structure. Something reminiscent of an exchange splitting in the adsorbate PDOS peaks can be seen in the energy range from $\sim$ -4 to -1 eV.

3. Adsorption of BN

In Fig. (8) we have plotted the energy levels of boron and nitrogen atoms together with the levels of the BN molecule. In a calculation without electron spin, the situation looks straightforward and the BN molecule has a closed-shell structure with $\pi_p$ (HOMO) and $\sigma_{pz}$ (LUMO) having a gap of $\sim$ 250 meV. The bond order is 2 and there is no net spin magnetic moment. When spin-polarization is allowed, a considerable rearrangement of the MOs due to the exchange splitting takes place: $\pi_p$ and $\sigma_{pz}$ orbitals slide through each other in the energy-level diagram ($\pi_p$ “down” states shift upwards, while $\sigma_{pz}$ “up” states shift down) and one of the $\sigma_{pz}$ states becomes occupied. BN molecule lowers its energy by 0.36 eV and obtains a net magnetic moment of 2 $\mu_B$.

It is very difficult to anticipate which one of the orbitals, $\pi_p$ or $\sigma_{pz}$, will dominate the adsorption, as they are very close to each other in energy. Magnetism makes this situation even more complicated, as the gap between these molecular orbitals can close up due to the exchange splitting. Both of these orbitals are of the bonding type, so at least BN should be stabilized on the adsorbant. We look again at the PDOS plots of Fig. (8) and identify the peaks with the energy levels of Fig. (7). We can see that both the $\pi_p$ and $\sigma_{pz}$ states coincide with the iron d-states and hybridize with them. There are even some
that the hybridization of the $\pi_p^*$ at Fig.(6) and comparing $B_2^*$ in $B_2^*$ states are then energetically closer to the iron d-states $\sim$ and $\sim$ related $B_2$ than in BN. Some one-electron states (from a SIESTA calculation) have been included in the insets: color red (blue) corresponds to positive (negative) values of the wavefunction.

The HOMO ($\pi_p^*$) and LUMO ($\sigma_{pz}^*$) states for an isolated $B_2$ molecule in Fig.(3) lie at energies of 0.0 eV and $\sim 0.18$, while for BN in Fig.(4) they lie at $\sim -0.15$ eV and $\sim 0.12$ eV. The HOMO and LUMO states of the BN molecule are then shifted slightly downwards, when compared to the same states of the $B_2$ molecule. These states are then energetically closer to the iron d-states in $B_2$ than in BN. Supporting this idea, when looking at Fig.(6) and comparing $B_2$-1 and BN-1, we can see that the hybridization of the $\pi_p$ and $\sigma_{pz}$ states with the iron d-states seems to be more pronounced in the case of $B_2$ and this implies that the adsorption through these bonding-type orbitals is stronger.

V. DISCUSSION AND CONCLUSIONS

We have performed an *ab initio* study of the energetics of the simplest chemical reactions involved in catalytic growth of boron nitride nanotubes (BNNTs). We studied adsorbed boron and nitrogen atoms ($N^*, B^*$) and all their adsorbed diatomic combinations ($N_2^*, B_2^*$ and $BN^*$) on an iron catalyst.

Our objective was to study the fundamental aspect of BN bond stabilization on iron (rather than modelling realistic reaction conditions, see Sec.(II F)). In order to do this, we mimicked the very first stages of a CVD synthesis of BN structures. We assumed that precursors (without defining them) have dissociated and donated individual adsorbed N and B atoms on the catalyst. In the very first stages of the synthesis, these atoms start to form either adsorbed $N_2$, $B_2$ or BN molecules. We believe that understanding when the BN bond is stabilized can provide help in understanding the BNNT synthesis in general. Specifically, we observed that $N_2$ is unstable, while $B_2$ and BN are stabilized on the iron catalyst (BN only at the step edge region). $N_2$ dissociates by adsorption on iron through antibonding orbitals, while $B_2$ and BN are stabilized by dominant adsorption through bonding-type orbitals.

On terrace regions of the iron catalyst, the reaction forming $B_2$ is energetically favorable, while the reaction forming BN is not. The energy barriers of the two competing reactions $B^*+B^* \rightarrow B_2^*$ and $B^*+N^* \rightarrow BN^*$ are the same order of magnitude for the two reactions. This implies that if B and N atoms are distributed on a flat iron surface, in the very first stages of the synthesis, large amounts of $B_2$ and individual nitrogen atoms adsorbed on iron will be formed, while very little BN molecules will form. If further boron cluster formation occurs, it is probably not favorable from the point of view of BNNT synthesis (as mentioned in Sec.(II), BNNT growth from boron has been observed only in very elevated temperatures).

The situation looks much more promising in the step edge region; the energetic balance is tipped into favor of BN formation and the energy barriers are again the same magnitude for both reactions $B^*+B^* \rightarrow B_2^*$ and $B^*+N^* \rightarrow BN^*$. This implies that when B and N atoms are distributed into the step edge, some $B_2$ molecules and considerable amount of BN molecule formation takes place. The formation of a large number of BN molecules on the catalyst could be very important for BNNT formation, provided that these molecules are mobile and do not poison the catalyst.

The stabilization of BN at the step edge can be explained in terms of atomic coordination: we observed that, within the computational unit cell we used, nitrogen preferred 3-4, while boron 5-6 fold coordination with iron and the only morphology where these two coordinations are simultaneously available, is found at the step edge.

Summarizing, according to our calculations, the BN bond is stabilized in step edge regions of the iron catalyst. This implies that the yield of BNNT in a CVD synthesis might be enhanced by altering the iron catalyst morphology to include more steps, instead of close-packed surface regions. Simply having step edges is not enough; having step edges, but long terraces, will result
Figure 8: (a-b) Energy level diagrams for individual B atoms and the B$_2$ molecule as calculated with VASP (a) without and (b) with spin-polarization. The B$_2$ energy levels are interpreted using the molecular orbital theory. (c-d) Energy level diagrams for individual B and N atoms and the BN molecule as calculated with VASP (c) without and (d) with spin-polarization. The BN energy levels are interpreted using the molecular orbital theory. Blue (red) color corresponds to spin up (down) states.

in more flat surface sites than step edge sites, lowering the free energy for flat surface sites. From the point of view of maximizing the BNNT yield, the terraces should then be very short. As creating a catalyst nanoparticle with a desired morphology is very difficult, the predictions on BN yield given in this theoretical work could be put to test in practice by using as a catalyst a high-index Fe surface with very short steps.

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