

FORMATION AND FUNCTIONALIZATION OF BORON PHOSPHIDE MONOLAYERS

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By
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PHIDE MONOLAYERS

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in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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Since the synthesis of graphene with its unique properties has increased the focus on novel two dimensional (2D) materials, successively new 2D materials from either layered or non-layered materials have been synthesized following the advances in thin film growth and characterization techniques. Hexagonal boron nitride (*h*-BN) is the runner-up material, which is structurally stable in hexagonal honeycomb form. *h*-BN is an insulator whereas, it is a good thermal conductor. However, the electronic and structural properties of these 2D materials are very susceptible to doping and adsorption, as such, these properties can be altered extensively. Therefore, we have examined the phosphorization of *h*-BN with varying concentrations, which leads to stable 2D boron phosphide at the ultimate limit. The lattice constant of the $\text{BN}_{16-x}\text{P}_x$ alloy have been found to increase with increasing x . The planar geometry of *h*-BN is deformed and alloy turns into buckled structure until $x > 0.75$ (corresponding to (75% P) concentration). Beyond this point, planarity is recovered and planar monolayer *h*-BP achieved when all N atoms are replaced with P. Although 2D BP has not been synthesized yet, phonon spectrum analysis and high temperature molecular dynamics calculations indicate the stability of the system. Interestingly, while *h*-BN is an insulator, *h*-BP is semiconductor with 1.3 eV direct band gap. Owing to decreasing of electronic band gap with increasing x , it is possible to tune the band gap of $\text{BN}_{16-x}\text{P}_x$ alloy, allowing various device applications in nanoelectronics.

After proving of the stability of *h*-BP in monolayer form, we have elucidated the effect of doping and adsorption on electronic and structural properties of monolayer BP with selected atoms from Group III-IV-V atoms. The Dumbbell phase has been found to play a key role to stabilize the monolayer BP upon adsorption, suggesting full coverage of the monolayer BP surface. Evenmore, this new phase forms exothermically. Adsorption also leaves monolayer BP as small

gap semiconductor with impurity characteristics of adsorbants. Also, we have shown that except for Al and Ga, these impurity adatoms carry small amount of magnetic moment in moderate temperatures.

In addition, we have studied the substitution of monolayer BP with Group III-IV-V atoms. Based on our calculations, we have found that C and N can substitute P atom under ambient conditions. Nonetheless, only N atom selectively substitute for P atom, whereas C atom substitutes both for B and P giving rise to possible chemical etching of monolayer BP in the presence of excess C atom. Substitution of C for B/P results in metallic state in monolayer BP, while substitution of N for P leaves monolayer BP direct gap semiconductor. It is also found that none of these substitutions makes substrate magnetic.

Using state-of-the-art computational tools based on the Density Functional Theory(DFT), we have calculated the structural and electronic properties of phosphorization of monolayer *h*-BN and doped monolayer *h*-BP.

Keywords: 2D materials, First principles calculations, Ab-initio, Density Functional Theory(DFT), Monolayer Boron Nitride, Monolayer Boron Phosphide, Phosphorization, Doping.

ÖZET

TEK ATOMİK KATMANLI BORON FOSFOR YAPILARININ OLUŞTURULMASI VE İŞLEVSELLETİRİLMESİ

Lütfiye Halhoğlu

Malzeme Bilimi ve Nanoteknoloji Bölümü, Yüksek Lisans

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2-boyutlu(2B) ve tek katmanlı grafenin sentezlenmesi ile elde edilen üstün özellikler, benzer malzemeler üzerinde araştırmaları yoğunlaştırmıştır. İnce-film büyütme ve karakterizasyonundaki gelişmeleri takiben, gerek katmanlı gerekse katmanlı olmayan 2B malzemeler (ard arda) sentezlendi. Yapısal olarak kararlı ve bal peteği örgüsüne sahip bir 2B yapı olan h -BN, en çok dikkat çeken malzemelerden biri olmuştur. h -BN elektriksel olarak yalıtkan olup, termal olarak iletkenidir. 2B malzemelerin katkılama ve adsorpsiyona çok elverişli olmaları, elektriksel ve yapısal özelliklerinin geniş çapta değiştirilebilmesine olanak sağlamaktadır. Bu çalışmamızda 2B ve tek katman BN yapısını, değişen oranlarda fosfor atomu ile katkılayarak, sistemdeki yapısal ve elektronik değişimleri *ab-initio* method kullanılarak inceledik ve tüm P atomları N atomlarının yerine geçtiğinde 2B Boron Fosfor (BP) elde edildiğini bulduk.

Yapısal olarak, düzlemsel bir örgüye sahip olan BN, P atomu ile katkılандığında düzlemsel yapısını kaybederek burgulu bir yapıya kavuşur. Katkılanan P atomu konsantrasyonu arttıkça BN yapısının burulma miktarı artar, ancak daha sonra (%75'ten sonra), bu burulma miktarı azalır ve nihayetinde BN, tamamen düzlemsel BP'ye dönüşmüş olur. Tüm N atomları P ile yer değiştirildiğinde elde edilen BP yapısının da yapısal olarak kararlı bir yapı olduğu sonucuna vardık. 2B BP deneysel olarak elde edilmemiş olsa da yapmış olduğumuz yüksek sıcaklık moleküler dinamik ve fonon hesaplamaları normal deneysel koşullarda bu yapının yapısal kararlılığını koruyabildiğini göstermiştir. Elektronik yapı analiz edildiğinde, BN yüksek bant aralıklı bir yalıtkan iken tek tabakalı BP yaklaşık direkt ≈ 1.3 eV bant aralığına sahip bir yarı iletkenidir. P katkılması ile bant aralığı kontrol edilebilir şekilde değiştirilen yalıtkan yarı iletken geçişi mümkün olmaktadır.

Yaptığımız çalışmalar sonucunda kararlı olduğunu bulduğumuz hekzagonal BP (h-BP)'ye Grup III-IV-V atomlarının katkılanması ve adsorpsiyonu ile oluşan yapısal ve elektriksel özelliklerdeki değişimi inceledik. Yapısal olarak yeni bir faz olan Dumbbell fazı, *h*-BP'nin adsorpsiyonu sırasında kilit role sahip olup ekzotermik olarak oluşmaktadır. Bu adsorpsiyon, safsızlık atomu karakteristiğine sahip atomlar sayesinde tek tabaka BP yi küçük bant aralıklı yarı iletkene dönüştürür. Al ve Ga atomları hariç eklenen atomlarla, makul sıcaklıklarda, bu alaşımlara küçük de olsa magnetik özellik kazandırılabilir.

Adsorpsiyona ek olarak, Grup III-IV-V atomlarıyla tek katmanlı BP'nin katkılanması da çalışıldı. Çalışmalarımız C ve N atomlarının, deney koşullarına bağlı olarak, P atomlarının yerine katkılanabileceğini göstermiştir. Bununla birlikte, N atomları katkılama P atomlarını tercih ederken C atomları hem B hem de P atomları yerine katkılanabilmektedir. C atomlarının B/P atomlarının yerine katkılanması sonucu katkılanan sistem metalik özellikler kazanırken, N atomlarının P yerine katkılanması sonucu sistem direkt bant aralıklı yarı-iletkenliğini korur. Katkılama sonucu hiçbir atom sisteme magnetik özellik kazandırmamıştır.

Yoğunluk Fonksiyonel Teori(YFT)'ye dayanan, son teknoloji bilgisayar hesaplamaları kullanarak P-katkılanmış h-BN and katkılanmış tek katmanlı boron fosforun yapısal ve elektriksel özellikleri incelendi.

Anahtar sözcükler: 2B malzemeler, Temel Prensipler, Ab-initio, Yoğunluk Fonksiyonel Teori(YFT), Tek Katmanlı Boron Nitrür, Tek Katmanlı Boron Fosfor, Fosforizasyon, Katkılama.

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Chapter 1

Introduction

Ever since the exfoliation and identification of graphene in 2004 [1], layered ultrathin two-dimensional (2D) nanomaterials have been the subject of intensive study over the last decade. The runner-up is 2D *h*-BN, or "white graphene". Addition to monolayer BN[2], also MoS2[3], TiS2[4], WS2[5], black phosphorus[6], which have layered bulk forms have been synthesized. Obtained 2D systems are not limited to materials with layered crystal but epitaxial growth techniques allowed to synthesize novel structures such as silicene[7], germanene[8], stanene[9] etc.

Due to constraints on the electronic wave functions in 2D, the electronic wave functions adopt leading to modify the electronic structures, leading to new devices in nanoelectronics with promising and novel properties ranging from high carrier mobility to half-integer quantum Hall effect[10]. Since ultrathin channels can control leakage pathways in FETs, 2D structures emerge as a good candidate for transistor applications[11]. Additionally, these 2D materials can be used in constructing heterostructures which are held through Van der Waals forces[12]. Moreover, these 2D materials have started playing a key role in various applications such as optoelectronics, spintronics, catalysts, chemical and biological sensors, supercapacitors, solar cells, and lithium ion batteries.[13]

Since *h*-BN is analogous to graphene which has sp^2 bonded carbon atoms those

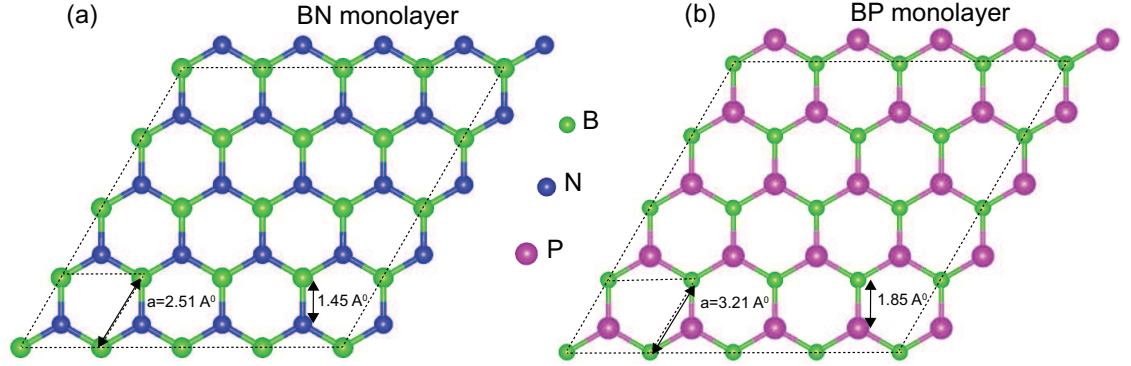


Figure 1.1: (a)Structure of monolayer BN in 4×4 supercell. (b)Structure of monolayer BP in 4×4 supercell. Boron, Nitrogen, and Phosphorus atoms are represented by green, dark blue and pink spheres, respectively.

have one atom thickness sheet in a honeycomb structure, it has been taken much attention due to its potential applications for nano electronics. *h*-BN is synthesized using both top-down and bottom-up approaches by chemical vapour deposition (CVD), highly crystalline BN nanosheets (BNNs) are also synthesized by utilizing liquid exfoliation. During liquid exfoliations, if the surface energy of the solvent is similar to that of the layered material, the energy difference between the exfoliated and reaggregated states will be very small, removing the driving force for reaggregation. Thus, if solvent are chosen accordingly, BNNs can be synthesized up to monolayers with large lateral sizes.

As shown in Figure 1.1a., BNNs have honeycomb structure that is in form of the $B_3N_3H_6$ borazine units. Covalently bonded B and N atoms form bonds at 1.45 Å and the distance between the two centers is 2.51 Å. Monolayer sheets of BN has no optical absorption in the visible range, giving rise to white colour of BNNs[14] BNNs are notable insulators due to their large bandgap.

Even though BNNs are electrically insulating, they are notable thermal conductors. C. Sevik et al.[15] calculated the thermal conductivity of BNNs to be between $300\text{-}2000\text{ Wm}^{-1}\text{K}^{-1}$ while that of graphene is between $1500\text{-}2500\text{ Wm}^{-1}\text{K}^{-1}$. The difference can be thought as the result of softer phonon modes of BNNs and B and N mass difference with respect to equal mass of C atoms[16].

Watanabe et al.[17] reported that the band gap of *h*-BN is ≈ 6 eV. CVD-grown BNNSs has absorption peak at ≈ 203 nm. CVD-synthesized BNNS monolayer shows bandgap at ≈ 6.07 eV[18] and few-layered at ≈ 5.92 eV[19]. This difference is a result of deficiency of interlayer interactions[22]. Since these nanosheets have higher surface/volume ratio compared to bulk form, they can be used as cheap lubricants. The lubricity is the result of weak forces between basal planes and slipping of layers in these nanosheets[20].

Owing to its high stability and insulator characteristics, few-layer crystals and monolayers of *h*-BN were used as gate dielectrics[21, 22], and tunnel barriers (2D *h*-BN can sustain biases up to about 0.8 Vnm[23] and be free from pinholes[24, 25]).

In this thesis, I have studied the structural and electronic properties of *h*-BN and *h*-BP. Both are functionalized via doping and adsorption. We have predicted a new way to synthesise *h*-BP starting with bare *h*-BN as precursor.

Obtaining semiconducting 2D structures with small band gap can open new possibilities in this field, especially for nanoelectronic applications. In that sense synthesis of 2D form of Group III-V elements can be a breakthrough step. Following the theoretical predictions, layered AlN have been experimentally synthesized. Interestingly, on the contrary to its nonlayered bulk structure, ultrathin 12 monolayers of AlN nanosheets has been epitaxially grown on Ag(111)[26]. The monolayer structure of AlN nanosheets had been verified by utilizing electron diffraction and scanning tunneling microscope measurements[26]. This blazes a trail for other possibilities in this group.

Among the III-V binary compounds boron phosphide(BP) has also attracted considerable attention. Zincblende phase of bulk BP[27, 28] is an indirect band gap semiconductor with a band gap of 2.02 eV[29]. In addition to the BP crystal, recent studies have revealed the importance of nanostructured BP for technological applications. Synthesis of BP nanostructures and the demonstration of BP-based electrode for photovoltaic solar cells were reported[30]. Stability, functionalization and various applications of BP nanotubes were also studied[31, 32]. It has

been shown that thin film BP with thickness of 5 nm used as a channel of FET[6] shows on-off current ratio exceeding 10^5 .

Moreover, the planar stable phase of monolayer BP having hexagonal crystal symmetry (*h*-BP) has been predicted.[33] Covalently bonded B and P atoms forms bonds at 1.85 Å and the distance between two centers is 3.21 Å. It has been theoretically shown that *h*-BP is a direct semiconductor with a band gap of 0.9 eV. Also, based on ab initio studies, p-n junction made of highly doped monolayer BP with ideal I-V characteristics have been demonstrated[34]. Additionally, Dong et al. recently reported that BP and silicon carbide nanoribbons can be used in the fabrication of promising nanoelectronic and spintronics devices[35].

It is known that functionalization of semiconductors by doping changes electronic properties significantly. In 2D systems, doping not only alter electronic properties but also modifies the structure drastically[36, 37]. For instance, Ge adatom adsorbed on germanene exothermically forms a dumbbell structure leading to electronic properties depending on the type of both supercell structure and size[36]. Furthermore, depending on the row number of adatoms and monolayer substrates, dumbbell structures forming upon adsorption are mobile resulting in new phases of these monolayers[37].

In the light of these information in this thesis, we have systematically doped *h*-BN with P atom, giving rise to monolayer *h*-BP. During phosphorization, the structural and electronical evolution has been extensively studied.

Then, we present a systematic study of the substitution and adsorption of selected adatoms from Group-III (B, Ga, Al), Group-IV (C, Si, Ge), and Group-V (N, P, As) on *h*-BP by using first principles calculations. We start with interaction of B and P atoms with *h*-BP and reveal the formation of dumbbell phase. Next, the study is extended to other Group III-IV-V as dopant (adsorption or substitution) in order to elucidate the effect of doping on structural, electronic and magnetic properties of *h*-BP.

Chapter 2

Theoretical Background

In order to describe the physical and chemical properties of matter, one needs to solve the many-body Schrödinger equation as a starting point of performing first-principle calculations.

$$H\psi_i(\mathbf{r}, \mathbf{R}) = E_i\psi_i(\mathbf{r}, \mathbf{R}) \quad (2.1)$$

The Hamiltonian of a many body problem can be written in a general form(1.2):

$$H = -\hbar^2 \sum_i \frac{\nabla_i^2}{2m} - \hbar^2 \sum_I \frac{\nabla_I^2}{2M_I} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_{i \neq j} \frac{Z_i e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (2.2)$$

That is, a system of many-body can be described by electrostatic interaction of electrons and nuclei. Although it is formulated in one equation, it does not mean that it allows a solution. Analytically it can be solved only for H and He atom. For realistic systems having many electrons and nuclei, it is not possible to solve the Schrödinger equation even numerically with High Performance Computers (HPC) yet. During calculations, one has to deal with $3n + 3N$ (n for electrons and N for nuclei) degrees of freedom, thus, some approximations are needed in order to get as closer as correct solutions to exact solution, numerically.

2.1 Born-Oppenheimer Approximation

In quantum chemistry, in order to make Schrödinger equation simple, some approximations are acceptable. The first approximation is to separate electrons as core and valence electrons. The core electrons are very close to nuclei and it is asserted as totally occupied orbitals; whereas valence electrons are treated in unoccupied orbitals. And the second approximation arises from the fact that the force and momentum between electrons and nucleus are the same result of attraction of the same magnitude of the electric charge. Comparison between nucleus and electrons' velocity, having the same magnitude of momentum leads to disproportional relationship with their mass and velocity. Thus, electron having less mass has much more velocity with respect to nucleus as being much heavier. In Born-Oppenheimer approximation, as the mass of electron is so small that can be neglected with respect to mass of nuclei, electrons are assumed to be moving and nuclei is as stationary. As a property of Hamiltonian, the eigenfunctions are products of each ones if Hamiltonian is separable into two or more terms. Thus, separating nuclei and electrons velocity and neglecting the velocity of nuclei leads to treat the Hamiltonian as (of electron positions $\mathbf{r}$ and nuclear positions $\mathbf{R}$)

$$\Psi_{molecule} = \Psi_{electrons}(\mathbf{r}_i, \mathbf{R}_j) \Psi_{nuclei}(\mathbf{R}_j) \quad (2.3)$$

Then, Hamiltonian equation can be written as;

$$\hat{H} = \hat{T}_e + \hat{V}_{n-e} + \hat{V}_{e-e} + \hat{V}_{n-n} \quad (2.4)$$

The many-body Schrödinger equation turns into having a solution for fixed nuclei due to these two approximations.

2.2 The Electronic Problem

In order to solve the many body Schrödinger equation, more approximations are needed. First step is the **Hartree Approximation** which states

that if electron-electron interaction must be calculated, Hamiltonian should be separated according to the fact that electrons are affected by their positions. Hartree thought that each electron moves in a field which is constructed by other electrons. This idea leads to electrons be in an electronic “sea”.

$$\sum_{i=1}^N \sum_{j>1}^N \frac{1}{\mathbf{r}_{ij}} \approx \sum_{i=1}^N v_i(\mathbf{r}_i) = \sum_{i=1}^N \int \frac{\rho(\mathbf{r}_j) - |\Psi(\mathbf{r}_j)|^2}{\mathbf{r}_i - \mathbf{r}_j} d\mathbf{r}_j \quad (2.5)$$

that outputs a set of “effective” one-electron potentials v_i and orbitals Ψ_i for each electron i . [38] By the way, individual electrons are only affected by other $N - 1$ electron densities δ , not itself, and after calculating Ψ_i , one can determine the potential. Then, one can express the total wave function as the Hartree product of the one-electron wave functions Ψ_i , i.e.,

$$\Psi = \varphi_1(r_1)\varphi_2(r_2)\dots\varphi_N(r_N) \quad (2.6)$$

Briefly, Hartree approximation states the potential can be separated into V_{elec} and V_{ion} . In other words, it is possible to write electronic wavefunction as the product of single electron wavefunctions. The lack of this approximation is that when one electron is removed from the total N electron cloud, this approximation only accounts the fields experienced by the electron from the rest and the discount of electrons behaviour as fermions. These calculations start with initial guess of orbitals, then a new potential is developed till the difference between Ψ_i and Ψ_{-i} are negligible. This process is called as **Self-consistency cycle**.

In computational techniques, the Hartree method is an essential step for the self-consistency. The next step called the **Hartree-Fock Approximation** which includes both electronic charge and spin. Due to Pauli exclusion principle, Hartree approximation is not enough because of electronic spin, thus, one should formulate a three dimensional orbital φ for electron i by writing it as the product of a purely space-dependent part ξ and a spin function, α or β , characterizing spin-up or spin-down electron, for example;

$$\varphi_i(x_i) = \xi_i(r_i)\alpha_i \quad (2.7)$$

here we use x to indicate a variable which includes both space $\mathbf{r}$ and spin α .

Then,

$$\Psi' = \xi_1(r_1)\alpha_1\xi_2(r_2)\beta_2 \quad (2.8)$$

but also as

$$\Psi'' = \xi_1(r_2)\alpha_2\xi_2(r_1)\beta_1 \quad (2.9)$$

Because electrons are fermions, then their wave functions should be antisymmetric. This leads the wave function turns into;

$$\Psi = \Psi' - \Psi'' = \xi_1(r_1)\alpha_1\xi_2(r_2)\beta_2 - \xi_1(r_2)\alpha_2\xi_2(r_1)\beta_1 = \begin{vmatrix} \xi_1(r_1)\alpha_1 & \xi_2(r_1)\beta_1 \\ \xi_1(r_2)\alpha_2 & \xi_2(r_2)\beta_2 \end{vmatrix} \quad (2.10)$$

this is also called as Slater determinant[39] and has antisymmetrized product wave function property. In order to consider the fermionic behaviours of electrons, Hartree-Fock approximation takes into account antisymmetry and focusing into φ again;

$$\Phi(x_1..x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \phi_3(x_1) & \dots \\ \phi_1(x_2) & \phi_2(x_2) & \phi_3(x_2) & \dots \\ \phi_1(x_3) & \phi_2(x_3) & \phi_3(x_3) & \dots \\ \vdots & \vdots & \vdots & \end{vmatrix} \quad (2.11)$$

In this determinant, due to normalization constant, it is prevented to go into same orbital if two electrons have the same spin. The mathematical feature of being more demanding, **Hartree-Fock(HF)** equations are much better to concern electronic exchange. However, electronic correlations are still missing in HF equations. However, these two approximations are also have problems. The more number of interacting particles a system has, the more computational cost increases. They are also bad at band and HOMO-LUMO gap values by overestimating them. Slater[40] is another method of approximating the nonlocal exchange potential by using electron density. Slater turns nonlocal exchange potential into so-called $\chi\alpha$ local potential. This leads to emerge Hartree-Fock-Slater(HFS) method which is much easier than HF. Again, HFS ignores electronic correlations, like in HF[38].

2.3 Density Functional Theory

By using Schrödinger equation, exact solutions are possible only for a few particles. Thus, bigger systems are treated as “pseudo” one-particle systems by introducing a ”centre-of-mass” coordinate systems in many-body problems.[41]

In Density Functional Theory (DFT) , “centre-of-mass” is the density of the system. Before focusing on density, the meaning of DFT should be understood deeply. Hohenberg and Kohn state that there is one-to-one correspondence between electron density of a system and the energy. Here, the density is function, energy dependence on density is functional (functional means function of a function, denoted with brackets, $F[f]$). In short, DFT is the theory of the function energy with respect to being function of density. Thus, density determination and correspondence with energy are the way of generation DFT. In theory, by solving many-body Schrödinger equation, all information about entire system can be expressed.

Wave function with concerning exchange and correlation can be explained by going from N-electron wave function Ψ and its corresponding Schrödinger equation to electron density $\rho(r)$ by a computational scheme. Thomas [42]and Fermi are the pioneers of a method of statistically revealing the distribution of electrons in an atom.

A DFT has the capability of calculating a host of properties of condensed matter and their accurate surfaces. Although there are other techniques in order to obtain closest solution of the many body Schrödinger equation, DFT aims to calculate the ground state electron density distribution, instead of many body density. Because real space has only 3 dimension, independently of the number of electrons, the requisite for density decreases to 3 variables, not $3N$ [43]. To this respect, for many electron systems, DFT is one of the best choice.

Afterwards the proof of Hohenberg and Kohn in 1964, within the ground state electronic function Ψ_0 , modern DFT used in electronic structure problem has risen. In short, DFT enables to functionalize the problem of interacting electron

gas to an only particle that has an actual nonlocal potential. The prominent aim in DFT is to replace wavefunction with density.

As described above detailed, Hohenberg and Kohn declared that a single value for functional of electron density can be used to find out the total energy of an electron gas. And, Kohn and Sham describe that the presentation of set of self consistent one-electron equations.

With beginning kinetic energy terms, Coulomb energy and exchange-correlation terms, DFT divides the total energy to three parts. Describing the van der Waals forces for thin materials and underestimation of the band gap of semiconductors and other extremely correlated systems are some of deficiencies of DFT.

2.3.1 Hohenberg-Kohn Approximation

On the contrary, DFT includes both exchange and correlation that leads DFT relation on two theorems of Hohenberg and Kohn[44] that declares that the wave function of ground state Ψ is a unique functional of $\rho(r)$, that is because of the dependence of energy on $\rho(r)$. Additionally, searching for the minimum energy wave function Ψ_0 can be represented by the minimum energy $\rho_0(r)$ that is called as **variational principle**. The ground state energy of the system can be found in terms of ground state electron density of the system, that is unique for a given potential function.

There are two prominent theorems of Hohenberg-Kohn formulations.

Theorem I: There is a mapping, that is the external potential is described by the electronic density. Because of the correlation of $\rho_{\mathbf{r}}$ and $V(\mathbf{r})$, one can easily have an idea of ground state wavefunction and the full Hamiltonian.

Theorem II: Instead of using trial wavefunctions, it is enough to reach minimal principle by using trial charge densities. That results in;

$$E = \min \frac{\langle \tilde{\Psi} | \mathbf{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \quad (2.12)$$

DFT has these two backbone theorems. Since Hohenberg-Kohn approximation calculates kinetic energy not accurate, the miscalculation of kinetic energy in HK approximation is ruled out by using Kohn-Sham equations.

2.3.2 Kohn-Sham Equations

Kohn and Sham[45] introduced of a reference system that consists of same density electron with no interaction as the real many-body system. The system turns into quasi-noninteracting system by introducing a bit of spin dependent additional potential.

Rewording, KS equations enable to have a methodology of minimizing the functional $E(\rho)$ by the help of variation of ρ through all densities of N electrons. Because DFT uses orbitals, exchange correlation energies and kinetic energy parts, DFT has a logical progress. Then DFT has a form of many-body problem replaced by the self-consistent, N Kohn-Sham equations solutions

$$-\frac{1}{2}\nabla^2 + v_{eff}(r)\Psi_i(r) = \varepsilon_i\Psi_i \quad (2.13)$$

with an effective one-particle potential of the form

$$v_{eff}(r) = v(r) + \int \frac{\rho'}{|r - r'|} dr' + v_{XC}(\mathbf{r}) \quad (2.14)$$

here, nuclei potential, potential with respect to Hartree, and exchange and correlation represented.

That are,

$$v_{XC}(\mathbf{r}) = \partial E_{XC}(\rho(\mathbf{r}))\rho(\mathbf{r}) \quad (2.15)$$

Due to including exchange and correlation potentials and self-consistency, DFT has advantages by a long way. DFT is quick, size-consistent, and orbital theory independent formulation for solving many body problem of electrons and nuclei. In conclusion, DFT is qualified to determine ground-state properties.

2.4 Functions of Exchange and Correlation

There are some approximations listed below in order to search for reliable exchange-correlation functions.

2.4.1 Local Density Approximation (LDA)

The other Exchange-correlation functional in DFT is LDA,

$$E_{XC}^{LDA} \rho(\mathbf{r}) = \int \rho(\mathbf{r}) \varepsilon_{XC}^{hom} \rho(\mathbf{r}) d\mathbf{r} \quad (2.16)$$

$\varepsilon_{XC}^{hom} \rho(\mathbf{r})$ represents the exchange correlation energy per particle of a homogeneous gas of electrons of density $\rho(r)$. [38] The main idea of LDA is to evaluate the exchange-correlation energy per electron at a point $\mathbf{r}$ in the electron gas as exchange-correlation energy per electron in a homogenous gas which consists of the same density as the electron at $\mathbf{r}$. LDA treats inhomogeneous electron gas as locally homogenous and solve this problem as homogenous.

Evidently, this approximation is used for systems which has small changes in density. In other words, LDA is interested in $\rho(\mathbf{r})$ at a point. Using LDA, it is possible to calculate structural, vibrational and elastic properties of materials very accurate. LDA is not accurate enough to give activation energies of reactions. As LDA does not take into account inhomogeneity of electron density, it is not applicable for such systems. This is why, we have chosen GGA approximation as an exchange correlation functional in our calculations.

2.4.2 Generalized Gradient Approximation (GGA)

Another approach describes local changes in electron density by taking into account the gradient of electron density in an exchange hole, and by the way, this improves the LDA in low density regions by counting on both $\partial\rho(r)/\partial r$ and $\rho(r)$.

This is called as generalized gradient approximation (GGA), and

$$E_{XC}^{GGA} \rho(\mathbf{r}) = \int \rho(\mathbf{r}) F(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|) d\mathbf{r} \quad (2.17)$$

In short, GGA is still local and uses both $\rho(\mathbf{r})$ and $|\nabla \rho(\mathbf{r})|$ that means GGA also accounts the gradually changing densities. GGA considers fluctuations in electron density which is given as the gradient of electron density with respect to reciprocal space coordinates. Thus, GGA successfully determines some ground state properties of materials in most cases. Although GGA corrects the problem of overbinding of LDA, GGA results in underbinding. In our calculations, we have used GGA approximation with a type of PBE(developed by **P**erdew, **B**urke and **E**rnzerhof) [46] flavor. Also, in order to increase accuracy, hybrids functionals are used which are mixtures of some fraction of HF.

2.4.3 Hybrid Functionals

Hybrid functionals are the mixture of exchange from HF theory with exchange and correlation from ab-initio or empirical methods. The meaning of “hybrid” is also a clue of this technique is a corporation with HF and DFT. Thereby, calculation of hybrid functionals cost too much computational time.

In this thesis, HSE06 type hybrid functionals are used which refers Heyd-Scuseria-Ernzerhof (HSE) which represents the change of screening parameter effects solid band gaps the most[47]. HSE06 hybrid functional is constructed by mixing 25% of the Fock exchange with 75% of the PBE exchange and 100% of the PBE correlation energy. HSE06 is also successful at calculating band gaps and lattice constants of solids.

2.5 Periodicity in Numerical Calculations

Most of the solid materials adopt a crystalline ordering due to the interactions of the atomic sites with the neighboring atoms having an increased stability in a

crystalline arrangement. The description of "crystal" according to the International Union of Crystallography (IUCr) is given as "any solid having an essentially discrete diffraction diagram"[43] but since the recently discovered quasi-crystals also fit in to this description, periodic crystals have become a subset of this concept. A unit cell, i.e. the repeating structural building block of the material in 3 directions is defined either by the 6 lattice parameters, namely the length of the three sides of the cell along with the angles between them; or by the 3 lattice vectors that defines the boundaries of the repetition pattern (giving rise to the periodicity). Considering these periodic translations, 14 basic lattice types (i.e., Bravais lattices) have been found to be compatible with the underlying periodicity, with any other proposed type of lattice being transformable to one of these. With the addition of point group symmetries to the aforementioned translations, 230 space groups have been defined for a 3 dimensional lattice. Due to the periodicity of the lattice, the potential must also be periodic. Defining a lattice translation vector $\mathbf{R}$ as the combination of lattice vectors, the potential should satisfy[48]:

$$U(r + R) = U(r) \quad (2.18)$$

Substituting this potential into the Schrödinger equation yields:

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(r)\right)\Psi = \varepsilon\Psi \quad (2.19)$$

and the free electrons are now considered as Bloch electrons due to the included potential[49].

2.5.1 Bloch Theorem

Theorem: Plane wave times a function i^{th} periodicity of Bravais lattice can be combinations of the eigenstates Ψ of the Hamiltonian $\hat{H}$. Such as,

$$\Psi_{nk}(r) = e^{ik \cdot r} u_{nk}(r) \quad (2.20)$$

where

$$u_{nk}(r + R) = u_{nk}(r) \quad (2.21)$$

n is the quantum number and called as the band index which can be $n=1,2,3,\dots$. Each number is the representation of different energy levels. Another form of Bloch theorem is such as

$$\Psi(r + R) = e^{ik \cdot R} \Psi(r) \quad (2.22)$$

that states that each Ψ taken for each corresponding a wave vector $\mathbf{k}$. [49]

Bloch theorem can be applied to solve electronic structure problem in 3D, just by reducing it in primitive cell. In order to solve electronic structure problem in 2D, vacuum is applied. Periodic boundary conditions guarantee that in the x and y directions, the slab is infinite, in the z direction, the slab and vacuum broaden infinitely[43].

Total energy of a crystal formulated over Brillouin zone is as;

$$E = \sum_{n \in occ} \int_{B \cdot Z} \varepsilon_n(\mathbf{k}) d^3k \quad (2.23)$$

Here, for **k-point sampling**, $\mathbf{k}$ represents wave vectors and electronic states are only allowed through the fringe points of the integral which depends on $\mathbf{k}$ points. Also, the number of $\mathbf{k}$ -points depends on the density of the solids. In other words, density of allowed $\mathbf{k}$ -points is proportional to volume of solid in reciprocal space. Electron potential that is contributed by occupied states at each $\mathbf{k}$ points requires plenty of calculations in order to calculate exact potential. Nevertheless, having close enough energy values helps to treat identical $\mathbf{k}$ -points for similar electronic wavefunctions. Bloch theorem enables to calculate infinite number electronic wavefunction in a finite Brillouin zone by utilizing periodicity of the reciprocal space. The application of Bloch theorem in reciprocal space is known as **k-points sampling**. [50] As for metals, in order to define the Fermi surface exactly, number of $\mathbf{k}$ -points are needed more than for semi-conductors and insulators. Calculating the total density requires the more $\mathbf{k}$ -point, or in other words **k-meshes**, which leads the more accurate the solution of integral. Although the accuracy increases with increasing the number of $\mathbf{k}$ -points, CPU time consumed in calculation increases. Thus Monkhorst and Pack method is used in order to obtain the desired number of **k-meshes**. This method divides the Brillouin zone uniformly through **k-points**[50]. **k-meshes** with having as close as identical values can be represented by a single **k-meshes**.

Also, Bloch theorem enables that discrete **plane-wave basis sets** are able to broaden the electronic wave functions at each **k**-meshes. When one solves the Schrödinger equation for periodic systems, which satisfies Bloch theorem, can be stated as

$$\phi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r}) \quad (2.24)$$

Here, u_k is $u_k = r + n_1 a_1 + n_2 a_2 + n_3 a_3$ which is periodic. Plane-wave basis sets are the directly outcome of Kohn-Sham orbitals of crystal feature. Both ions and corresponding potentials are organized regularly. This enables to be solved for each independent **k** values.

Also, one can have the density of the system by the solutions of Schrödinger equation. Then, DFT becomes suitable for solving **k** not in terms of **r**. Thus, by using this information, plane waves are called by $\exp^{i\mathbf{k}\cdot\mathbf{r}}$. While, **r** vectors form real space, and **k** vectors form reciprocal space. Then, **a**₁, **a**₂, and **a**₃ vectors are converted to **b**₁, **b**₂, and **b**₃ reciprocal vector, respectively, by using formula given in equation;

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}, \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)} \quad (2.25)$$

Real lattice vectors and reciprocal lattice vectors are inversely proportional. The bigger magnitude of length of real lattice vector is, the smaller of reciprocal has, and vice versa. With the help of real lattices, primitive cells are defined which has the minimum volume that is enough to show all information to form the system. Here, one should consider the difference between real and reciprocal lattices; real lattice is the indication of locations of atoms; reciprocal lattice shows direction and size of momentum.

Because u_k is periodic which means

$$u_k(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (2.26)$$

Here, **G** is reciprocal space; $\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$ which has relationship between real space vector $\mathbf{G} \cdot \mathbf{a}_i = 2\pi m_i$. Then, solutions of Schrödinger equation leads kinetic energy as

$$E = \frac{h^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \quad (2.27)$$

And, in order to have minimum kinetic energy; one needs to make some reduction;

$$E_{cut} = \frac{h^2}{2m} G_{cut}^2 \quad (2.28)$$

Kinetic energy cut-off E_{cut} in DFT is an easy way of describing $\mathbf{k}$ points. With the help of E_{cut} , one has a finite plane waves. However, one should not ignore the errors of E_{cut} thus, the bigger it is, the less the accuracy error the system has. But computational time is also another issue one should take care of it during calculations, thus convergence tests of E_{cut} enables to save time and effort.

In order to apply Bloch theorem a system, this system should be periodic in 3D. The applied plane-wave basis set should be continuous. Thus, the **supercell approximation** enables us to adjust non-periodic structures. Periodic unit cells should be treated as having three dimensional periodicity even it does not, by putting inside very large supercell and making no interaction of each periodic cells by applying vacuum.

2.6 Pseudopotential Approximation

It is hard to expand the tightly bounded core electrons because of large number of plane waves. This leads to require highly large plane-wave basis sets. Including all electrons increase the computational time, thus, in order to decrease the time and high plane-wave necessity, pseudopotentials are used.

A pseudopotential refers not exact potentials of electron-ion potential, instead replacing it a much weaker one that leads all the prominent features of a moving valence electrons.[51] What makes pseudopotentials preferable is to make easier to solve Schrödinger equation by enabling expansion of wavefunctions in a very small plane-wave arrangement.

This approach is almost true because valence electrons of solids have the most important role in the most of physical properties with respect to core electrons. It is also asserted by Pauli exclusion and wavefunction orthogonality feature as valence

electron wavefunctions only oscillates fast in the core shells. Pseudopotential approach treats the core electrons as frozen and regards only valence electrons, by the way, the system has lower plane waves. The system has a cut-off radius which sets the wavefunctions all same after the radius.

There are two types of pseudopotentials; ultrasoft(US)[52] and projector augmented plane waves (PAW).[53]The difference occurs because of the core region. PAW treats superpositions of atomic orbitals. US is more flexible, only norm conservation should be considered. In this thesis, PAW potentials implemented in VASP are used. PAW potentials are better for calculating the accuracy of magnetic materials.

Although using pseudopotentials leads to lack of accuracy, advantages of using it overweigh. Kohn-Sham equations are needed to solve lower dimensional matrices that decrease basis sets and computational time.

2.7 Computational Employment of DFT

As the combinations of all above, in order to perform such calculations, we have used Vienna Ab-initio Simulation Package (**VASP**)[54]. This program enables to modelling materials at atomic scale for electronic structures, quantum mechanical calculations and so on. VASP calculates the many-body Schrödinger equations within using DFT with Kohn-Sham equations. The combination of both DFT and HF calculations are hybrid functionals are used in this thesis in order to find more accurate band gap of the systems. We use the property of VASP such that plane wave basis sets are used for local potentials and interactions of electrons with ions described PAW method. Because the system is periodic supercell, VASP fits with it by completely symmetric code by also using Monkhorst Pack special points.

In this chapter, methodology of this thesis is mentioned. DFT and its origin,

nuts and bolts are discussed. In order to sum up all procedure above, a self-consistent cycle is represented and easily understandable scheme is below. Briefly explanation of self-consistent cycle is an iterative cycle that depends on solution of Kohn-Shan equations. First one should start with an input density ρ_{in} as initial guess and get effective potential V_{eff} . After enough calculation of Kohn-Sham Hamiltonian, the output density ρ_{out} should be close enough with ρ_{in} . In other words, from a to z, a routine DFT calculation start from a guess of Hartree-like potential by solving Schrödinger equation; first cycle, one gets a density that yields a new potential, then after enough cycle, until self-consistency is achieved.

The Self-consistent field method

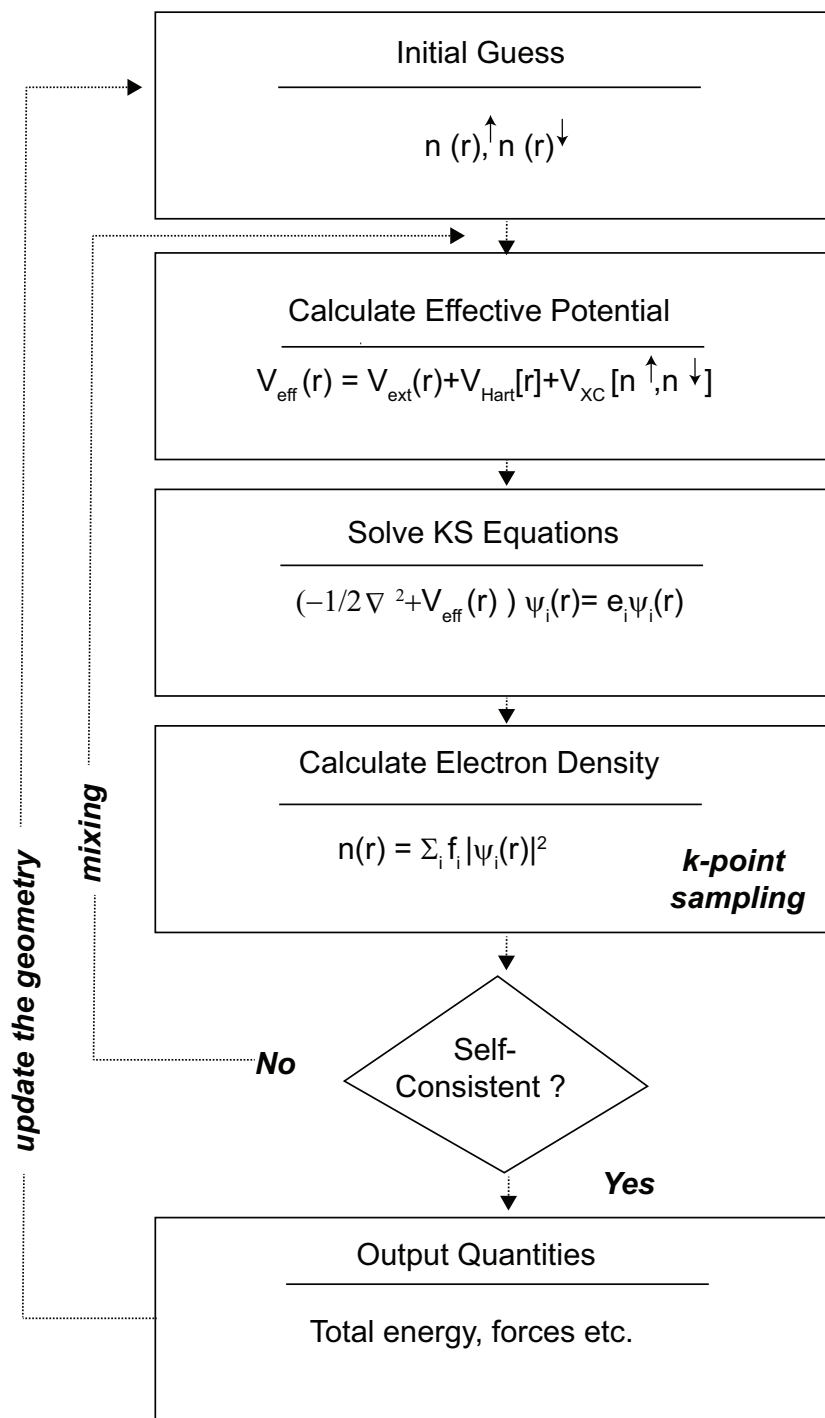


Figure 2.1: The scheme for self-consistent DFT calculation.

Chapter 3

Results

3.1 Phosphorization of Monolayer Boron Nitride: Stable Monolayer $\text{BN}_{16-x}\text{P}_x$ Alloy

In our calculations, we use the state-of-the-art first-principles plane-wave calculations within the density functional theory (DFT)[55, 44]. VASP is used to carry out the numerical computations. Also projector augmented-wave (PAW) potentials and generalized gradient approximation (GGA) are used. The Brillion zone of the primitive unit cell of boron nitride sheets are sampled by $5 \times 5 \times 1$ $\mathbf{k}$ -points in the Monkhorst-Pack scheme[50]. Between two consecutive steps, 10^{-5} eV is chosen as the convergence energy. The system is treated as periodic and the 4×4 supercell is used when absorptions are considered.

Since BP does not have layered bulk structure like graphite or BN, the synthesis of monolayer BP should follow a new path; like synthesis of monolayer AlN [26] epitaxially grown on single crystal Ag (111). Although this is one possibility of getting monolayer BP, in this thesis, we are suggesting another way of achieving 2D BP by phosphorization of monolayer BN. By this method, it is possible to obtain $\text{BN}_{16-x}\text{P}_x$ alloy and at the end to achieve monolayer BP.

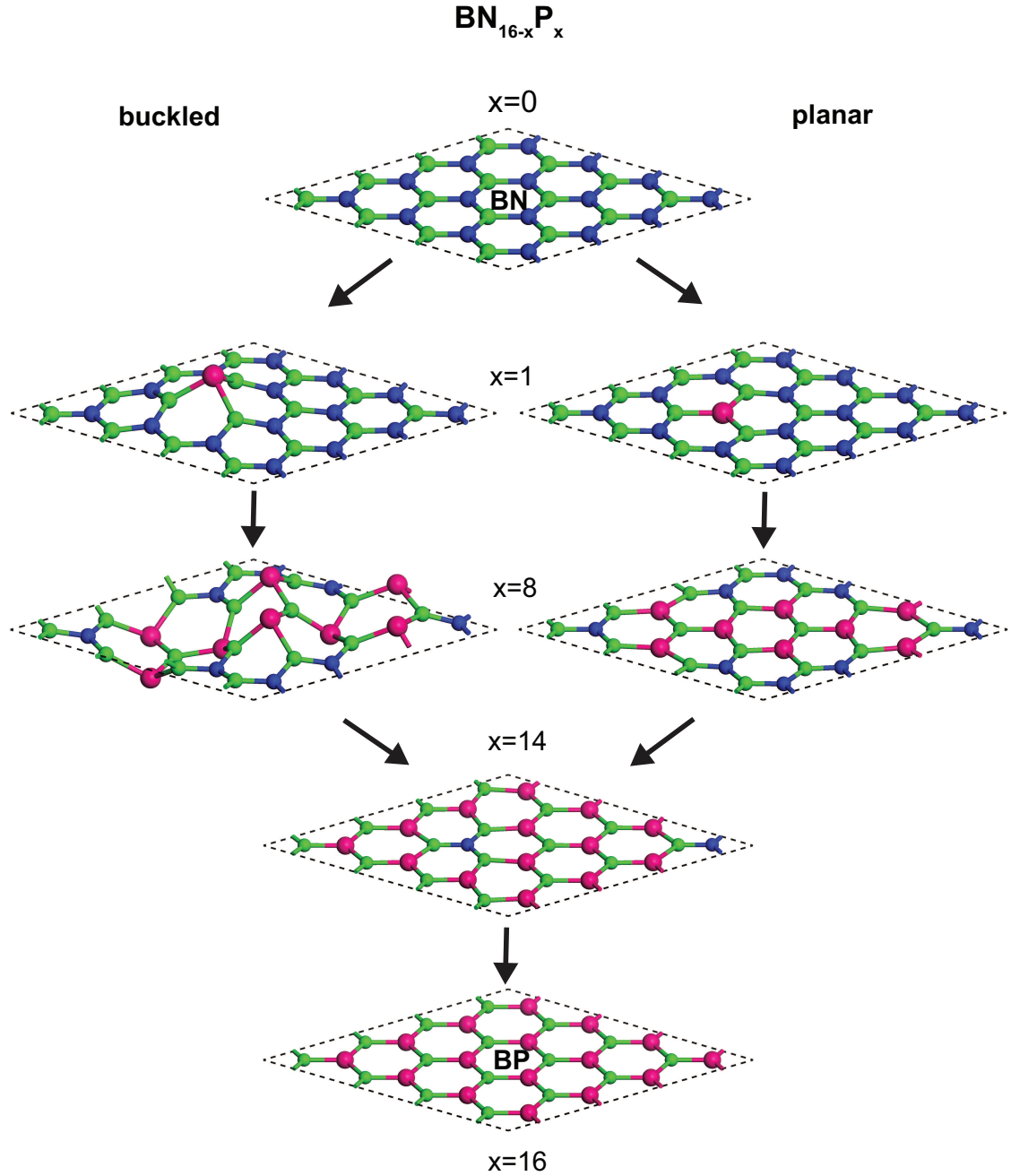


Figure 3.1: The predicted chemical route to synthesise *h*-BP via phosphorization in various concentrations starting with bare *h*-BN. x denotes doping concentration of P atom. Green, dark blue, pink spheres represent B, N, P atoms, respectively.

Firstly, we consider 4×4 supercell of BN (16B and 16N atoms) as prototype system and start replacing N atoms with P. For each case, we determine the lowest energy configuration. As shown Figure 3.1, starting from first substitution, $BN_{16-x}P_x$ alloy has a tendency of getting buckled structure until 87.5% ($x = 14$). The lattice constant of alloy enlarges with increasing P concentration. This can be expected since P is larger than host N atom. The monotonic increase of lattice constant with x is illustrated in Figure 3.2a. This trend also supports the shift from pure monolayer BN lattice constant(2.51 Å) and pure monolayer BP lattice constant(3.21 Å). Here, it is possible to refer Vegard's law which states that the lattice parameter of a solid solution of two constituents is approximately equal to a rule of mixtures of the two constituents' lattice parameters at the same temperature:[56, 57]

$$a_{A_{1-x}B_x} = (1 - x)a_A + xa_B \quad (3.1)$$

As the alloy is bucked, it is interesting to analyze the deviation from ideal planar geometry. In this sense we define a buckling parameter (Δ), which is the average deviation distance of each atom in z -direction. Δ is first increases with x , and then sharply decreases as shown in Figure 3.2b due to the planarity tendency of the monolayer BP.

As can be seen from Figure 3.3a, the buckled geometry is energetically more favorable when compared to planar one. The ground state configuration has an asymmetric nature, preferred to symmetric cases, for instance a configuration where all P atoms move upwards. The substitution of N with P is an endothermic process and requires energy. Thus can be feasible at high temperatures or with help of catalyzers. Here, we define the associated substitution energy either by single P atom doping or excessively doping in our calculations. Either case, substitution energy E_{sub} decreases with increasing of doping concentration x (Figure 3.3b). The electronic properties of BN also modify upon P substitution. The large band gap of BN decreases with increasing P concentration as shown in Figure 3.4. As band gap values are underestimated at standard DFT level, we also calculated them with HSE06 hybrid functional method (The details are given in the Method section). Our results indicate that however BN is an insulator, BP is a direct band gap semiconductor.

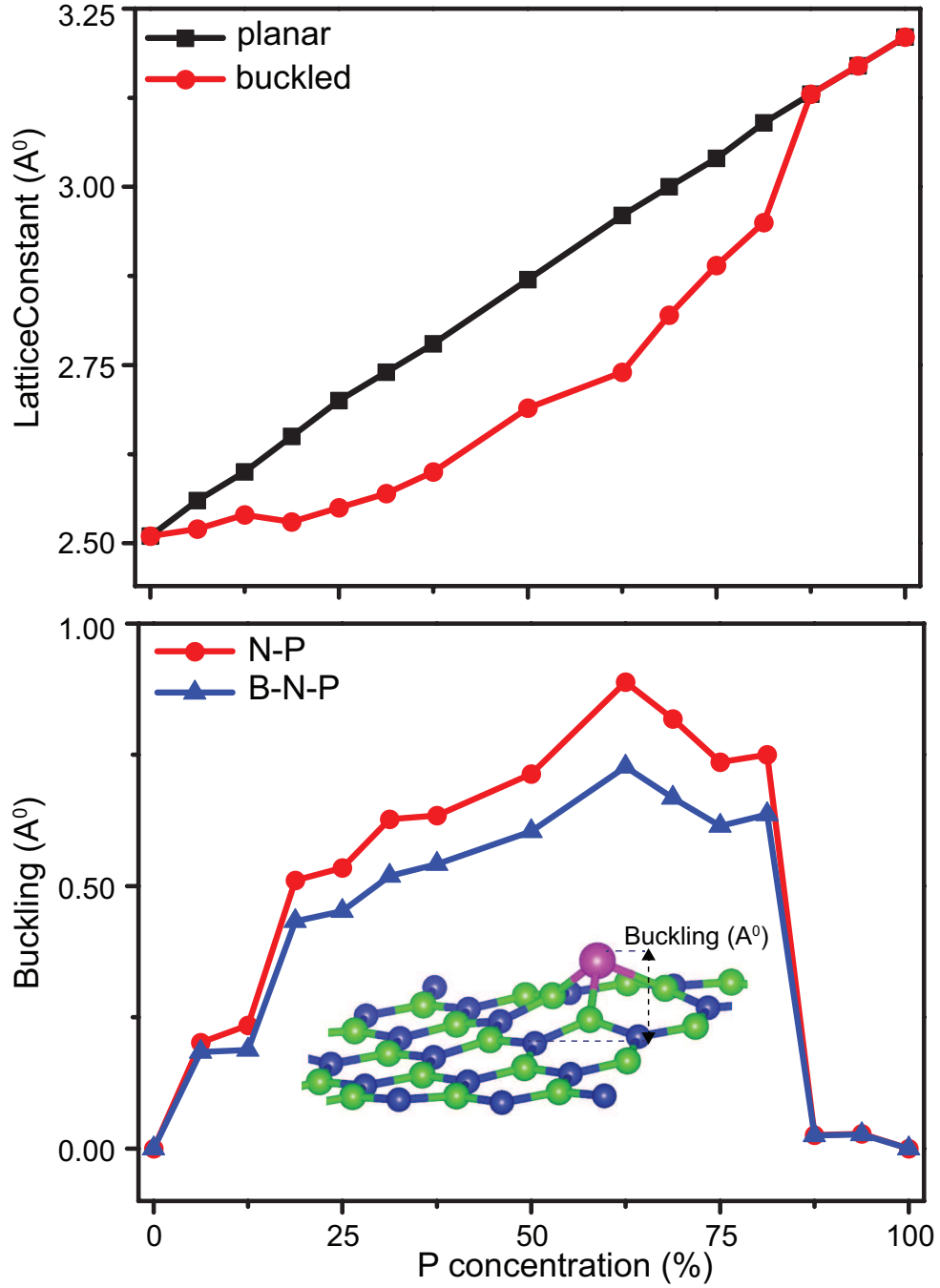


Figure 3.2: Top: Lattice constant evolution with respect to varying P concentration for both buckled and planar structures. Bottom: Buckling vs. concentration of P atom for both buckled and planar structures.

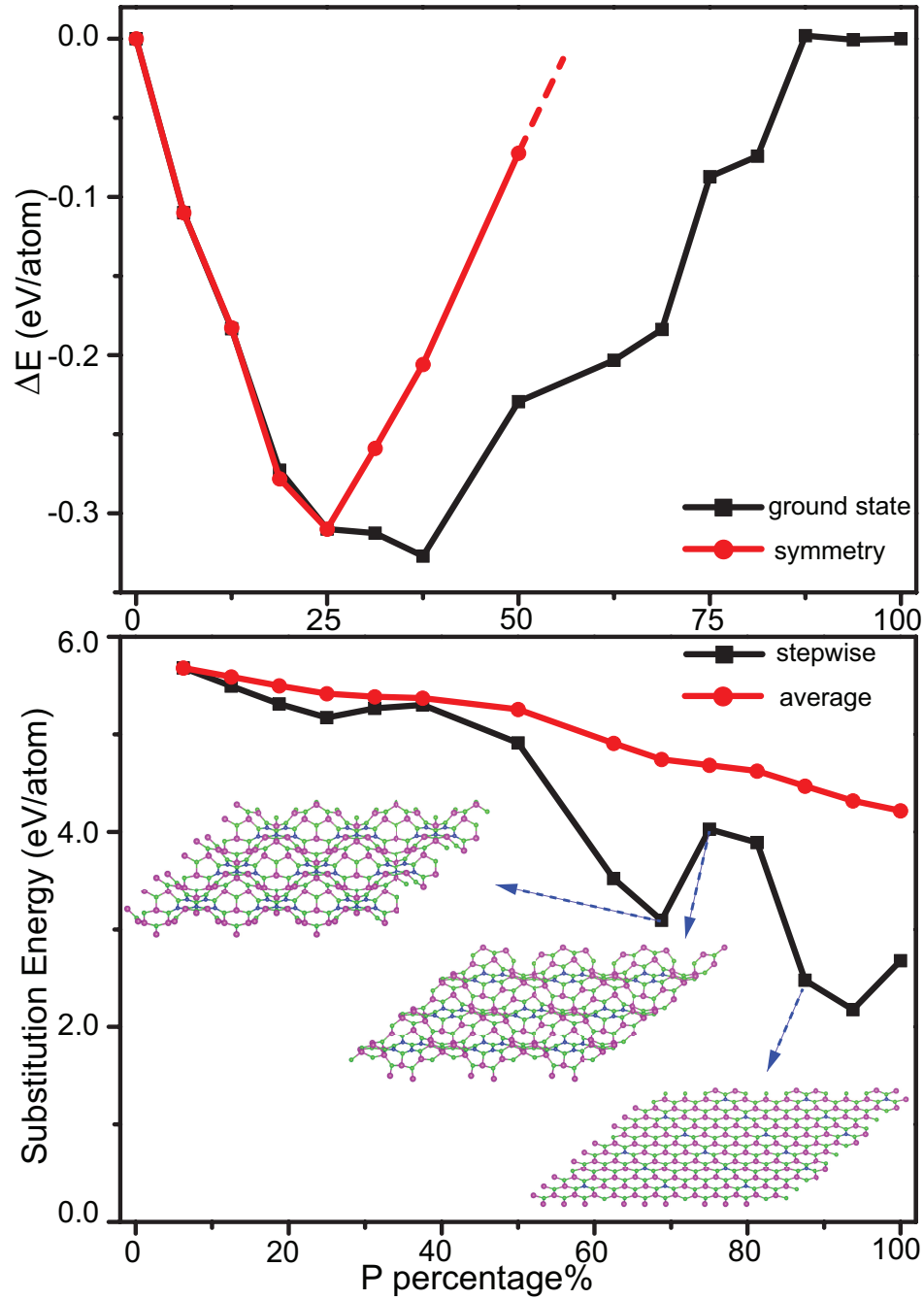


Figure 3.3: Top: The energy difference showing the structural deviation from ideal planar geometry to buckled one with respect to concentration of P atom. Black and red curves indicate ground state and symmetry configurations. Bottom: The variation of substitution energy with P concentration. Black curve corresponds to stepwise substitution of P atoms and red curve indicates the average substitution energy.

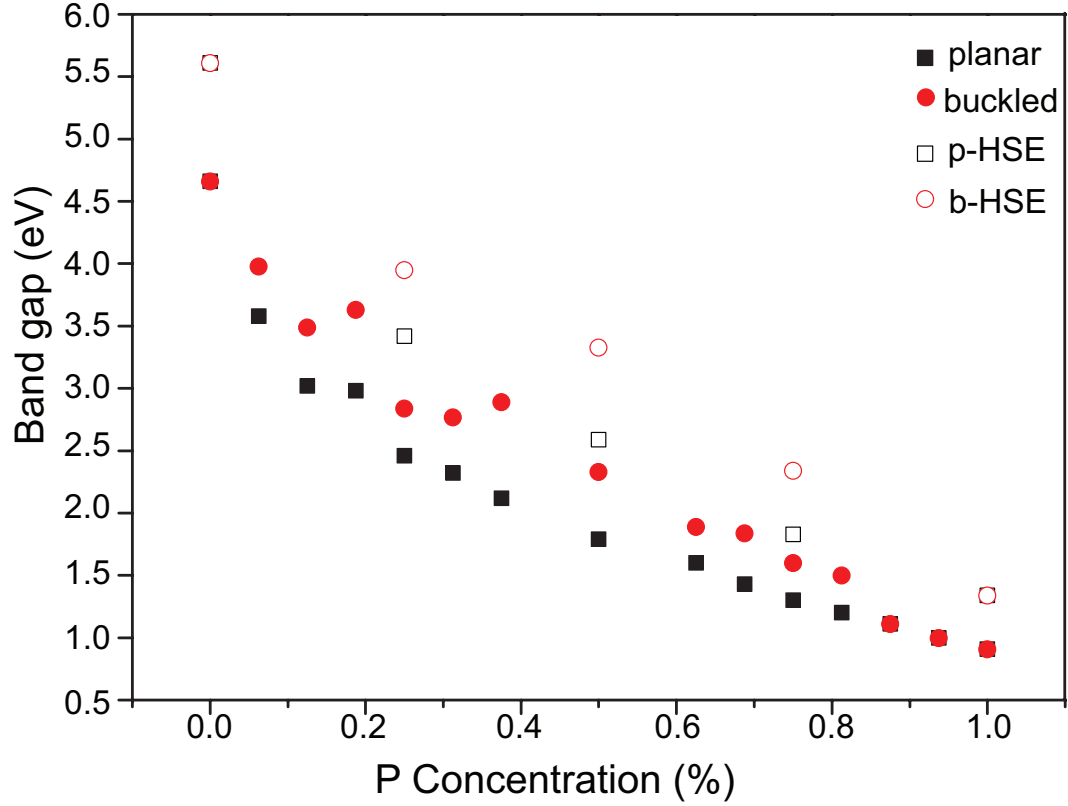


Figure 3.4: Band gap vs percentage of P adatoms, with respect to planar-DFT, buckled-DFT, planar-HSE, buckled-HSE calculations.

Briefly, as mentioned above, with the support of phonon stability calculations, it is possible to obtain stable monolayer $BN_{16-x}P_x$ alloy and also bare BP by phosphorization of h -BN. By this, it is possible to control E_{gap} by P concentration (band gap engineering). Being a direct band gap semiconductor, monolayer BP can be suitable for nanoelectronic applications. In that sense in the following sections, we will study the structural and electronic properties of doped BP monolayers.

3.2 Dumbbell Phase of Monolayer BP

In this work, we performed spin polarized first-principles calculations based on density functional theory (DFT) [55, 44] within generalized gradient approximation (GGA) including van der Waals corrections [58]. The pseudopotentials of elements were described by projector augmented-wave method (PAW)[59] using a plane-wave basis set with a kinetic energy cutoff of 500 eV and the exchange-correlation potential is approximated with Perdew-Burke-Ernzerhof (PBE) functional [46]. Although various supercell sizes of monolayer have been taken into account, all analyses on doping are carried out for 5×5 supercell ensuring minimum dopant-dopant distance. Self-consistent calculations are converged for the $11 \times 11 \times 1$ $\mathbf{k}$ -point sampling for the unitcell and then scaled accordingly for larger supercell sizes.

All structures are relaxed without any constraints by setting convergence criteria on the total energy and force to 10^{-5} eV and 10^{-4} eV/ $\text{\AA}$, respectively. Since the band gaps are underestimated by standard-DFT methods, we also carried out calculations using the HSE06 hybrid functional[60] for better estimation of actual band gap values.

It has been shown that excess presence of B atoms during growth make BP thin films *p*-type semiconductor, whereas excess P would make it *n*-type depending on the both growth temperature and flow concentration of atoms[61]. The thickness and crystalline ordering of the thin films are controlled by the cooling rate and by the concentration of constituent atoms. Evenmore, adsorption of excess atoms on the growing layer rules the growth thermodynamics of the subsequent layers under given conditions. Therefore, it is inherently significant to determine the structural evolution of monolayers in the presence of excess constituent atoms.

The structural properties of *h*-BP is expected to change and show dependency on the size of the growing layer in the presence of excess B/P atoms. Thus, we study the structure of *h*-BP with varying sizes upon interaction with B/P adatoms. The relaxed atomic structures display only on-top adsorption geometries, indicating

that the adsorptions on other sites are energetically favourable. Specially, it has been observed that B/P adatom on monolayer BP forms dumbbell(DB) structure by pushing down host atom lying below (B or P) as shown in Figure 3.5.

Interestingly, adatom B on-top of host B atom energetically favors symmetrical DB, whereas it favors asymmetrical DB on-top of host P atom. Since B atoms could favor trimer boron structures[62], B adatom on P can share its available valence electrons seamlessly with the nearest B atoms without disturbing bonding between B and P atoms underlying of adatom B. However, adatom P is found to form slightly symmetric DB and to have weak bonds with the nearest neighbors regardless of host atom lying below adatom P due to already saturated bonds of host atoms identical to pristine as shown in Figure 3.5. Additionally, adatom P on-top of host B atom has covalent tenuous bonding with the nearest host P atoms since bonding energy between host B-P atoms are much higher than that of between P atoms in that structure. Thereby, resulting weak trimer bonding between adatom P and host P atoms leads to localised charge on adatom P as shown in Figure 3.5. Although adatom has covalent bonding with the nearest host atoms of monolayer BP, no chemical bonding forms between adatom and host atom that is pushed down by adatom upon adsorption.

The construction of a single DB does not involve any energy barrier, thus the formation of a DB structure is expected as long as a free B/P atoms are present at the close proximity of the surface.

The associated binding energy of adatom, E_b , is calculated using the expression $E_b = E_T(BP) + E_T(X) - E_T(BP + X)$ in terms of the optimized total energies of pristine planar BP, single B/P atom ($X = B, P$) and doped BP system all calculated in the same supercell. E_b is calculated for a single DB in the $n \times n$ hexagonal supercells for $n = 1, \sqrt{3}, 2, 3, 4$, and 5. Positive values of E_b show that the adsorption of the adatom is an exothermic process and is energetically favorable as depicted in Figure 3.6a. Since the formation of DB phase is a novel property followed by adsorption of B/P adatoms regardless of the size of the cell, DB phase has high cohesive energy as shown in Figure 3.6b. Specifically, cohesive energy (E_c) is calculated for different supercell sizes as such that $E_c =$

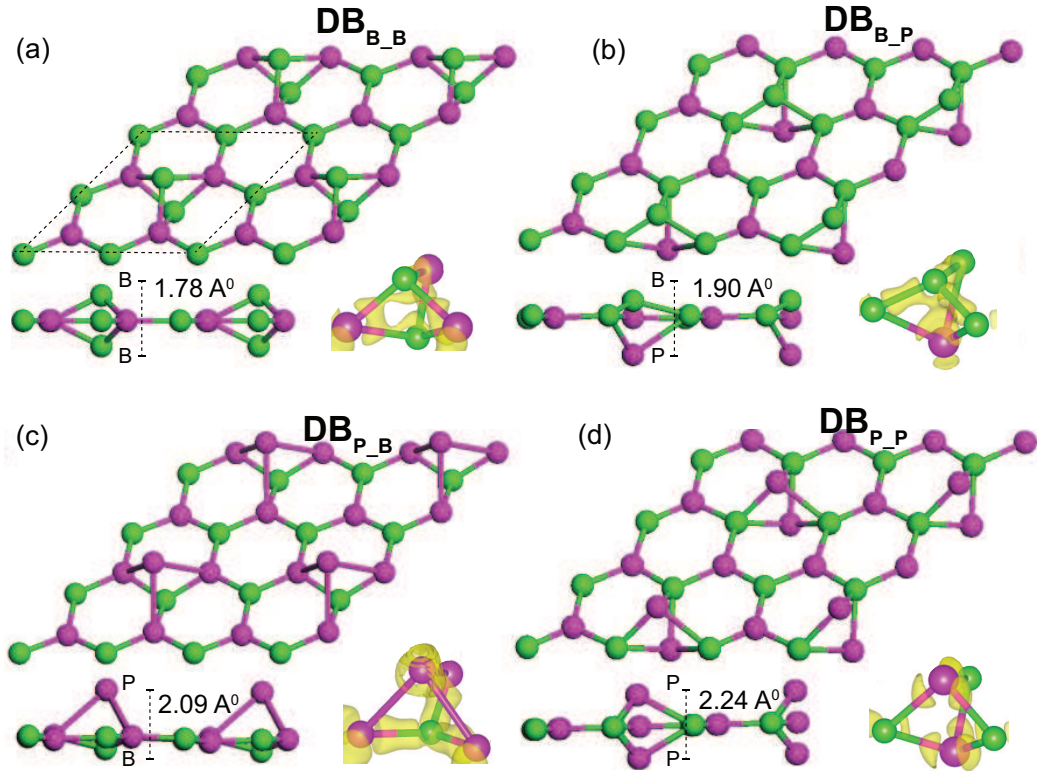


Figure 3.5: Side and top views of various types of equilibrium atomic structures, which represents DB structures of monolayer BP built up by B and P adatoms with all possible minimum energy configurations. (a) B adatom on top host B (DB_{B-B}), (b) B adatom on top host P (DB_{B-P}), (c) P adatom on top host B (DB_{P-B}), (d) P adatom on top host P (DB_{P-P}). The height of the adatom is given relative to bottom host atom. Total charge density isosurfaces with isovalue of $0.11 \text{ e}/\text{\AA}^3$ are also given in nearby side views of DBs. Green and pink spheres represent B and P atoms, respectively.

$[nE_T(B) + mE_T(P) - E_T(BP + X)]/(n + m)$ $n \times n$ to the single atom energies of B/P; n and m refers to the number of B/P atoms, respectively. It plays a crucial role to determine whether if the adsorbed atom will behave as an impurity for a given supercell size and the DB phase will grow on monolayer BP. Because each DB constructed on monolayer BP lowers the energy, high cohesive energies for all given supercell sizes is a sign of energetically favorable formation of DB phase.

The interaction energy between DBs plays a distinctive role to determine the phase of the growing monolayer BP following adsorption B/P adatoms. For instance, an attractive interaction between two DBs can induce domain structure in growing layer. However, a repulsive interaction at a small DB-DB distance is expected to favor phases with uniform coverage of DB. We have calculated interaction of DBs given as $E_{int} = E_T(pureBP) + E(B)_{vacuum} - E(P)_{vacuum} - E(dopedBP)_y$ where y refers to distance between DBs in order to clarify what happens if a B/P adatom is introduced in addition to an existing DB. Our calculations show that rather than bonding to DB atoms on the surface of BP, additional adatom forms another DB. Notably, each adatom introduced to the surface of BP favors the construction of a new DB, provided that a position is available for the next DB. Therefore, we found that forming of second DB nearby the first one is energetically favorable as depicted in Figure 3.6c. Recently, periodic coverage of silicene and germanene derivatives with DBs has been shown to be energetically favorable[37]. Furthermore, by utilizing the STM data, DB based silicene derivatives are shown to stack to form multilayers[63]. Remarkably, periodic coverage of DBs on silicene or germanene has been shown to play key role in growth of multilayer silicene and germanene on Ag and Au substrates, respectively[36, 64, 65].

Having found that DB structure on P is the most favorable position for B and P adatom on pristine h -BP, the band structure evolution with respect to varying supercell sizes has been calculated and illustrated in Figure 3.7.

It is notable that the impurity bands belonging adsorbed adatoms emerges in close proximity to Fermi level starting from 4×4 supercell. Due to having covalent bonds of adatom B with the nearest host B atoms as shown in total charge density

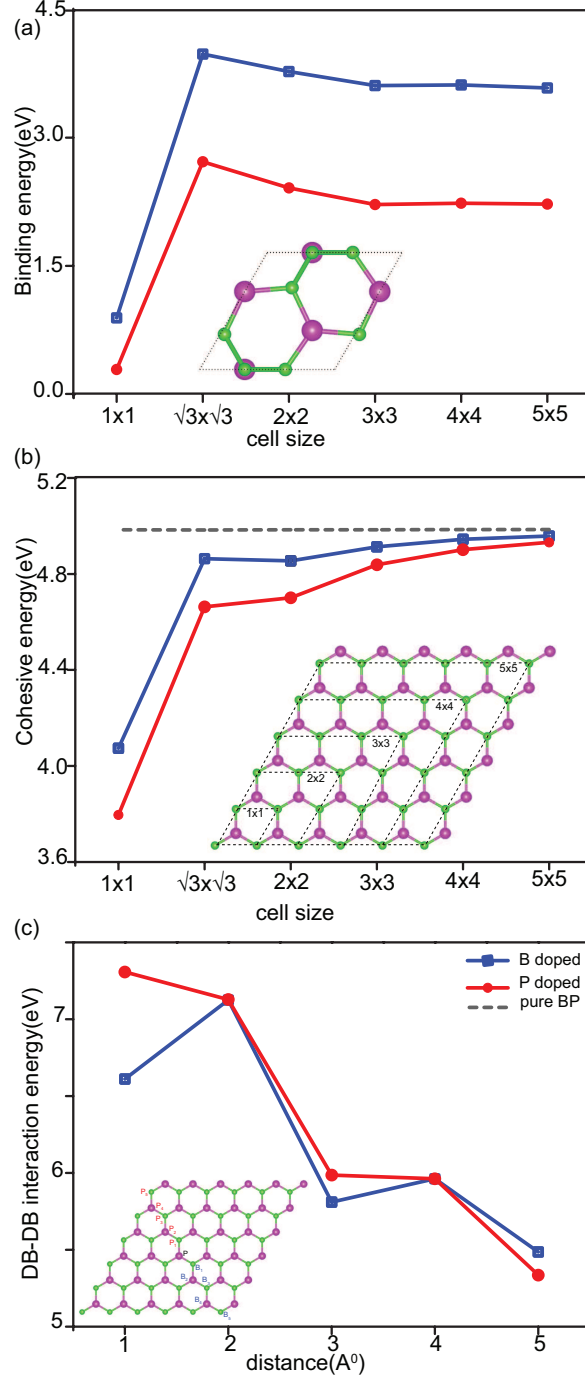


Figure 3.6: Dependence of (a) Binding energy, and (b) Cohesive energy of B/P absorbance on-top host P atom on varying supercell size. (c) DB-DB interaction energy is given with respect to distance between DBs.

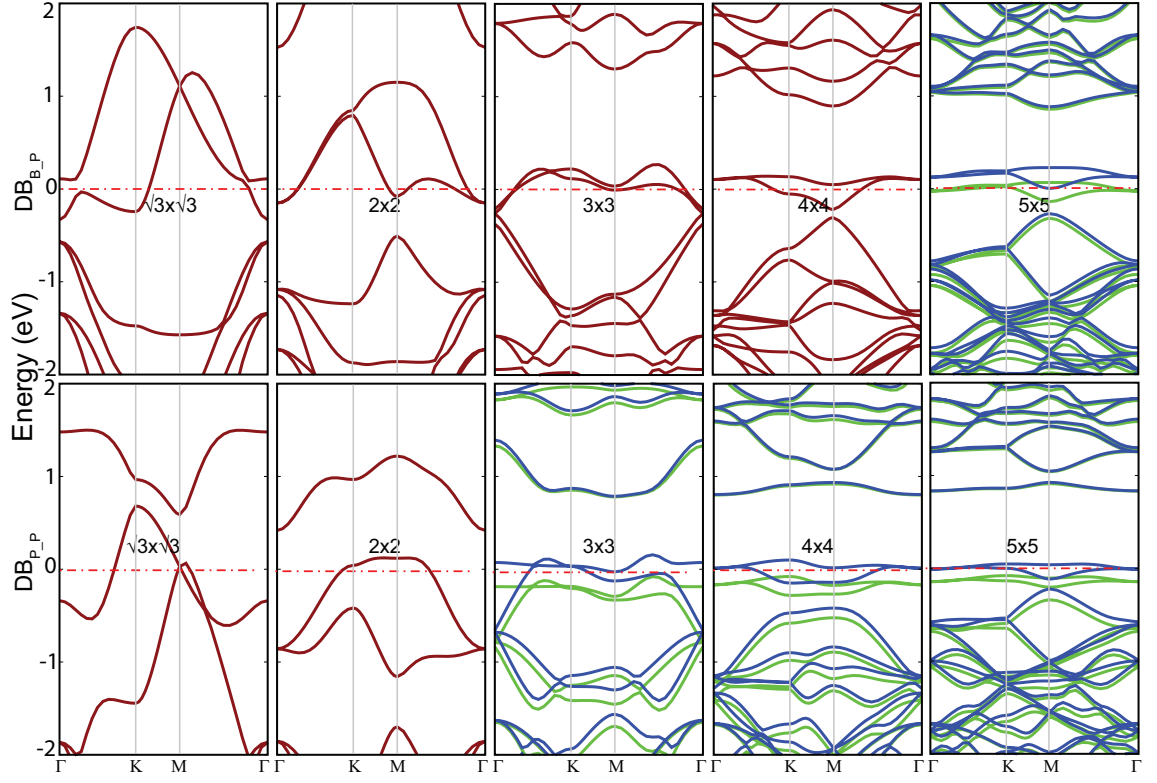


Figure 3.7: Electronic band structures for DB_{B-P} and DB_{P-P} optimized structures in various supercell sizes at top and bottom, respectively. The zero of energy was set to the Fermi level indicated by light red dash-dotted line. Non-spin polarized bands are depicted with dark red lines, whereas spin-up and spin-down bands are specified with green and blue lines, respectively.

plot in Figure 3.5, B adatom on-top host P gives rise to charge localization at host P atom. It is clear that the coverage of DBs modifies electronic properties of *h*-BP significantly as seen in these band structures. The DBs constructed by on-top P and on-top B make substrate metallic with no spin polarization both for $\sqrt{3} \times \sqrt{3}$ and 2×2 supercells. However, a significant difference is clearly seen in the band structures of on-top B and on-top P with 3×3 supercell. While on-top P adsorption leads to magnetic DBs, on-top B does not carry any magnetic moment in that supercell size. Following with the 4×4 supercell size, the impurity states starts showing up nearby Fermi level. Finally, the DB formation by either on-top P or on-top B adsorption in 5×5 supercell makes the BP substrate both magnetic and small gap semiconductor (which is confirmed by HSE calculations).

3.3 Interaction with Group III-IV-V Atoms

Since DB phases of 2D structures, in turn, can pave the way for novel thin films with diverse properties which are otherwise not accessible with pristine 2Ds, we have also studied adsorption of elements from Group-III (Al, B, Ga), IV (C, Si, Ge), and V (N, P, As) adatoms on BP. Having found that adsorption of B/P adatoms on *h*-BP leads to forming of impurity levels with 5×5 supercell, all properties accompanying to adsorption of these elements are calculated at this size. The initial positions for adsorption of adatoms Al, B, Ga, Ge, Si, C, N, P and As onto monolayer BP as depicted in Figure 3.8 are as follows: i) top of B atom ii) top of P atom iii) hollow site(H) of hexagon constructed by B and P atoms iv) bridge position(B) constituting bond between B and P atoms. Additionally, the excess charge on the adatom (δ) is calculated by subtracting the charge at the adatom gathered at the end of self-consistent calculation, ρ_A , from the valance charge of the adatom, Z_A , in the framework of Bader analysis. That is, $\delta = Z_A - \rho_A$, as such that $\delta < 0$ implies excess electron charge localized at the adatom site.

Al, B and Ga adatoms from Group-III have been found to prefer asymmetrical DB on-top of host P atom as in the case of B adatom on-top of host P atom due to

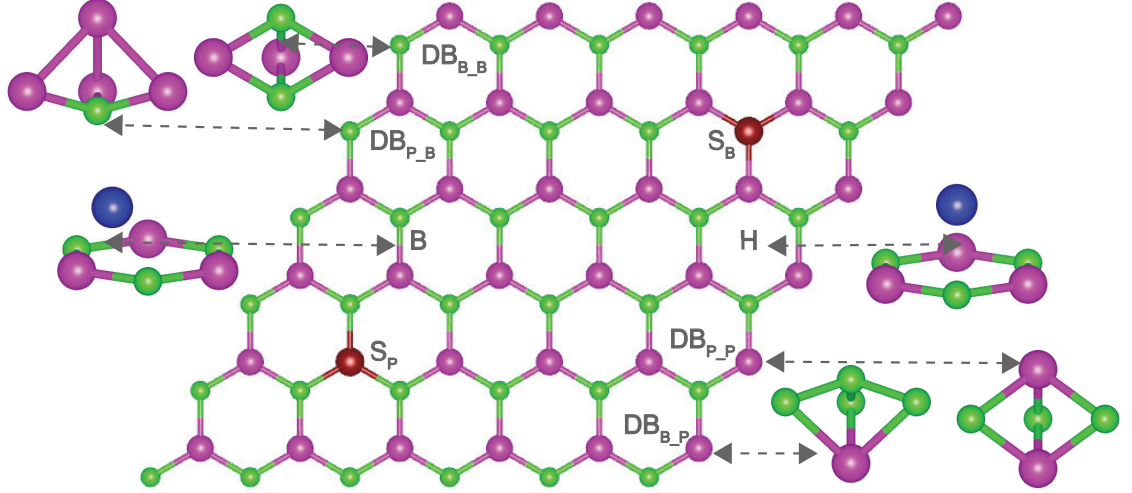


Figure 3.8: Hollow(H), bridge(B) and various DB positions representing possible adsorption geometries of adatoms on monolayer BP.

electronegativity difference in the nearest neighbor atoms. Specifically, Ga atom is known to be a fast diffuser over Boron terminated BP(100) surface[66]. For this reason, DB on P for adatom Ga is much more favorable when Ga becomes the neighbor of host B atoms. Interestingly, Ga and Al atoms may also prefer H site rather than stay on-top host P, since the total energy differences between DB phase and H site phase are only 0.22 eV and 0.13 eV, for Ga and Al atoms, respectively. Adsorption of Ga or Al adatoms on-top P do not change the nearest neighbor distance between host B and P atoms significantly (1.87 Å and 1.83 Å for adsorbed BP and pristine BP, respectively), revealing easy covalent sharing of available $3p^1$ valence electrons of adatoms with host atoms. Moreover, Al/Ga adsorption does not make substrate magnetic due to not existence of available unpaired electrons. Being in the same group as B, Al and Ga has similar electronic properties and has localized states in the band gap just above the valence band originating mostly from their p orbitals (Figure 3.12). Since Al and Ga has less electronegativity compared to substrate, electronic charge transfer occurs from adatoms to substrate giving rise to positively charged DBs of adatoms, as shown in Table 3.1.

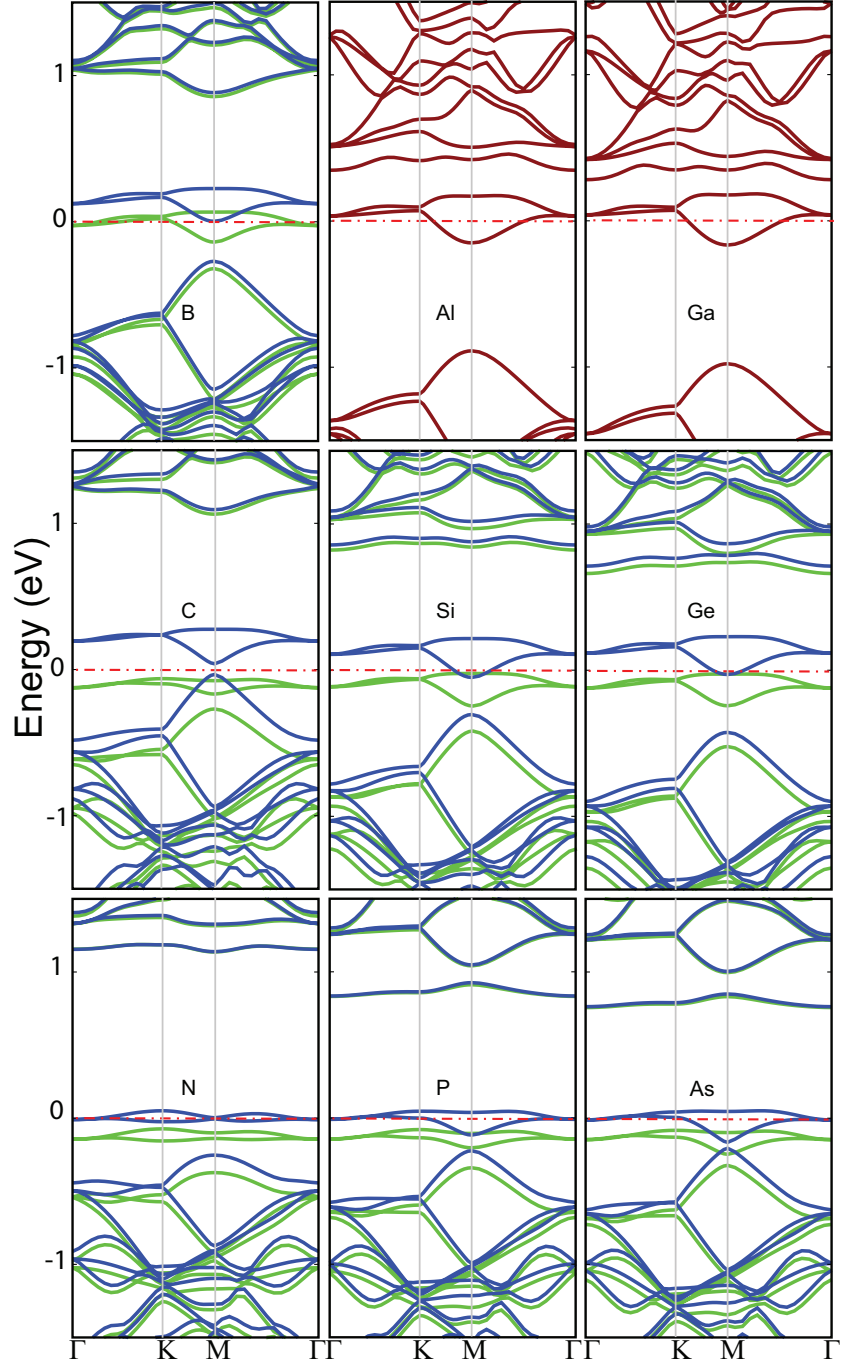


Figure 3.9: Electronic band structures of all adatoms in DB phase. Description of lines are the same as given in Figure 3.7.

Table 3.1: General trends of adsorption of specific adatoms (B, Al, Ga, C, Si, Ge, N, P, and As) on monolayer honeycomb structure of BP in 5×5 supercell. d_{B-X} Å indicates distance of adatom to the nearest host B atom, while d_{DB-X} Å implies height of DB from adatom to bottom host atom. $\mu(\mu_\beta)$ denotes magnetic moment per supercell. E_b gives binding energies of adatoms. δ indicates excess charge on the adatom.

Adatom	d_{B-X} Å	d_{DB-X} Å	$\mu(\mu_\beta)$	E_b (eV)	Δ^{un-sp} (meV)	δ
B	1,74	1,91	0,97	3,59	9	0,11
Al	2,61	2,55	0,00	2,14	0	0,75
Ga	2,85	2,64	0,00	1,99	0	0,43
C	1,61	1,89	2,02	5,18	86	-1,97
Si	2,14	2,29	1,82	2,57	31	0,87
Ge	2,33	2,41	1,85	1,87	56	0,45
N	1,60	1,89	1,09	3,25	15	-1,99
P	2,04	2,23	1,10	2,23	16	-0,12
As	2,21	2,35	1,10	1,44	15	-1,16

As for adsorbing of Group IVA elements on *h*-BP, C adsorption on-top of host P atom is found to be different from Si and Ge adsorption from electronic structure point of view. In particular, the energy difference between $2s^2$ and $2p^2$ states of C atom is much higher than that of Si atom, leading to rather special electronic character for C atom. Namely, contribution ratio of C states becomes rather different compared to Si/Ge atom when these atoms form a bond with the same atom. The symmetric DB structure forms when Si/Ge forms weak three-fold coordinated bonds with the nearest host B atoms on-top of host P atom as if they had sp^3 hybridized orbitals.

On the other hand, C adatom involves in forming bonds with three boron neighbors by moving P atom out of substrate and readily settles into substrate without any deformation in hexagonal structure. This predicts that carbon atom would prefer substituting of P rather than adsorbing onto monolayer BP which is revealed by the highest binding energy of C atom among all other adatoms as given in Table 3.1. Owing to difference in electronegativity of C atom and substrate, C atom mostly undergoes charge transfer with the substrate and has -1.97 excess negative charge. Despite the dissimilarity of the equilibrium structures of C and

Si/Ge adatoms on monolayer BP, all these adatoms make substrate spin polarized. However, this induced spin polarization can only survive at low temperature due to low exchange splitting energy in these structures.

Adsorbing of Group VA elements on BP substrate have also been scrutinized. The DB phase is found to be energetically favorable for P, N and As atoms on-top P revealed by the positive binding energies of these adatoms on-top host P atom. Yet, the binding at B site is a local minimum for N atom adsorption which is supported by higher binding energy of as much as 0.06 eV for that position.

While the adatoms C, N, and As have negative excess charge upon adsorption, Si, Al, B, and Ga adsorption on-top host P have positive excess charge. Consequently, adsorption of monolayer BP results in charged surface, so that it can improve the tribological and catalytic properties of monolayer BP.

Interestingly, a recent theoretical study has shown that adatoms of Si, Ge and Sn can form stable DB structures on silicene and germanene giving rise to promising electronic, magnetic and optical properties. It also reveals the mobility of DB structures of Si, Ge and Sn on silicene and germanene[37].

Except C adsorption on-top host P atom, the rest of the adatoms under study seems to make substrate metallic as shown in Figure 3.12. But adsorption brings out impurity bands localized nearby Fermi level for 5×5 supercell size, suggesting impurity character for these adatoms in DB phase. This naive expectation is confirmed by identifying orbital contribution of adatoms for a given state (PDOS). As such that impurity bands has contributions from p state orbitals of adatoms and p state orbitals of host atom that is pushed down upon adsorption as revealed by projected density of states given in Figure 3.11b. However, s orbitals of adatoms mostly lie in valance band. Moreover, impurity bands leads to charge localization nearby adatom, as shown in Figure 3.10b. Having clarified that the levels crossing Fermi level belongs to impurity atoms, ruling out the metallic electronic state of these structures, we have also calculated the band structures of B, P and Si adsorbed onto monolayer BP in 5×5 supercell by using hybrid

functionals. These calculations confirmed ferromagnetic and semiconductor characteristics of these systems as shown in Figure 3.11. These impurity bands are shown to exist in Group IV adsorbed silicene, graphene, germanene and silicene, too with similar characteristics as a by-product of DB structure[37].

To be able to find applications in nanoelectronics of novel 2Ds, obtaining suitable impurity levels is a must. Upon the adsorption of adatoms from Group III-IV-VA on *h*-BP, semiconducting state of bare monolayer BP is conserved which can be crucial for electronic device applications.

3.4 Substitution of Group III-IV-V Atoms

We finally examined the role of specific atoms for substitution B with (Al, Ga, C, Si, and Ge) and P with (N, As, C, Si, and Ge) atoms, respectively. Naive expectation for proper substitutionally doping of monolayer BP is that the potential dopants should be stabilized in threefold coordination and have the right atomic size, namely, they should induce minimal protrusions with respect to the surrounding BP. The verification of this naive expectation strongly depends on the nature of the interaction between the dopant atoms and the *h*-BP. In order to evaluate suitability of dopant for substitution, substitution energy has been calculated using the formula $E_{subs} = E_{5 \times 5 pure BP} + E_X - E_{subs.system} - E_{B/P}$, referring to adding one doping atom to the site of P/B atom that is removed from the monolayer BP. Positive substitution energy is a signature for seamlessly accommodation of substituted atom in monolayer BP lattice.

Based on substitution energies in Table 3.2, although both C and N have positive substitution energies, we suggest that only N atom can selectively dope monolayer BP owing to having positive substitution energy as much as 2.27 eV. Remarkably, N substitution results in a network that resemble the hexagonal lattice of BN. Hence, introduction of N atom to the monolayer BP neither destroys the atomic structure nor the electronic structure. Thereby, selective growth of in-plane heterostructures made of monolayer BP and *h*-BN can be envisaged. In

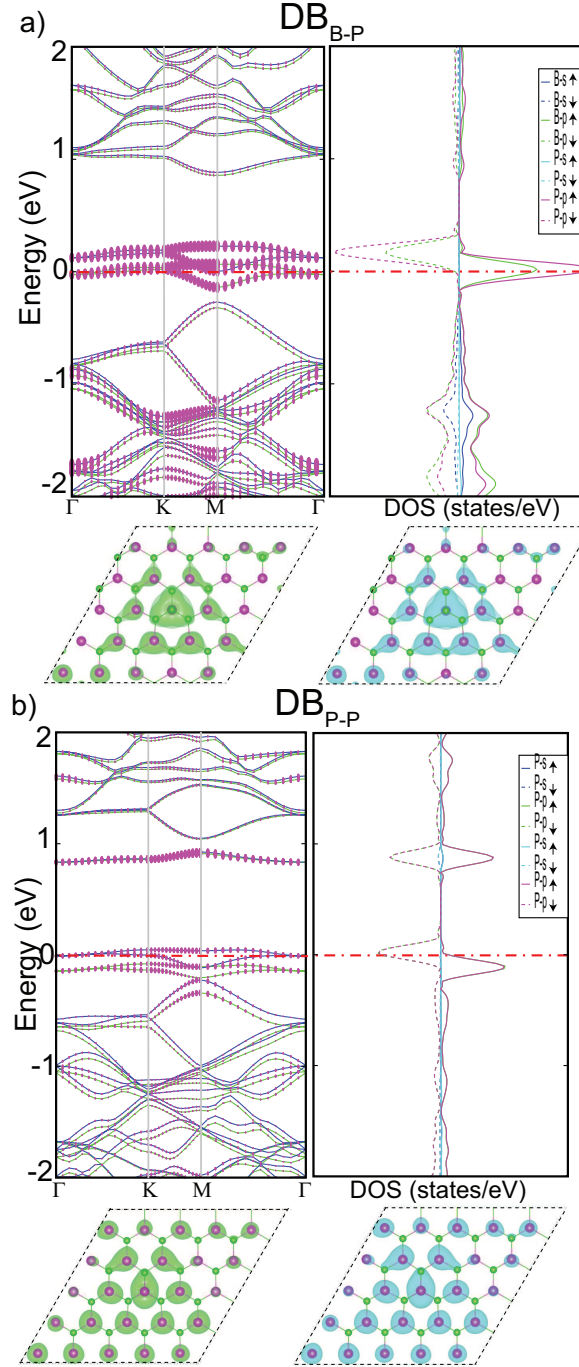


Figure 3.10: Orbital decomposed energy band structure, and Partial density of states (PDOS) that belongs to s and p orbitals of adatom and host P atom, Charge density isosurfaces of p orbitals of adatoms. Green localized charge density plot refers to the states of spin-up, whereas blues one represents states of spin-down of a) DB_{B-P} , and b) DB_{P-P} structures, respectively.

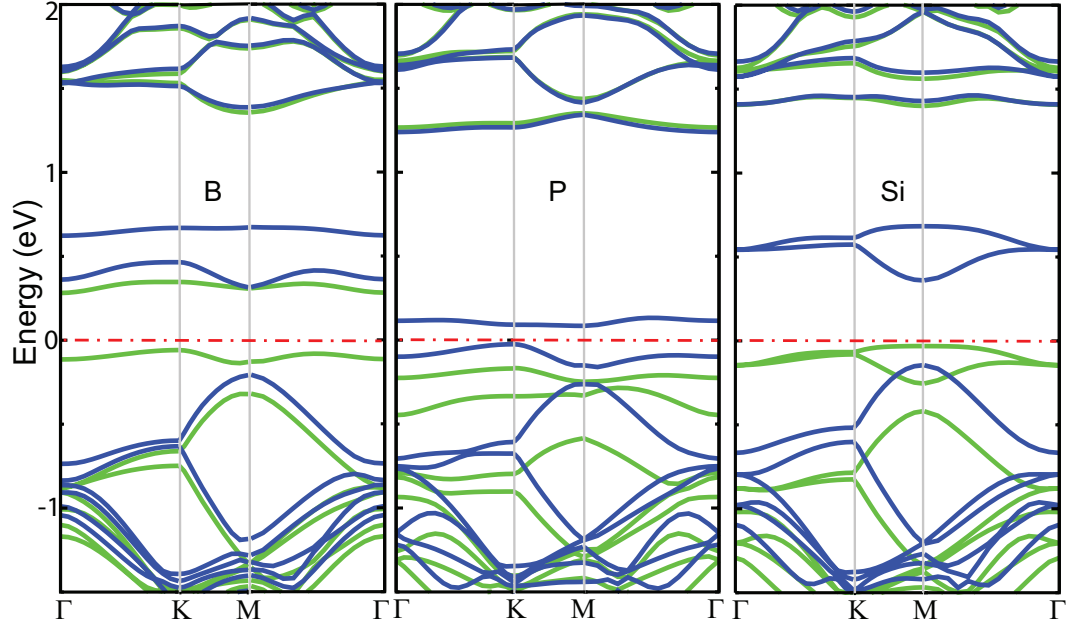


Figure 3.11: Electronic band structures, calculated by using HSE, for monolayer BP with adsorption of adatoms B, P, and Si.

fact, due to the limited lattice substitution of graphene by B or N atoms concomitant to etching/growth process, both in-plane (*h*-BN-G) and stacked (G/*h*-BN) heterostructures are synthesized more recently[67]. Since substitution energy required for substitution of P by C is also positive, C substitution is an exothermic reaction. However, the substitution energy for P is only 2.66 eV larger than substitution of B by C. This suggests that C atom can deteriorate the hexagonal structure of monolayer BP by moving out both B and P, as long as there

Table 3.2: Substitution energies of Al, Ga, C, Si, and Ge adatoms for host B atom and N, As, C, Si, and Ge adatoms for host P atom in 5×5 supercell.

-	-	Al	Ga	C	Si	Ge	N	As
substitution _B	energy (eV)	-3.78	-4.69	0.43	-4.01	-5.46	-	-
substitution _B	bader	2,01	0,72	-1,66	1,80	0,47	-	-
substitution _P	energy (eV)	-	-	3.09	-0.72	-1.94	2.27	-1.40
substitution _P	bader	-	-	-1,98	1,64	0,48	-2,01	-0.17

are available C atoms during reaction. Additionally, substitution of C atom for P makes substrate metallic, with a half-filled state near fermi level resulting in electronically reactive site due to rehybridization of nearby orbitals as shown in Figure 3.12. This metallic state has contributions from electronic states of substrate, revealing highly mixing of dopant and host atoms. However, substitution of N for P leaves monolayer BP direct gap semiconductor owing to belonging to the same group as P. None of these substitutions makes substrate magnetic.

Given that most compounds of Si, Ge, Al, Ga, and As all tend to have tetrahedral bonds, these atoms do not satisfy bonding coordination for substitutionally doping. Therefore, all substitution energies are negative for these dopants.

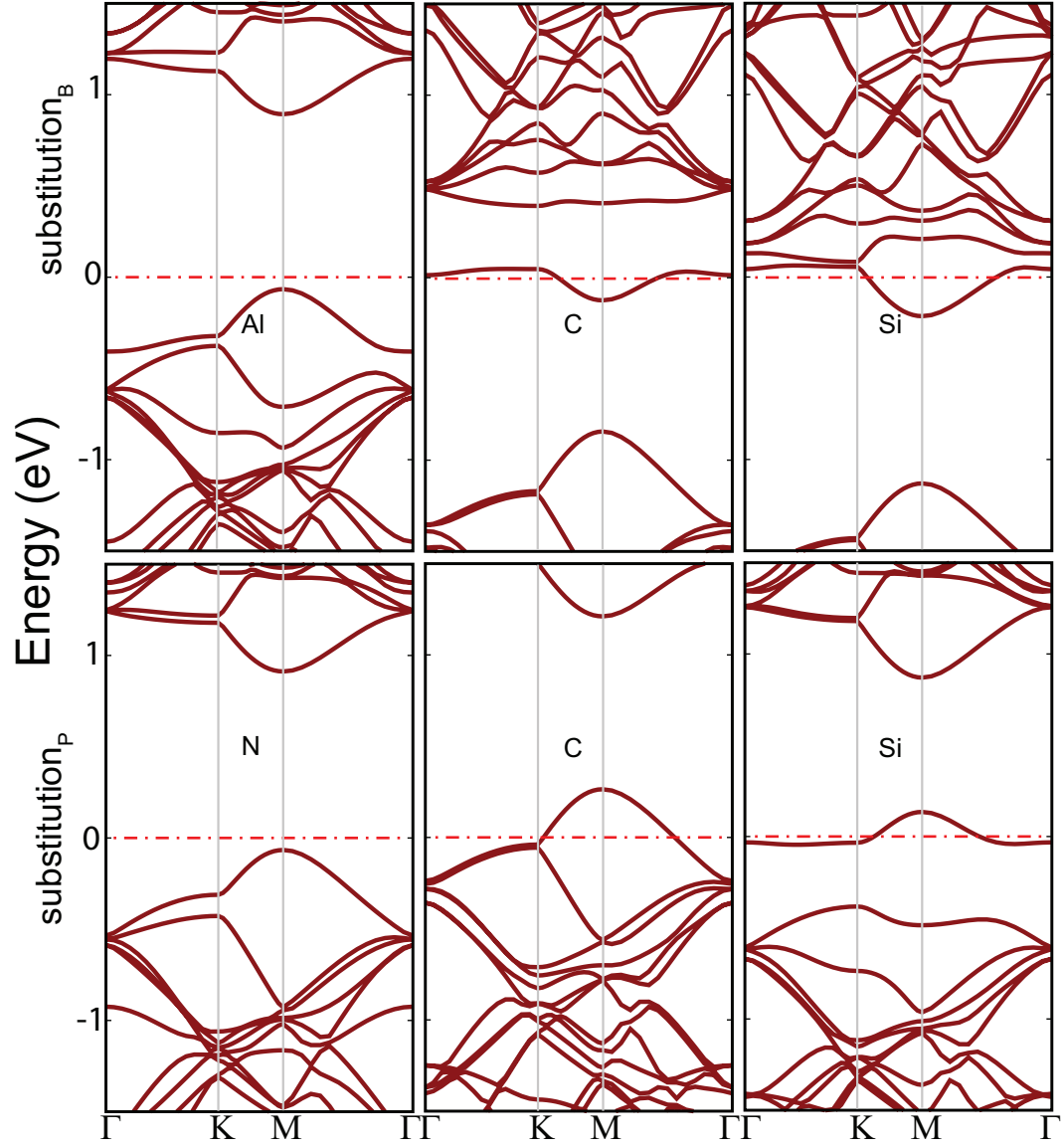


Figure 3.12: Electronic band structures of substitutionally doped *h*-BP. Top: Substitution of B with Al, C, Si atoms, respectively. Bottom: Substitution of P with N, C, Si atoms, respectively. All bands are non spin polarized and fermi level is denoted as dotted red line.

Chapter 4

Conclusion

In brief, our first principles calculations reveals that phosphorization of *h*-BN results in achieving alloys with controllable electronic band gaps ranging from ≈ 6 eV down to 1 eV. Notably, it is possible to make bandgap engineering by utilizing phosphorization in various concentrations. In turn, the phosphorization can lead to synthesising of monolayer BP.

Then, we investigate the atomic structure, energetics, and the electronic structure of monolayer BP doped or substituted by selected atoms from Group III-IV-V row. We find that adsorption of Group III-IV-V elements are much favorable on-top P position giving rise to DB phase in small supercell sizes exothermically. Although adsorption site does not show any dependency on the supercell size of monolayer BP, the electronic characteristics of the whole structure exhibits size dependency, enforcing the adatoms to be doping atoms in small supercell sizes. However, when the supercell size reaches 4×4 , the dopant atoms electronically behaves as if they were impurity atoms. The impurity contribution of electronic states explicitly becomes clear nearby Fermi level. The HSE corrected band structure of these adsorbed systems reveals that these impurity states make the system smallgap semiconductor which is also confirmed by projected density of states analyses. Also, except for Al and Ga, these impurity adatoms carry small amount of magnetic moment in 5×5 supercell as a low temperature property due

to low exchange splitting energy. Since high mobility and small electronic band gap (around 0.4 eV) are prerequisites what recent nanoelectronics look for, these structures can be candidate as a building block for nanoelectronic devices such as FETs. Remarkably, DB-DB interaction in all doped systems with 5×5 supercell size is attractive in small distances of neighbour DBs, suggesting the possibility of full coverage of monolayer BP surface with DBs in a periodic fashion. Moreover, DB formation upon adsorption provides energy gain to the system. In turn, it gives rise to increasing of structural stability as revealed by positive cohesive energies.

In addition, we consider the substitution reaction for these adatoms on BP monolayer surface. Interestingly, C and N atoms goes under substitution reaction with P atom without inducing any deformation on hexagonal structure of monolayer BP.

Covering the monolayer BP with adatoms would make novel heterostructures feasible built up by these single layers either via by substitution or adsorption.

Bibliography

- [1] K. S. Novoselov, A. K. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, , I. Grigorieva, and A. Firsov, “Electric field effect in atomically thin carbon films,” *science*, vol. 306, no. 5696, pp. 666–669, 2004.
- [2] D. Pacile, J. Meyer, C. O. Girit, and A. Zettl, “The two-dimensional phase of boron nitride: Few-atomic-layer sheets and suspended membranes,” *Applied Physics Letters*, vol. 92, no. 13, p. 133107, 2008.
- [3] Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang, and L. Cao, “Controlled scalable synthesis of uniform, high-quality monolayer and few-layer MoS₂ films,” *Scientific reports*, vol. 3, 2013.
- [4] M. Tan, Z. Wang, J. Peng, and X. Jin, “Facile synthesis of large and thin tis2 sheets via a gas/molten salt interface reaction,” *Journal of the American Ceramic Society*, vol. 98, no. 5, pp. 1423–1428, 2015.
- [5] A. L. Elías, N. Perea-López, A. Castro-Beltrán, A. Berkdemir, R. Lv, S. Feng, A. D. Long, T. Hayashi, Y. A. Kim, M. Endo, *et al.*, “Controlled synthesis and transfer of large-area WS₂ sheets: From single layer to few layers,” *ACS nano*, vol. 7, no. 6, pp. 5235–5242, 2013.
- [6] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang, “Black phosphorus field-effect transistors,” *Nature nanotechnology*, vol. 9, no. 5, pp. 372–377, 2014.
- [7] N. W. Johnson, P. Vogt, A. Resta, P. De Padova, I. Perez, D. Muir, E. Z. Kurmaev, G. Le Lay, and A. Moewes, “The metallic nature of epitaxial

- silicene monolayers on ag (111),” *Advanced Functional Materials*, vol. 24, no. 33, pp. 5253–5259, 2014.
- [8] M. E. Dvila, L. Xian, S. Cahangirov, A. Rubio, and G. L. Lay, “Germanene: a novel two-dimensional germanium allotrope akin to graphene and silicene,” *New Journal of Physics*, vol. 16, no. 9, p. 095002, 2014.
- [9] F.-f. Zhu, W.-j. Chen, Y. Xu, C.-l. Gao, D.-d. Guan, C.-h. Liu, D. Qian, S.-C. Zhang, and J.-f. Jia, “Epitaxial growth of two-dimensional stanene,” *Nature materials*, 2015.
- [10] Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, “Experimental observation of the quantum hall effect and berry’s phase in graphene,” *Nature*, vol. 438, no. 7065, pp. 201–204, 2005.
- [11] M. Jeong, B. Doris, J. Kedzierski, K. Rim, and M. Yang, “Silicon device scaling to the sub-10-nm regime,” *Science*, vol. 306, no. 5704, pp. 2057–2060, 2004.
- [12] A. Geim and I. Grigorieva, “Van der waals heterostructures,” *Nature*, vol. 499, no. 7459, pp. 419–425, 2013.
- [13] H. Pang, S. Wang, W. Shao, S. Zhao, B. Yan, X. Li, S. Li, J. Chen, and W. Du, “Few-layered cohpo 4· 3h 2 o ultrathin nanosheets for high performance of electrode materials for supercapacitors,” *Nanoscale*, vol. 5, no. 13, pp. 5752–5757, 2013.
- [14] X. Huang, Z. Zeng, and H. Zhang, “Metal dichalcogenide nanosheets: preparation, properties and applications,” *Chemical Society Reviews*, vol. 42, no. 5, pp. 1934–1946, 2013.
- [15] C. Sevik, A. Kinaci, J. B. Haskins, and T. Çağın, “Characterization of thermal transport in low-dimensional boron nitride nanostructures,” *Physical Review B*, vol. 84, no. 8, p. 085409, 2011.
- [16] C. Li, Y. Bando, C. Zhi, Y. Huang, and D. Golberg, “Thickness-dependent bending modulus of hexagonal boron nitride nanosheets,” *Nanotechnology*, vol. 20, no. 38, p. 385707, 2009.

- [17] K. Watanabe, T. Taniguchi, and H. Kanda, “Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal,” *Nature materials*, vol. 3, no. 6, pp. 404–409, 2004.
- [18] K. K. Kim, A. Hsu, X. Jia, S. M. Kim, Y. Shi, M. Hofmann, D. Nezich, J. F. Rodriguez-Nieva, M. Dresselhaus, T. Palacios, *et al.*, “Synthesis of monolayer hexagonal boron nitride on cu foil using chemical vapor deposition,” *Nano letters*, vol. 12, no. 1, pp. 161–166, 2011.
- [19] Y. Shi, C. Hamsen, X. Jia, K. K. Kim, A. Reina, M. Hofmann, A. L. Hsu, K. Zhang, H. Li, Z.-Y. Juang, *et al.*, “Synthesis of few-layer hexagonal boron nitride thin film by chemical vapor deposition,” *Nano letters*, vol. 10, no. 10, pp. 4134–4139, 2010.
- [20] Y. Lin and J. W. Connell, “Advances in 2d boron nitride nanostructures: nanosheets, nanoribbons, nanomeshes, and hybrids with graphene,” *Nanoscale*, vol. 4, no. 22, pp. 6908–6939, 2012.
- [21] L. Ponomarenko, A. Geim, A. Zhukov, R. Jalil, S. Morozov, K. Novoselov, I. Grigorieva, E. Hill, V. Cheianov, V. FalKo, *et al.*, “Tunable metal-insulator transition in double-layer graphene heterostructures,” *Nature Physics*, vol. 7, no. 12, pp. 958–961, 2011.
- [22] I. Meric, C. R. Dean, A. F. Young, J. Hone, P. Kim, and K. L. Shepard, “Graphene field-effect transistors based on boron nitride gate dielectrics,” *arXiv preprint arXiv:1101.4712*, 2011.
- [23] J. Orenstein and A. Millis, “Advances in the physics of high-temperature superconductivity,” *Science*, vol. 288, no. 5465, pp. 468–474, 2000.
- [24] G.-H. Lee, Y.-J. Yu, C. Lee, C. Dean, K. L. Shepard, P. Kim, and J. Hone, “Electron tunneling through atomically flat and ultrathin hexagonal boron nitride,” *Applied Physics Letters*, vol. 99, no. 24, p. 243114, 2011.
- [25] L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, M. I. Katsnelson, L. Eaves, S. V. Morozov, A. S. Mayorov, N. M. Peres, *et al.*, “Electron tunneling through ultrathin boron nitride crystalline barriers,” *Nano letters*, vol. 12, no. 3, pp. 1707–1710, 2012.

- [26] P. Tsipas, S. Kassavetis, D. Tsoutsou, E. Xenogiannopoulou, E. Golias, S. Giamini, C. Grazianetti, D. Chiappe, A. Molle, M. Fanciulli, *et al.*, “Evidence for graphite-like hexagonal aln nanosheets epitaxially grown on single crystal ag (111),” *Applied Physics Letters*, vol. 103, no. 25, p. 251605, 2013.
- [27] P. Popper and T. Ingles, “Boron phosphide, a III–V compound of zinc-blende structure,” 1957.
- [28] P. Kocinski and M. Zbroszczyk, “Calculated structural and electronic properties of boron phosphide under pressure,” *Semiconductor science and technology*, vol. 10, no. 11, p. 1452, 1995.
- [29] J. Ejembi, I. Nwigboji, L. Franklin, Y. Malozovsky, G. Zhao, and D. Bagayoko, “Ab-initio calculations of electronic, transport, and structural properties of boron phosphide,” *Journal of Applied Physics*, vol. 116, no. 10, p. 103711, 2014.
- [30] E. Schroten, A. Goossens, and J. Schoonman, “Large-surface-area boron phosphide liquid junction solar cells,” *Journal of The Electrochemical Society*, vol. 146, no. 6, pp. 2045–2048, 1999.
- [31] S. Z. Sayyad-Alangi, M. T. Baei, and S. Hashemian, “Adsorption and electronic structure study of thiazole on the (6, 0) zigzag single-walled boron phosphide nanotube,” *Journal of Sulfur Chemistry*, vol. 34, no. 4, pp. 407–420, 2013.
- [32] S. Z. Sayyad-Alangi, S. Hashemian, and M. T. Baei, “Covalent functionalization of pristine and ga-doped boron phosphide nanotubes with imidazole,” *Phosphorus, Sulfur, and Silicon and the Related Elements*, vol. 189, no. 4, pp. 453–464, 2014.
- [33] H. Sahin, S. Cahangirov, M. Topsakal, E. Bekaroglu, E. Akturk, R. T. Senger, and S. Ciraci, “Monolayer honeycomb structures of group-iv elements and iii-v binary compounds: First-principles calculations,” *Physical Review B*, vol. 80, no. 15, p. 155453, 2009.

- [34] D. Çakır, D. Kecik, H. Sahin, E. Durgun, and F. M. Peeters, “Realization of ap–n junction in a single layer boron-phosphide,” *Physical Chemistry Chemical Physics*, vol. 17, no. 19, pp. 13013–13020, 2015.
- [35] J. Dong, H. Li, and L. Li, “Multi-functional nano-electronics constructed using boron phosphide and silicon carbide nanoribbons,” *NPG Asia Materials*, vol. 5, no. 7, p. e56, 2013.
- [36] V. O. Ozcelik, E. Durgun, and S. Ciraci, “New phases of germanene,” *The Journal of Physical Chemistry Letters*, vol. 5, no. 15, pp. 2694–2699, 2014.
- [37] V. O. Ozcelik, D. Kecik, E. Durgun, and S. Ciraci, “Adsorption of group iv elements on graphene, silicene, germanene, and stanene: Dumbbell formation,” *The Journal of Physical Chemistry C*, vol. 119, no. 1, pp. 845–853, 2014.
- [38] R. Dronskowski, “Computational chemistry of solid state materials.”
- [39] J. C. Slater, “Note on hartree’s method,” *Phys. Rev.*, vol. 35, pp. 210–211, Jan 1930.
- [40] E. Baerends, D. Ellis, and P. Ros, “Self-consistent molecular hartreefock-slater calculations i. the computational procedure,” *Chemical Physics*, vol. 2, no. 1, pp. 41–51, 1973.
- [41] F. Jensen, *Introduction to computational chemistry*. John Wiley & Sons, 2013.
- [42] L. H. Thomas, “The calculation of atomic fields,” in *Mathematical Proceedings of the Cambridge Philosophical Society*, vol. 23, pp. 542–548, Cambridge Univ Press, 1927.
- [43] A. Michaelides and M. Scheffler, “An introduction to the theory of crystalline elemental solids and their surfaces,” *Surface and Interface Science, ISBN*, pp. 978–3, 2012.
- [44] P. Hohenberg and W. Kohn, “Inhomogeneous Electron Gas,” *Phys. Rev.*, vol. 136, pp. B864–B871, nov 1964.

- [45] J. A. Pople, P. M. Gill, and B. G. Johnson, “Kohnsham density-functional theory within a finite basis set,” *Chemical physics letters*, vol. 199, no. 6, pp. 557–560, 1992.
- [46] J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” *Phys. Rev. Lett.*, vol. 77, pp. 3865–3868, Oct 1996.
- [47] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, “Influence of the exchange screening parameter on the performance of screened hybrid functionals,” *The Journal of chemical physics*, vol. 125, no. 22, pp. 224106–224106, 2006.
- [48] N. A. Gershenfeld, *The physics of information technology*, vol. 25. Cambridge University Press Cambridge, 2000.
- [49] N. Ashcroft and N. Mermin, *Solid State Physics*. Philadelphia: Saunders College, 1976.
- [50] H. J. Monkhorst and J. D. Pack, “Special points for brillouin-zone integrations,” *Phys. Rev. B*, vol. 13, pp. 5188–5192, Jun 1976.
- [51] M. C. Payne, M. P. Teter, D. C. Allan, T. Arias, and J. Joannopoulos, “Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients,” *Reviews of Modern Physics*, vol. 64, no. 4, p. 1045, 1992.
- [52] D. Vanderbilt, “Soft self-consistent pseudopotentials in a generalized eigenvalue formalism,” *Physical Review B*, vol. 41, no. 11, p. 7892, 1990.
- [53] P. E. Blöchl, “Projector augmented-wave method,” *Physical Review B*, vol. 50, no. 24, p. 17953, 1994.
- [54] M. M. Georg Kresse and J. Furthmüller, “Vasp introduction,” 2015.
- [55] W. Kohn and L. J. Sham, “Self-Consistent Equations Including Exchange and Correlation Effects,” *Phys. Rev.*, vol. 140, pp. A1133–A1138, nov 1965.

- [56] L. Vegard, “Die konstitution der mischkristalle und die raumfüllung der atome,” *Zeitschrift für Physik A Hadrons and Nuclei*, vol. 5, no. 1, pp. 17–26, 1921.
- [57] A. R. Denton and N. W. Ashcroft, “Vegard’s law,” *Phys. Rev. A*, vol. 43, pp. 3161–3164, Mar 1991.
- [58] S. Grimme, “Semiempirical GGA-type density functional constructed with a long-range dispersion correction.,” *J. Comput. Chem.*, vol. 27, no. 15, pp. 1787–1799, 2006.
- [59] P. E. Blöchl, “Projector augmented-wave method,” *Phys. Rev. B*, vol. 50, pp. 17953–17979, Dec 1994.
- [60] J. Heyd, G. E. Scuseria, and M. Ernzerhof, “Hybrid functionals based on a screened coulomb potential,” *The Journal of Chemical Physics*, vol. 118, no. 18, pp. 8207–8215, 2003.
- [61] Y. Kumashiro, K. Sato, S. Chiba, S. Yamada, D. Tanaka, K. Hyodo, T. Yokoyama, and K. Hirata, “Preparation of boron and boron phosphide films by photo- and thermal chemical vapor deposition processes,” *Journal of Solid State Chemistry*, vol. 154, no. 1, pp. 39 – 44, 2000.
- [62] F. Moscardó, “Molecular properties of the boron trimer obtained by combined hartree-fock and density-functional calculations,” *Phys. Rev. A*, vol. 45, pp. 4731–4733, Apr 1992.
- [63] S. Cahangirov, V. O. Özçelik, L. Xian, J. Avila, S. Cho, M. C. Asensio, S. Ciraci, and A. Rubio, “Atomic structure of the $\sqrt{3} \times \sqrt{3}$ phase of silicene on Ag(111),” *Phys. Rev. B*, vol. 90, p. 035448, Jul 2014.
- [64] S. Cahangirov, V. O. Özçelik, A. Rubio, and S. Ciraci, “Silicite: The layered allotrope of silicon,” *Phys. Rev. B*, vol. 90, p. 085426, Aug 2014.
- [65] V. O. Ozcelik and S. Ciraci, “Local reconstructions of silicene induced by adatoms,” *The Journal of Physical Chemistry C*, vol. 117, no. 49, pp. 26305–26315, 2013.

- [66] V. Ferreira and H. L. Alves, “Boron phosphide as the buffer-layer for the epitaxial iii-nitride growth: a theoretical study,” *Journal of Crystal Growth*, vol. 310, no. 17, pp. 3973–3978, 2008.
- [67] T. Gao, X. Song, H. Du, Y. Nie, Y. Chen, Q. Ji, J. Sun, Y. Yang, Y. Zhang, and Z. Liu, “Temperature-triggered chemical switching growth of in-plane and vertically stacked graphene-boron nitride heterostructures,” *Nature communications*, vol. 6, 2015.