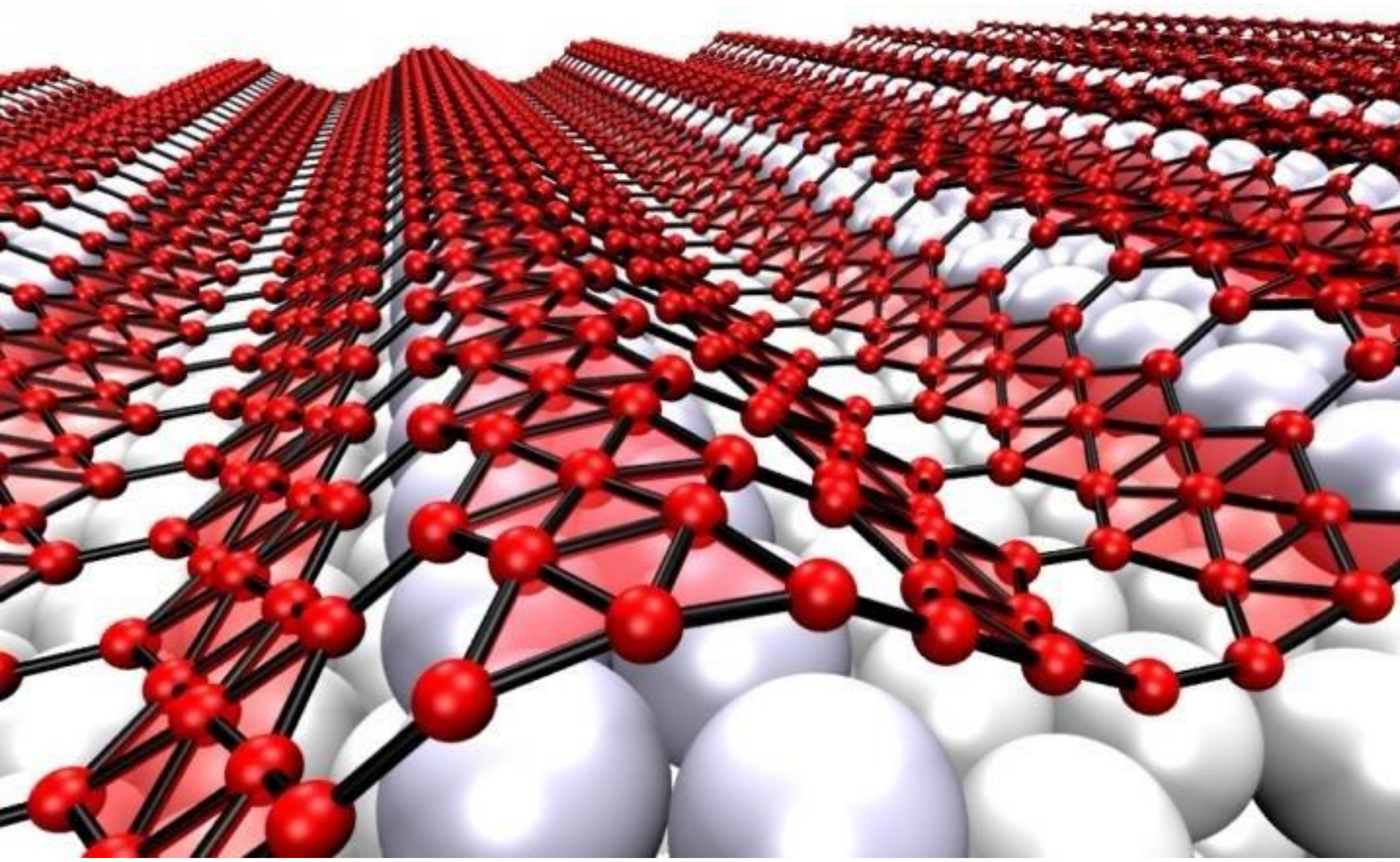
Prateek Jain

Computational Exploration of Chemical Stability under Oxidation for 2D Boron-based Compounds:

A DFT based study



Borophene on silver (Ag (111)) substrate moulded by the corrugations. [1]

Computational Exploration of Chemical Stability under Oxidation for 2D Boron-based compounds:

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By

Prateek Jain

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Student number:	5136075	
Thesis committee:	Dr. Poulumi Dey, Supervisor	TU Delft
	Dr. Othon Moultos, Supervisor	TU Delft
	Mr. Parsa Habibi, Daily Supervisor	TU Delft
	Prof.dr.ir. Thijs J.H. Vlugt,	TU Delft

Imagination is more important than knowledge.

Albert Einstein

Abstract

Boron-based two-dimensional materials showcase promise in variety of fields like hydrogen storage, fabrication of electronic devices and catalytic applications. These materials have garnered interest owing to their unique properties such as high electron mobility, high gravimetric capacity for hydrogen especially after metal decoration, thermal conductivity and tensile strength amongst others. However, for sustained operations of the devices involving these materials, their chemical stability against oxygen is of paramount importance. Especially in the applications involving exposure of the material to air. Abundance of oxygen in the air and its high reactivity increases the likelihood of oxidation of the material. In this work, chemical stability of hydrogen passivated 2D Boron structures; Borophane and 2D Boron Hydride against oxygen were analysed. First-principles calculations reveal that Borophane and 2D Boron Hydride have a less negative binding energy thus indicating that the oxygen binds less strongly to compared to Borophene which does not possess surface passivation by hydrogen. Experimental studies in the literature involving synthesis of 2D Boron Hydride reported presence of vacancies. The effect of vacancy site towards the reaction with oxygen was therefore analysed to maintain consistency with the synthesized materials. The simulations were performed on Borophane and 2D Boron Hydride by introducing a Boron vacancy in the system. The DFT simulation of defect containing Borophane revealed that oxygen binds less strongly in the physisorbed state and more strongly in the chemisorbed state, relative to the values obtained for Borophane without any defects. In case of 2D Boron Hydride it was observed that the vacancies provide a stable site for oxygen, for both physisorbed and chemisorbed state. From these simulations we can conclude that presence of vacancies in Boron based 2D materials generally leads to a stable site for oxygen.

Acknowledgements

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1 Introduction

Recent development in the field of two-dimensional (2D) materials has led to an increased interest in exploring their applications in a myriad different field. The unique properties of this class of materials have made them ubiquitous due to their high electron mobility, thermal conductivity and tensile strength amongst others. Graphene has been the most widely researched material but other materials like Silicene, Phosphorene and, Boron-based materials have also garnered interest. [2]–[6]

Boron is unique compared to other elements of the periodic table due to *electronic frustration.* The valance shell of Boron has only 3 electrons which are insufficient to form covalent bonds to reach closed-shell configuration. Moreover, since the size of Boron is small it is not electropositive enough to form metallic bonding, while it is also not electronegative to a degree to form ionic bonds. Hence, Boron forms a unique multicentre bonding configurations in many of its forms. One of the most prominent types of bonding found in Boron allotropes is three-centre two-electron (3c2e) bonding. This unique chemistry of Boron lends several useful properties to the 2D materials mainly, mechanical compliance, optical transparency, anisotropic plasmonics, ultrahigh thermal conductance, 1D nearly-free electron state, and the presence of metallic Dirac fermions and superconductivity. The presence of these properties has ensured a sustained interest in the theoretical and experimental study of Boron-based 2D materials. [3], [4], [7]–[11]

Several Boron-based 2D structures have been studied theoretically, however recently synthesis of these materials have been realized [4], [11]–[14]. Theoretical studies indicate that Boron-based 2D structures are stable with an ordered distribution of vacancies, however, experiments report that structure can also exist without vacancies.[2], [12]

The biggest hurdle in developing devices with Boron-based 2D materials is their stability when exposed to ambient environment. The main component of air which causes instability is oxygen, which reacts readily with the reactive 2D materials. Oxidation of 2D materials lead to a change in material properties. Saturation of surface with oxygen reduces the gravimetric capacity for hydrogen storage while mechanical degradation was observed in Phosphorene within hours after exfoliation. Oxidation experiments were conducted on Borophene; a Boron analogous of Graphene suggests that buckled Borophene gets partially oxidized whereas the planar sheets appeared to be inert. [2]–[4], [8], [9], [15]–[18]

Recent studies showed that hydrogenation of the Boron sheet display a remarkable improvement in chemical stability when exposed to air. The electron deficient Boron atom has three valance electrons resulting in an incomplete shell through bonding, hydrogenation of the structure provides the electron in exchange for the metallic surface and forms a free-standing configuration. An added advantage of using this method is its reversibility via annealing at low temperatures. [15], [19], [20]

Process of oxidation in materials is a complex process involving both the ground state of the oxygen molecule known as the triplet state and first excited state known as the singlet state. Both these states interact differently with the substrate. In case of Borophene it was reported that the oxygen molecule undergoes triplet to singlet state transition in the absence of silver substrate. Hence illustrating the importance of encompassing the possibility of state transition while conducting a theoretical study involving Boron-based 2D material. [21]

1.1 Thesis Motivation

With the recent advances in the synthesis of Boron-based 2D materials and their remarkable properties, nanomaterials show potential to be part of several application areas including energy storage. Several research groups are working on metal decoration of Boron-based 2D materials for hydrogen storage for mobility sector [5], [22]–[24]. The backbone of extraordinary properties of 2D materials is the characteristic high surface area to volume ratio. However, this leaves the material susceptible to unwanted reactions especially oxidation. Abundance of oxygen in the ambient environment and a high reactivity of most materials towards it makes it the most important factor to consider for chemical stability of materials [2], [25]. While collating literature review on various 2D materials, only a handful of papers tackle the oxidation of 2D Boron-based materials. Moreover, there is a gap in the literature related to the chemical stability of Boron-based structures that are passivated with hydrogen. Furthermore, the synthesis of 2D

Boron-based materials have revealed presence of vacancies. However, majority of first principles calculations were performed without taking into account the effect of these defects. [5], [19], [26], [27]

The aim of this thesis is to conduct a chemical stability analysis for these promising materials to validate their practical concerns of oxidation of these materials in real world applications.

1.2 Thesis Objectives

The high reactivity and abundance of oxygen in the atmosphere makes it the biggest roadblock in the realisation of 2D materials for applications. Especially for the applications which involves a direct contact of the material with air. The overall objective of this thesis is to gain insights into the chemical stability of Borophane and 2D Boron Hydride against oxygen. The hypothesised shielding effect of surface hydrogen in these structures could potentially provide an answer for real world applications of these materials.

The lack of detailed investigation of chemical stability of these materials and their promise of stability against oxidation defined the choice of these materials. The overall objective is to gain insights into the reaction of oxygen with these materials through first principles calculations by DFT framework. The sub-objectives of the thesis are:

- Investigate reactivity of Borophane and 2D Boron Hydride with oxygen
    - Determine the optimum system size and input parameters to simulate the materials as bulk.
    - Evaluate the most stable binding configurations for oxygen on the Borophane and 2D Boron Hydride surface using DFT framework.
    - Create configurations for chemisorption of oxygen on the substrate.
    - Evaluate binding energies of the different configurations and compare it with Borophene.
- Analyse the effect of vacancies on binding energy of oxygen to the substrate.
    - Create vacancies in the Borophane and 2D Boron Hydride.

- Determine the effect of vacancy on the oxidation process by simulating different configurations around vacancy.

1.3 Thesis Organisation

The thesis is organised in the following manner: Chapter 2 summarises the literature which served as a bedrock for the thesis to build upon. This chapter is used to establish the methodology for the analysis. Careful alterations are made to the methodology to cater to Borophane and 2D Boron Hydride. Chapter 3 lays down the theoretical background of the computational technique used in this work. Chapter 4 expands upon the methodology and creating a benchmark with interaction of oxygen with Borophene. Borophene as a benchmark is then used in the later chapters for comparison with Borophane and 2D Boron Hydride. Chapter 5 encompasses the chemical stability analysis of both Borophane and Boron Hydride. Chapter 6 summarises the work done in the thesis and directions which can be explored through this work in the future.

2 Literature Review

The basis of this study has been built up on the works of Alvarez et al. [2] on oxidation of free standing and supported Borophene and Rojas et al. [19] on Chemical stability of hydrogen boride nanosheets in water. Furthermore, the work of Singh et al [28] on Computational exploration of Borophane-supported single transition metal atoms as potential oxygen reduction and evolution electrocatalysts was used as a benchmark for the structure of Borophane.

2.1 Oxidation of Borophene

Motivation of studying oxidation of Borophene arises from the previously conducted experiments on 2D materials such as Phosphorene [29]. The experiments revealed that Phosphorene is very unstable in ambient conditions and undergoes oxidation within first few hours of synthesis. Oxidation of Phosphorene causes a degradation of mechanical properties in the 2D material [27]. It has been reported that oxidation of Borophene can tune electronic and optical properties [21], [25], [30]. Work of Guo et al. put light on the spin triplet-to-singlet conversion is important during oxidation of freestanding Borophene [29]. Another research group concluded that the transition does not take place in presence of Ag(111) substrate [2]. A study by Luo et al. neglected the triplet to singlet conversion [10]. However previous works done on oxidation of silicon surface [16], Phosphorene [27] and free stranding Borophene [29] underline the importance of this conversion.

The buckled configuration proposed in the works of Mannix et al. was used as a basis for simulations [31]. Oxidation of Borophene was modelled using the first principles calculations based on DFT [32]. VASP was used to solve the Kohn-Sham equations. The work of Alvarez et al takes into account the possibility of triplet to singlet transition when the sheet is oxidized. For modelling the triplet state of oxygen, spin polarized calculations were used by providing parallel spin on the oxygen for initialization. While the spin on Borophene sheet was distributed into equal number of spin up and spin down orientations. The GGA approximation with Perdew-Burke-Ernzerhof (PBE) parametrization is used for calculation of the exchange correlation functional and Van der Waals forces are taken into account via optB88-vdW functional (vdW-DF). [2], [33], [34]

Modelling of oxidation of Borophene sheet is done in a series of steps to identify the likelihood started with identification of unique configurations to find out the most stable adsorption configurations. Different orientations were used and configurations with both the singlet and triplet states were simulated. Finally, the binding energy of the oxygen molecule to the substrate was calculated by the equation:

$$E_b = E_T - \left(E_B + E_{O_2}\right) \tag{2.1}$$

Where, the E_T, E_B and E_{O2} are the total energies of oxidized sheet, energy of pristine Borophene and the energy of triplet state of oxygen molecule. [2]

2.2 *Effect of vacancies on chemical stability*

The work of Rojas et al. provides a holistic solution while investigating the chemical stability of Boron Hydride in water. Their approach combined experimental results with theoretical study which illustrated on the presence of vacancies during synthesis of Boron Hydride nanosheets. Hence, underlining the importance of including vacancies in the theoretical study to mimic the experimental setup. However, since the work pertains to the application of Boron-based 2D materials for use in electronic and catalytic applications, chemical stability in presence of water held more importance than oxygen in this particular case. Modelling of water on the Boron Hydride sheet followed a similar methodology as done in the work of Alvarez et al. [2]

The analysis of the chemical stability of Boron Hydride and Borophane in an oxidizing environment was carried out by following the methodologies established in the literature, while the procedure was altered to cater to the systems being analyzed in this study. Oxidation of Borophene was carried out in the study to setup a benchmark. This benchmark is then used to compare the effect of passivating the structure with hydrogen on its chemical stability in presence of oxygen. The passivated structures considered in this study are Boron Hydride and Borophane.[5], [19].

3 Theoretical Foundation

3.1 The many-body problem

While dealing with multiple atoms, the investigation of electronic properties involves taking into account a substantial number of electrons. To setup the problem and solve to obtain the material properties of the system an associated many-body problem is used. To solve a many-body problem, a Hamiltonian is constructed and is then used to solve Schrödinger equation.

The Schrodinger's equation is expressed as

$$\hat{H}\Psi = E\Psi \tag{3.1}$$

Where, Ĥ represents the Hamiltonian, Ψ is the electronic wavefunction of the system and E is the energy of the system.

The Hamiltonian is expressed as

$$\hat{H} = \widehat{T_e} + \hat{T}_n + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne} \tag{3.2}$$

The equation for Hamiltonian accounts for kinetic energy of the electrons and nucleus, and coulomb like interactions between the nuclei, electrons and nucleus-electrons. Where, $\widehat{T_e}$ is the electronic kinetic energy contribution, $\hat{T}_n$ is the kinetic energy of the nucleus, $\hat{V}_{nn}$ is the nucleus-nucleus potential energy, $\hat{V}_{ee}$ is the electron-electron potential energy and $\hat{V}_{ne}$ is the nucleus electron potential energy.

The Hamiltonian can be further expressed as:

$$\hat{H} = \frac{\hbar^2}{2m_e}\sum_{i}^{N_e}\nabla^2 - \frac{\hbar^2}{2}\sum_{k}^{N_n}\frac{\nabla^2}{M_k} + \frac{1}{2}\sum_{i\neq j}^{N_e}\frac{e^2}{|r_i - r_j|} + \frac{1}{2}\sum_{k\neq l}^{N_n}\frac{Z_k Z_l e^2}{|R_k - R_l|} - \sum_{i,k}^{N_e,N_n}\frac{Z_k e^2}{|r_i - R_k|}$$

(3.3)

Where, i, j indices are for the electrons and k, l denote different nucleus. Z_k and Z_l are the atomic number of the nucleus, m_e and M_k are the mass of the electron and nucleus. [35]

3.2 Born Oppenheimer approximation

Schrödinger's equation can be solved exactly for the hydrogen which has a proton and an electron. The equation already gets complicated for the next atom in periodic table, Helium. To resolve the practical constraints of the equation approximations are used. Born Oppenheimer approximation involves an assumption that nucleus is heavier in contrast to electrons and hence we can divide the equation into a nucleic and electronic contributions. While solving the electronic part of the equation an extra term is added to take into account the effect of nucleus known as external potential. [35]

$$\hat{H} = \frac{\hbar^2}{2m_e}\sum_{i}^{N_e}\nabla^2 + \frac{1}{2}\sum_{i\neq j}^{N_e}\frac{e^2}{|r_i - r_j|} + \hat{V}_{ext}$$

(3.4)

Where, $\hat{V}_{ext}$ is external potential.

3.3 Hohenberg-Kohn Theorems

Hohenberg-Kohn theorems provide an approximation for the electronic interactions. To take into account effect of all the electrons, the theorems propose usage of electron density to be instead of individual interactions. This approach is the bedrock of Density Functional Theory (DFT) formed to obtain an exact theory of many body systems.

The following are the two Hohenberg-kohn theorems:

1. *The ground state electron density determines the external potential for a system of interacting particles.*

   The theorem posits that since the Hamiltonian is fully determined, except for a constant shift in energy, the many-body wavefunctions for all states (ground and excited) are determined. Hence, all properties of the system depend completely on only the ground state density.

2. *For any external potential, a universal energy functional exists. The minimum value of the energy functional for a specific external potential is the ground state energy where the density that minimises the functional is the ground state density.*

   The second theorem asserts that the universal functional is self sufficient to determine the exact ground state energy and density. However, the excited states if the electrons must be determined through other means.

The potential of the system hence is only dependent on the electronic density and the ground state electronic density is the minima of the energy function. [35]

3.4 Kohn-Sham Ansatz

Density functional theory is widely applicable in the present times due to an approach proposed by Kohn and Sham which replaces the original many-body problem by an auxiliary independent particle problem. This assumption involves independent particles but an interacting density. The Kohn-Sham Ansatz replaces one problem with another, albeit to a relatively easier to solve problem. The ansatz assumes that ground state density of the system can be equated to another non interacting system. This approach leads to formulation of independent-particle equations for the auxiliary system which is solvable by numerical methods. Whereas, all the many-body terms are clubbed together in an *exchange correlation functional of the density.*

According to Kohn-Sham ansatz, the ground state energy of the system can be defined by the following equation:

$$E_0[\rho(r)] = T[\rho(r)] + \int V_{ext}(r)\rho(r)dr + \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|}dr\,dr' + E_{xc}[\rho(r)] + E_{II}$$

(3.5)

Since all electrons are affected by a charge density and they don’t interact with the other electrons, we can let every electron have its own eigen-function. Now, we need to determine effective potential and the eigenfunctions.

$$\left\{-\frac{1}{2}\nabla^2 + V_{eff}(r)\right\}\Psi_i(r) = \varepsilon_i\Psi_i(r)$$

(3.6)

$$\rho(r) = \sum_{i=1}^{N}|\Psi_i(r)|^2$$

(3.7)

The above equations determine the electronic density and the effective potential. The two equations are solved through a self-consistency loop until the ground state energy of the system is found. [35]

3.5 Exchange-Correlation Functional

The effective potential from above equation can be segmented into three parts $V_{eff} = V_{hartree} + V_{ext} + V_{xc}$, where $V_{hartree}$ and V_{ext} are solvable with exact solutions. The V_{xc} term needs approximations to solve. Two types of approximations are widely applied for calculation of exchange-correlation functionals, Local Density Approximation (LDA) and Generalised Gradient Approximation (GGA). LDA function makes use of electron gas of the particles to estimate the exchange correlation functional. However, it tends to underestimate the lattice parameters and band gap. LDA also overestimates binding energy.

GGA is an improved alternative to LDA, instead of using only the electron density, there is a change of rate at which the density changes i.e. the gradient. [35]

$$\mathbf{E}_{\chi C}^{LDA}[\boldsymbol{\rho}(\mathbf{r})] = \int_{\mathbf{r}} \varepsilon_{\chi C}(\boldsymbol{\rho})\, \boldsymbol{\rho}(\mathbf{r})\mathbf{dr} \tag{3.8}$$

$$\mathbf{E}_{\chi C}^{GGA}[\boldsymbol{\rho}(\mathbf{r})] = \int_{\mathbf{r}} \varepsilon_{\chi C}(\boldsymbol{\rho}, \nabla\boldsymbol{\rho})\, \boldsymbol{\rho}(\mathbf{r})\mathbf{dr} \tag{3.9}$$

3.6 Projector Augmented Wave (PAW) Formulation

Even after taking into account all the approximations and correlations, the electronic structure calculations still require a lot of computational resources. An approach to reduce the computational expense is PAW formalism. The core region of an atom or the electrons near the nucleus are described separately using a smooth wave function, since only the electrons in the outer shells interact with neighbouring atoms. A real description of core electrons would involve fast oscillating wave functions, which makes it difficult for Fourier transformation. The PAW method instead uses pseudo wave functions and then these wavefunctions are transformed by an operator $\hat{T}$ into the real Kohn-Sham single particle wave functions.

$$|\Psi\rangle = \hat{T}|\Psi'\rangle$$

(3.10)

Where, $|\Psi\rangle$ is the real single particle wave function and $|\Psi'\rangle$ is the pseudo wave function.

Formulation of the operator is based on the consideration that the wave functions are the same outside the core region. Inside the core region, the smooth partial waves are used as follows:

$$|\Psi\rangle = \sum_{i} |\phi_i'\rangle c_i = \hat{T}|\Psi'\rangle$$

(3.11)

The total single particle wave function is described in the following equations where T_c is only applicable inside core region.[35]

$$|\Psi\rangle = \sum_{i} |\phi_i'\rangle c_i = \hat{T}|\Psi'\rangle$$

(3.12)

$$\hat{T} = 1 + \sum_{C} T_c$$

(3.13)

$$c_i = \langle \hat{\rho}_i | \Psi' \rangle$$

(3.14)

$$\langle \hat{\rho} | \phi_j' \rangle = \delta_{ij}$$

(3.15)

$$\boldsymbol{\sum_i |\,\phi_i^{'}\rangle\,\langle\widehat{\rho_i}\,| \;=1}$$

(3.16)

$$\boldsymbol{T_C|\,\Psi^{'}\rangle = \sum_i T_C\,|\,\phi_i^{'}\rangle\, c_i = \sum_i \left(|\phi_i\rangle - |\,\phi_i^{'}\rangle\right)\langle\widehat{\rho_i}|\Psi^{'}\rangle}$$

(3.17)

$$\hat{T} = 1 + \sum_i (|\phi_i\rangle - |\phi_i'\rangle)\langle\widehat{\rho_i}\,|$$

(3.18)

Vienna Ab-initio Simulation Package (VASP) was used to perform the electronic structure calculations in this work, which is based on the PAW formalism and pseudo-potentials for every element in the structure. Pseudo-potential uses the core electrons to screen the nuclear charge as an approximation since only valence electrons are involved in interatomic interactions.

4 Methodology

4.1 Benchmarking Borophene sheet

Borophene sheet considered for benchmarking in this study is the striped Borophene sheet, with 32 Boron atoms.

4.1.1 Visualisation of the Borophene sheet

Visualisation of the Borophene sheet was done with the help of the software called Visualization for Electronic and Structural Analysis (VESTA), which helps in creating graphics for molecular structures. The unit cell lattice parameters were chosen from the paper by Alvarez et al. where the free-standing structure was relaxed and the lattice parameters were found to be a = 1.61 Å and b = 2.87 Å with a buckle height of 0.91 Å. An interlayer separation of 20 Å was chosen to prohibit inter-layer interactions.

4.1.2 Creation of a supercell

Formation of supercell is an important part of mimicking the bulk behaviour of the material, choice of the number of atoms is usually a trade-off between the computational expense and accuracy of simulating a bulk material.

- Creation of a supercell was done by first obtaining an electronically relaxed conventional unit cell, the lattice parameters were then compared with the values stated in the paper by Alvarez et al. the results matched and corroborated the lattice parameter of the relaxed structure.
- The relaxed unit cell is then converted from POSCAR file format obtained from VESTA into a CIF (Crystallographic Information Framework) file format.

- A script called Cif2Cell is then used to convert the CIF file into a supercell CIF file, in our case we used 4x4 Supercell which generated a system of 32 Boron atoms. The output file can then be converted into a POSCAR file format which is compatible with VASP. [36]

4.1.3 DFT calculations for modelling interaction of oxygen with Borophene sheet

oxygen molecule in the triplet state was then added to the Borophene sheet at a distance of 3.2 Å. DFT calculations were carried out using a plane-wave basis set through VASP 5.3.5. PAW method is used and the GGA is applied with PBE to approximate the exchange correlation functional. Van der Waals forces are especially important when the oxygen stays in the triplet state, these forces were accounted for by including a dispersion corrected Van der Waals framework (DFT-D2). Cut-off energy was selected as 600 eV for the plane-wave basis set and Monkhorst-Pack k-point mesh of 4 x 4 x 1 was used for the calculation. The energy convergence criteria for self-consistent electronic loop were set to 10-8 eV and all the lattice parameters and atomic positions are relaxed until the forces acting on atoms were below 1 meV/Å. Gaussian smearing with sigma of 0.1 was used for Brillouin-Zone integration. [2]

4.1.4 Configurations of oxygen molecule on Borophene sheet

To model the oxidation of Borophene sheets, the most stable configuration for adsorption was identified as the bridge configuration. To map the difference of adsorption on bridge configuration, two configurations were made. In the first configuration the oxygen atom is in valley position (configuration a) and in the second configuration the oxygen molecule is in the peak position (configuration b).

Furthermore, to test the triplet to singlet transition two configurations were made with oxygen atoms in singlet state bonded to the sheet (configuration c and configuration d). [2]

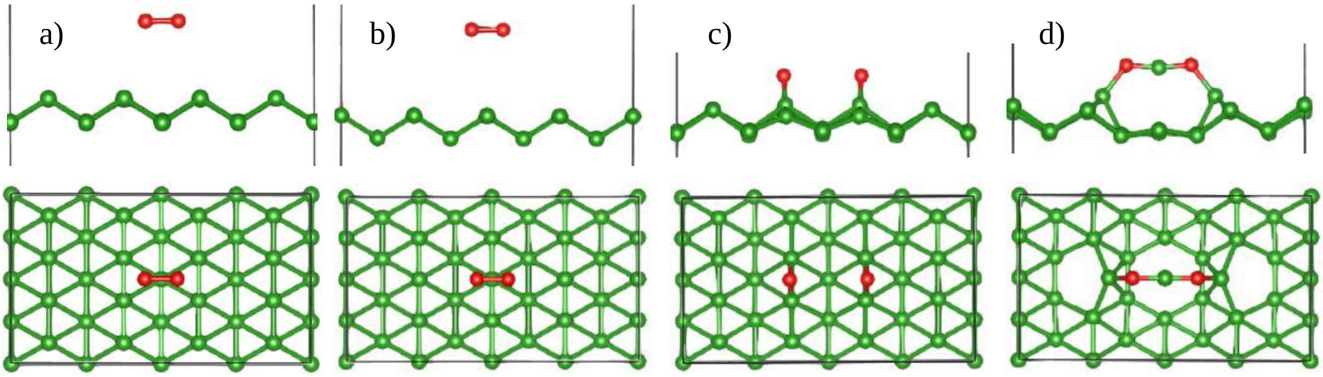

Figure 1 Top view and front view of converged Borophene sheet with 32 Boron atoms. These configurations were found to be most stable for oxygen. (Green atoms – Boron and red atoms – oxygen)

Spin Polarized DFT calculations were performed with setting initial magnetic moment for oxygen molecule as 3.0 μB, an overestimation which gets corrected in the calculation. The spins were set as parallel and equal number of spin up and spin down orientations were chosen for Boron atoms.

The calculations were run at varying distances of oxygen molecule and showed a tendency for chemisorption onto the Borophene sheet in singlet state.

Further, the binding energies of pristine Borophene sheet and oxygen were calculated through the same procedure. Resultingly, now all the elements for calculation of binding energy of oxygen on Borophene sheet are available.

Table 1 Binding energy of Borophene with oxygen at Configuration a, b, c and d.

Configuration	Binding Energy eV)
a	-1.14
b	-1.14
c	-7.17
d	-8.02

4.1.5 Optimisation of size of the system

The next step in setting Borophene sheet as a benchmark for further comparison with the hydrogenated structures is the determination of a system size which accurately represents the bulk material. The aim of testing different system sizes is for identification of the plateau after which increasing the number of atoms does not necessarily increase the accuracy while significantly increasing the computational time. For the study, an effort was made to build systems which are closer to a square plane, this approach allows an easier visual identification of the source of warpage, if the system undergoes deformation.

System sizes of 4x4 (32 Boron atoms), 4x6 (48 Boron Atoms), 4x8 (64 Boron atoms) and 5x10 (100 Boron atoms) were made for the most stable configurations from the above step. The singlet state corresponding to configuration C and D were hence chosen. This selection lent an additional advantage of a higher chance of deformation on the Borophene sheet since it involved chemical bonding, hence a note can be made on warpage.

After calculating the binding energies of these two configurations for varying system sizes, it was discovered that the difference in binding energies of two configurations for system with 48 Boron atoms and 64 Boron atoms was less than 0.1 eV and hence was chosen as the system size for this study.

Table 2 System size effects

System Size	Binding Energy Configuration C (eV)	Binding Energy Configuration D (eV)	Difference in Binding Energy C – D (eV)
4x4	-7.17	-8.02	0.853
4x6	-7.27	-7.75	0.472
4x8	-7.31	-7.86	0.553
5x10	-7.62	-7.62	0.357

4.1.6 Sensitivity Analysis

The sensitivity analysis is the next optimization step to obtain input parameters for the system. This optimization follows a similar route as compared to system size effect where we are trying to find the value beyond which the accuracy is not increased. The parameters which are optimized in this study are the cutoff energy of the plane-wave basis set, the k-point mesh and gaussian smearing sigma.

The value for ENCUT was changed from 400 eV to 800 eV in intervals of 50 eV, k-point mesh was changed from 4x4x1, 6x6x1 to 8x8x1. While the sigma was changed from 0.05, 0.1 and 0.2. Furthermore, a reference system was calculated with ENCUT as 1200 eV, a KPOINT mesh of 27x27x1 and sigma as 0.01.

These calculations were carried out only for configuration D, since it was the most stable configuration. The resulting values were then compared to the reference value. Then to establish the optimum parameters the difference in energies were calculated between two increments. The parameters chosen had a difference around 0.001 eV from the next increment.

The optimum parameters found after applying these constraints are:

- ENCUT = 600 eV
- K-point mesh = 4x4x1
- Sigma = 0.1

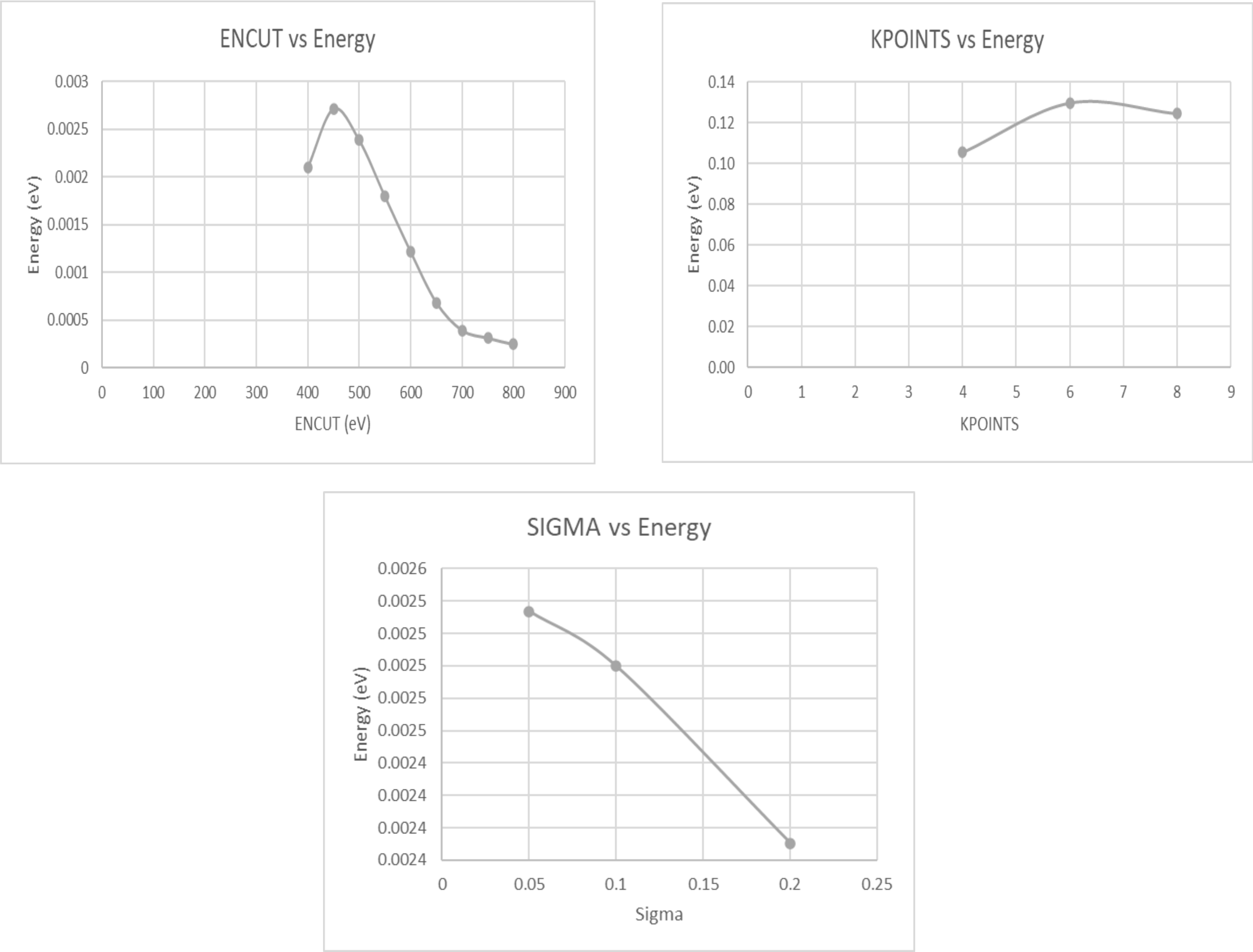

Figure 2 Sensitivity analysis results (*top left)* cut off wavelength (eV) vs energy (eV), *(top right)* KPOINTS vs Energy (eV), *(bottom centre)* Gaussian Smearing parameter SIGMA vs Energy.

5 First Principles Calculations to analyse chemical stability of Borophane and Boron Hydride

5.1 Borophane

5.1.1 Introduction

Borophane polymorphs can be synthesised through hydrogenation of Borophene. The synthesis is done via a two-step procedure, namely Boron deposition, followed by hydrogenation in ultrahigh vacuum (UHV) chamber. Deposition of Boron is conducted using electron beam evaporation (Focus EFM 3) of solid Boron rods as precursor. Borophene is then grown on a ~600 nm thick Ag (111) on mica substrate. The substrates are kept at 400-550 ˚C during deposition. A flux of 10-15 nA is then maintained for 20-30 min for growth of Borophene monolayer. The hydrogenation of Borophene substrate is then carried out by exposing the sample to atomic hydrogen. Atomic hydrogen is generated by splitting molecular hydrogen using a tungsten filament at ~ 1600 ˚C. The sample is kept at room temperature and it directly faces the filament at an approximate distance of 10 cm. [20], [28]

hydrogenation of Borophene to form Borophane is a reversible change, with hydrogen release on thermal annealing. Hence, hydrogenation of Borophene into Borophane can be considered as a reversible passivation scheme. [20]

5.1.2 Computational Details

The structure of Borophane resembles the structure of striped Borophene with the difference that each Boron atom has formed bond with a hydrogen atom. To analyse the chemical stability of the system, the methodologies established in the previous chapters are applied.

Firstly, a supercell of Borophane with 48 Boron atoms was created from the relaxed conventional unit cell of Borophane. First principles calculations were performed based on DFT framework via VASP. PAW method was used with GGA approximations wand PBE functional for approximation of exchange correlation. Van der Waals forces were taken into account by including dispersion corrected van der Waals framework (DFT-D2). The parameters for running the simulation were chosen based on the data from sensitivity analysis. The cut-off energy was selected as 600 eV for the plane-wave basis set and the Monkhorst-Pack K-Point mesh of 4 x 4 x 1 was selected to set up the simulation. The energy convergence criteria for self-consistent electronic loop were set to 10^{-8} eV and all the lattice parameters and atomic positions were relaxed till forces acting on the atoms were below 1 meV/Å. Gaussian smearing with sigma of 0.1 was used for integrating Brillouin Zone. Spin-Polarised calculations were performed for cases where the oxygen was in triplet state. As learnt from the experience of simulating Borophene, negligible difference was found by including spin polarised calculations for singlet state, hence chemisorption calculations were performed without spin polarisation. The initial magnetic moment on oxygen was chosen to be 3 μB, in parallel orientation. Magnetic moment of hydrogen was considered 0 μB and the Boron atoms were initialised with magnetic moment of 1 μB in anti-parallel orientation.

Secondly, five unique configurations were identified on the symmetrical molecule, to map out all the possibilities of the interaction of oxygen molecule with the Borophane sheet. The configurations were chosen as follows: configuration a – top of Boron atom, configuration b – top of hydrogen atom, configuration c – centre, configuration d – diagonal bridge and configuration e – straight bridge and can be visualised in fig 3 (a). These configurations were used to find the most stable position of physisorption of oxygen molecule i.e., in its triplet state. Furthermore, to identify the preferred orientation of oxygen molecule with respect to the Borophane, three different orientations were simulated at each configuration namely, vertical, horizontal and diagonal orientations of the oxygen molecule. Those results are added in the appendix.

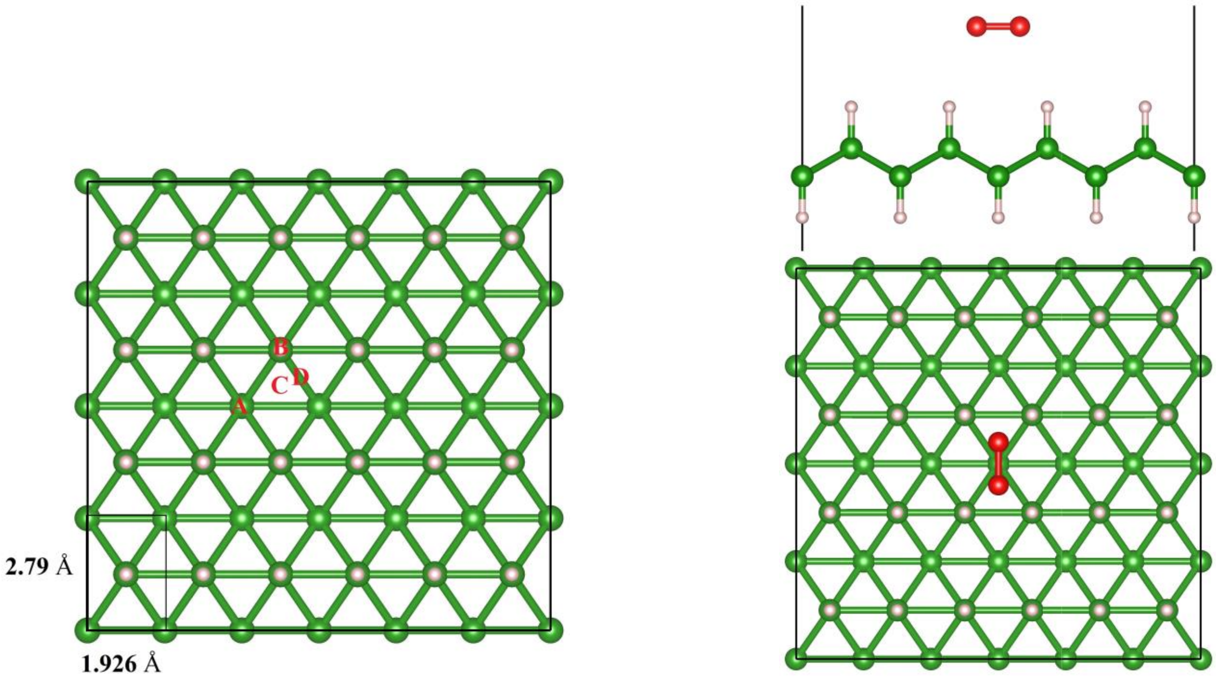

Figure 3 (left) Unique locations for oxygen adsorption on Borophane sheet due to symmetry, (right) oxygen adsorption on configuration b on Borophane sheet. (Green atoms – Boron, red atoms – oxygen and pink atoms - hydrogen)

Furthermore, two configurations (configuration e and configuration f) were created with initial setup in which the oxygen was in singlet state. These two configurations were created to cover the possibilities of chemisorption and the likelihood of all the structures that can be formed. Simulations for configurations in which oxygen was in singlet state was run with both the inclusion and exclusion of spin polarisation. Negligible effect in the final configurations prompted that the calculations can be run without spin polarisation. The final structures obtained from the configurations where oxygen was in singlet state show a possibility of configurations where the oxygen gets chemisorbed on the surface.

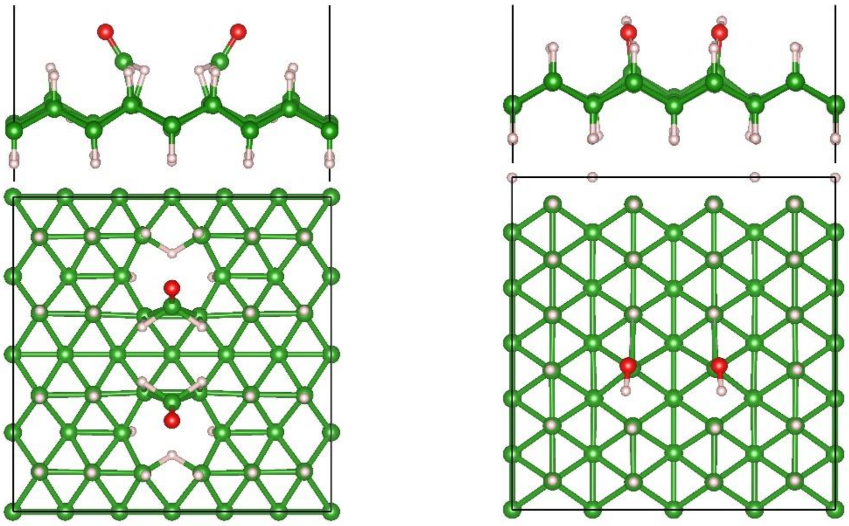

Figure 4 (left) Top view and front view of chemisorption of oxygen in configuration f, (right) top view and front view of chemisorption of oxygen in configuration g. (Green atoms – Boron, red atoms – oxygen and pink atoms - hydrogen)

5.1.3 Structural Characteristics of Borophane

The relaxed structure of Borophane can be seen in fig 3 (a). The lattice parameters of the unit cell were determined to be a = 1.9266 Å and b = 2.799 Å, giving good agreement with the studies done on Borophane in the literature [28]. The structure has a periodic lattice in a buckled arrangement. Each Boron atom is bonded to one hydrogen atom in an alternating up and down positions. The structure shows no presence of vacancies. The effect of hydrogenation can be seen on the Borophene substrate, the unit cell parameters for Borophene are a = 1.67 Å and b = 2.89 Å. Hence the effect of hydrogen on Borophene results in stretching of lattice constant a and b is decreased.

5.1.4 Adsorption of oxygen on Borophane

A comprehensive configuration sampling for oxygen on Borophane was performed. oxygen was placed in the 5 unique configurations on Borophane owing to its symmetry. oxygen was the rotated in three different orientations to obtain the most stable adsorption configuration. The binding energies of oxygen at each configuration and orientation varies but through extensive sampling of the Borophane the most stable configurations were obtained. The most stable configuration was found to be configuration D with horizontal orientation, further the binding energies for each configuration with the most preferred orientation for that configuration has been tabulated in table 3. Compared to binding energies of oxygen on Borophene as reported in Alvarez et al [2], a lowered value is found for the Borophane. The lowered binding energy on Borophane indicates the effect of passivating the Borophene structure with hydrogen impacts the oxidation. Furthermore, it hints toward a relative chemical stability under oxidation since the oxygen's binding energy to the substrate has been lowered.

The configurations (f and g) indicate the possibility of splitting of oxygen molecule and bonding with the Boron from Borophane sheet. The final configurations in both the cases show that the bond between hydrogen and Boron has been broken and replaced by oxygen. The configurations also show significant structural changes, which can lead to altered material properties.

Table 3 Binding Energy of oxygen molecule at different configurations of Borophane

Configurations	Binding Energy (eV)
a	-1.1600399
b	-1.1713199
c	-1.1884399
d	-1.1932599
e	-1.1837199
f	-5.2027499

g	-6.1478399

Binding energies from configuration a to configuration e fall in a similar range, since the oxygen was physisorbed on each of these configurations. From the calculations it can be concluded that configuration d is the most stable configuration amongst configurations where the oxygen was physisorbed. Comparing the binding energy of oxygen on the most stable configuration of Borophane with the binding energy of oxygen on Borophene reveals that oxygen is slightly more stable on Borophane. This can be explained by the interaction of the hydrogen on the surface of Borophane and oxygen. However, on comparison of binding energies of chemisorbed configurations of Borophene and Borophane, there is a clear marked difference of lower binding energy in case of Borophane. These results indicate that the presence of hydrogen on the surface of Borophane reduces the stability of oxygen. The steric effect of hydrogen could explain the lowering of binding energy of oxygen, another reason could be the charge passivation of the substrate with hydrogen reduces the susceptibility of oxidation of Boron atoms.

5.1.5 Effect of Vacancies

In addition to pristine Borophane sheet, this section looks into the effect a vacancy imparts on the reactivity of the substrate. Allotropes of Borophene except striped Borophene indicate a periodic presence of vacancies in their relaxed structures [12]. Furthermore, the experimental studies conducted on 2D Boron Hydride also report presence of vacancies[19]. These studies indicate the ubiquity of vacancies in real systems. Hence to present a thorough picture of chemical stability of Borophane on oxidation, vacancies were created.

A Boron-hydrogen pair was removed from the Borophane sheet to mimic a vacancy. Four different configurations were then created, two each for the singlet and triplet state of oxygen. The aim of this setup was to identify if the presence of vacancies leads to a reactive configuration.

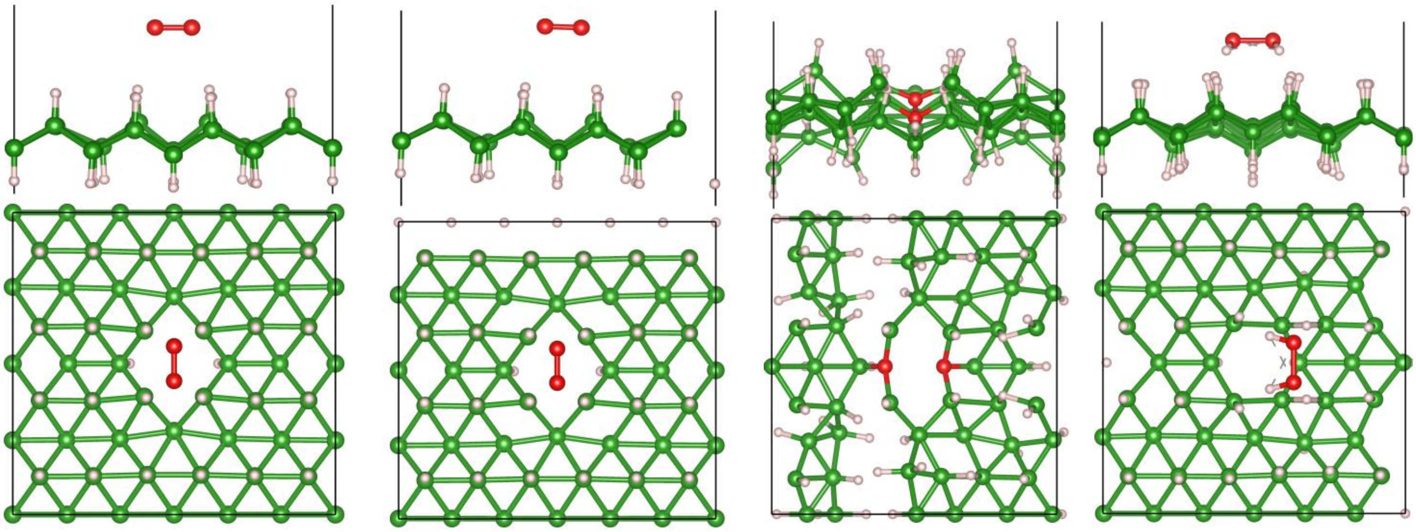

Figure 5 (left to right) Top and front view of configurations (a-d) of borophane sheet with a Boron vacancy. (Green atoms – Boron, red atoms – oxygen and pink atoms - hydrogen)

5.1.5.1 Structural Characteristics

The relaxed structures from the configurations a and b both indicate a movement of oxygen molecule towards the vacancy. This result is also intuitive since the presence of a vacancy disrupts charge balance and provides a more reactive configuration for oxygen. Furthermore, presence of vacancy has an effect on the structure as well. The lattice constants of the unit cell after the introduction of a vacancy are a = 1.9562 Å and b = 2.6942 Å. Compared to lattice parameters of pristine Borophane sheet, a = 1.9266 Å and b = 2.799 Å, a stretch in lattice parameter a and a shrinkage in lattice parameter b due to the presence of a vacancy is observed. Furthermore, warpage around the vacancy is more pronounced than on the edges, this can be visualized from fig 5 (b).

An effort was made to simulate chemisorption of oxygen on the Borophane sheet. Contrasting results were obtained, configuration c predicts a structure which breaks the periodic lattice of Borophane. The oxygen atoms in this configuration, bonded with the Boron atoms from the Borophane sheet, resulting in distortions which breaks Boron-Boron bonds from the adjacent configuration. This configuration reveals that chemisorption of oxygen in presence of a vacancy can cause severe deformations.

Configuration d, visualized in figure 6 (c and d) caused a distortion around the vacancy, however the effect was much less pronounced compared to configuration c. The bond length of oxygen in this configuration is 1.4776 Å, compared to 1.208 Å, the experimental value of oxygen molecule bond length. This shows a stretching of the oxygen molecule. Furthermore, we see a bond between the stretched oxygen and hydrogen thus indicating a possibility of formation of hydrogen peroxide. The oxygen bond length is also consistent with the oxygen-oxygen bond length in hydrogen peroxide.

5.1.5.2 Oxygen Adsorption on Defective Borophane

To understand the effect of vacancy in Borophane sheet, four different configurations were conceptualised. The first two configurations (a and b) were used to determine the effect of vacancy on oxygen molecule near the vacancy and on top of the vacancy.

Two more configurations (c and d) were initialised with atomic oxygen on top of Boron atoms closest to vacancy and on top of hydrogen atoms near the vacancy. Further, in the configuration c, the oxygen atoms were placed close to the Borophane sheet to characterise the effect of distance of oxygen molecule with the substrate.

Binding energy of oxygen on defective Borophane sheet for the different configurations are tabulated in table 4. Calculation of binding energy of oxygen on defective Borophane sheet, required binding energy of defective Borophane sheet without oxygen. Electronic relaxation of defective Borophane sheet without oxygen was performed with the same parameters as mentioned in section 5.1.2. The pseudopotentials were altered to exclude the effect of oxygen for this calculation.

Configurations a and b show comparable binding energies, which is consistent with the final relaxed structure obtained. These results further corroborate the prediction that oxygen molecules near the vacancy move towards the vacancy since it provides a more stable configuration. Moreover, comparing the binding energies of configuration, a and b, with the physisorbed configurations of pristine Borophane, we can easily see a significantly lower binding energy. This indicates that the Boron vacancy does not provide a site for oxygen to stabilise when the oxygen is physisorbed on the vacancy.

Configuration c shows significant distortion. The relaxed structure shows that oxygen is in singlet state, the binding energy is quite high. Each oxygen atom in configuration c forms bonds with three Boron atoms near the vacancy. The existence of this structure indicates that oxidation of Borophane in presence of vacancy can lead to an exothermic reaction and distortion.

Configuration D as expected from a chemisorbed state, revealed a higher binding energy of oxygen, the final relaxed structure indicated that oxygen preferred to stay near the vacancy. Moreover, formation of hydrogen peroxide was observed, indicating the possibility that vacancies can lead to lowered binding energy of hydrogen and hence formation of oxygen-hydrogen bond.

Table 4 Binding Energy of oxygen molecule at different configurations of Borophane with a Boron vacancy

Configurations	Binding Energy (eV)
a	-0.18561990
b	-0.18719990
c	-15.811920
d	-3.7371399

5.2 Boron Hydride

5.2.1 Introduction

Boron forms a unique multicenter bonding configurations in many of its forms. One of the most prominent types of bonding found in Boron allotropes is three-center two-electron (3c2e) bonding. Boron Hydride showcases this type of bonding, which interacts at an intermediate strength with hydrogen. Pure hexagonal Boron layer is not stable due to electron deficiency, however introducing electron donors can stabilize it. Similar model is proposed for stability of Boron Hydride, instead of metals as typical electron donors, hydrogen is introduced to the electron deficient hexagonal Boron network by formation of 3c2e bonds. In-plane Boron atoms are bonded to each other by sp^2 hybridization. [7], [37]–[40].

Pair of hydrogen atoms are bonded to hexagonal Boron plane (above and below). The weakly bonded hydrogen is the key to the formation and stability of Boron network. Moreover, this bond ensures a release of hydrogen in practical conditions and preservation of backbone of Boron structure ensures cyclicity. [41]–[43]

5.2.2 Computational Details

The structure of 2D Boron Hydride resembles the structure of Graphene. The difference being the presence of hydrogen on bridge configurations to stabilise the planar structure of the material. To analyse the chemical stability of the system, the methodologies established in the previous chapters are applied.

Firstly, a supercell of Boron Hydride with 48 Boron atoms was created from the relaxed conventional unit cell of Borophane. The methodology followed for simulation of oxygen on Borophane were used to keep the consistency for comparison. First principless calculations were performed based on DFT framework via VASP. PAW method was used with GGA approximations wand PBE functional for approximation of exchange correlation. Van der Waals forces were taken into account by including dispersion corrected van der waals framework (DFT-D2). The parameters for running the simulation were chosen based on the data from sensitivity analysis. The cut-off energy was selected as 600 eV for the plane-wave basis set and the Monkhorst-Pack K-Point mesh of 4 x 4 x 1 was selected to set up the simulation. The energy convergence criteria for self-consistent electronic loop were set to 10^{-8} eV and all the lattice parameters and atomic positions were relaxed till forces acting on the atoms were below 1 meV/Å. Gaussian smearing with sigma of 0.1 was used for integrating Brillouin Zone. As learnt from the experience of simulating borophene, negligible difference was found by including spin polarised calculations for singlet state, hence chemisorption calculations were performed without spin polarisation. The initial magnetic moment on oxygen was chosen to be 3 μB, in parallel orientation. Magnetic moment of hydrogen was considered 0 μB and the Boron atoms were initialised with magnetic moment of 1 μB in anti-parallel orientation

Chemical stability of Boron Hydride for oxidation was analyzed by identifying four different configurations which are candidates for the most stable position for oxygen. These four configurations are as follows: configuration a – center of the hexagonal ring, configuration b – top of Boron atom, configuration c – top of hydrogen atom and configuration d – bridge.

These configurations were used to find the most stable position of physisorption of oxygen molecule i.e., in its triplet state. Furthermore, to identify the preferred orientation of oxygen molecule with respect to the Boron Hydride, three different orientations were simulated at each configuration namely, vertical, horizontal and diagonal orientations of the oxygen molecule. Those results are added in the appendix.

Lastly, two symmetrically unique configurations were identified for chemisorption of oxygen atom. Configuration e was constructed to check the chemisorption on Boron atom and configuration f was constructed to check the chemisorption on hydrogen atom.

5.2.3 Structural Characteristics of 2D Boron Hydride

2D Boron Hydride has hexagonal arrangement of Boron atoms. Moreover, the planar structure is stable in 2D Boron Hydride due to electron donation from hydrogen atom. The lattice constants of the unit cell of relaxed 2D Boron Hydride were found to be a = 3.002 Å and b = 5.295 Å. These results closely resemble the values found in the literature with a = 3.015 Å and b = 5.29 Å. The slight change can be attributed to inclusion of van der Waal’s forces in the simulations carried out in this study [19].

No significant buckling was observed in configurations a, b, c and d, the oxygen stayed in triplet molecular state. There was a slight change in the bond length of oxygen from 1.208 Å to 1.269 Å, this change indicates interaction of oxygen with the Boron Hydride substrate. Furthermore, a slight change in the lattice constants was observed with a = 3.0003 Å and b = 5.288 Å, indicating that both the lattice constants shrunk in value.

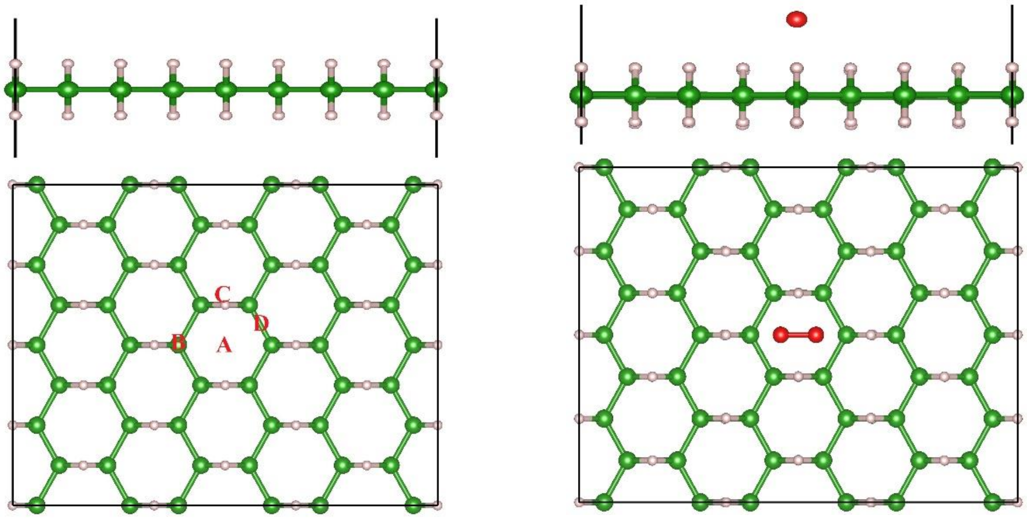

Figure 6 (left) Unique locations for oxygen adsorption Boron Hydride sheet due to symmetry, (right) Top and front view of physisorption of oxygen on Boron Hydride sheet in configuration a. (Green atoms – Boron, red atoms – oxygen and pink atoms - hydrogen)

Furthermore, two configurations for chemisorption of oxygen molecule on Boron Hydride sheet were relaxed, and the significant visual distortion was observed. The lattice constants for configuration e changed to a = 3.0064 Å and b = 5.28067 Å. It was also observed in this configuration that the oxygen replaced hydrogen from the bridge configuration, and binds to both Boron and hydrogen directly, but breaks the bond between hydrogen and Boron.

Configuration f further indicates that atomic oxygen prefers to go into the bridge configuration of Boron Hydride, the oxygen atoms in this case were placed on top of hydrogen atom and it replaced the hydrogen atom and bonded with Boron in the bridge configuration as well. The lattice constants for this configuration were found to be a = 2.992 Å and b = 5.309 Å.

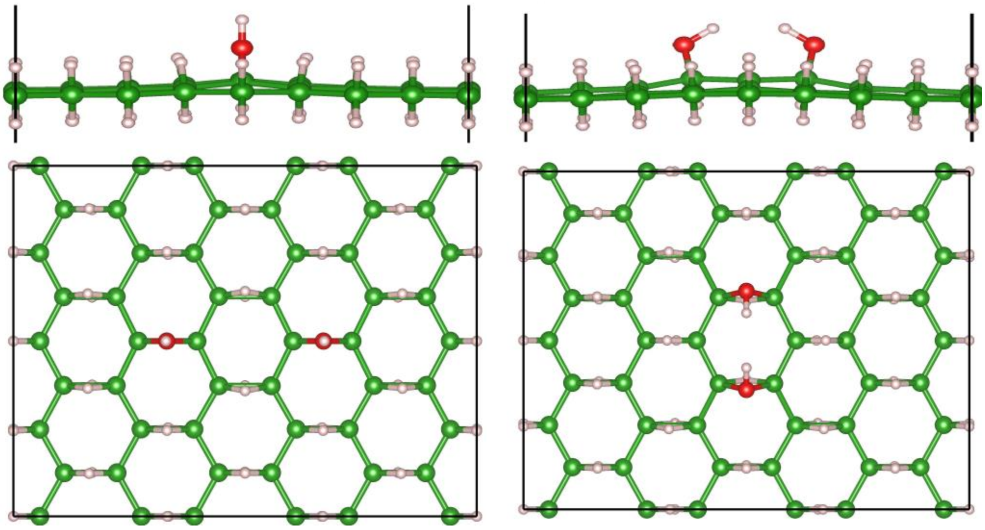

Figure 7 (left) Top view and front view of chemisorption of oxygen in configuration e on Boron Hydride, (right) top view and front view of chemisorption of oxygen in configuration f on Boron Hydride. (Green atoms – Boron, red atoms – oxygen and pink atoms – hydrogen)

5.2.4 Oxygen Adsorption on Boron Hydride

A comprehensive configuration sampling for oxygen on Boron Hydride was performed similar to the one achieved for Borophane. However, Boron Hydride presents four unique configurations for oxygen adsorption owing to its symmetry unlike five in case of Borophane. oxygen was then placed on these configurations and was rotated in three different orientations to obtain the most stable adsorption configuration. The binding energies of oxygen at each configuration and orientation varies but through extensive sampling of the Borophane the most stable configurations were obtained. The most stable configuration was found to be configuration c with diagonal orientation of oxygen molecule, further the binding energies for each configuration with the most preferred orientation for that configuration has been tabulated in table 5. Compared to binding energies of oxygen on Borophene as reported in Alvarez et al [2], a lowered value is found for the Boron Hydride. The lowered binding energy on Boron Hydride indicates the effect of passivating the Borophene structure with hydrogen impacts the oxidation. However, binding energy of oxygen for configuration c is higher than the one reported for Borophene. This indicates that the bridge configurations are more much more susceptible to oxidation. However, the binding energy value for configuration C was comparable to the value calculated for Borophane. This is expected since the bridge configurations of Boron Hydride resemble the dangling surface hydrogen on Borophane.

Comparing the chemisorbed configurations Boron Hydride has lower binding energy of oxygen compared to both Borophene and Borophane this indicating its superior chemical stability against oxidation.

The configurations (e and f) indicate the possibility of splitting of oxygen molecule and replacing hydrogen from the bridge configurations with atomic oxygen. The final configurations in both the cases show that the bond between hydrogen and Boron has been broken and replaced by oxygen. The configurations also show some structural changes, which can lead to altered material properties. The trend of chemisorbed species having a significant larger binding energy has also been observed in Boron Hydride, configuration f is the most stable configuration.

Table 5 Binding Energy of oxygen molecule at different configurations of Boron Hydride

Configurations	Binding Energy (eV)
a	-0.9261999
b	-0.9336799
c	-1.1884399
d	-1.0263899
e	-4.7688799
f	-5.7111099

5.2.5 Effect of Vacancies

In the works of Rojas et al. it was experimentally realized that Boron Hydride sheet has vacancies [19]. An effort is made to check the interaction of oxygen with the vacancy. The defects in general provide more reactive configurations. Further, inclusion of defects in the simulation mimics the reality better than pristine substrate.

Hence to present a thorough picture of chemical stability of Borophane on oxidation, vacancies were created. A Boron vacancy was created by removal of a single Boron atom from the Boron Hydride sheet to create a vacancy. Four different configurations were then created, two each for the singlet and triplet state of oxygen. The aim of this setup was to identify if the presence of vacancies leads to a reactive configuration.

5.2.5.1 Structural Characteristics

Vacancy had a pronounced effect on the warping of the structure. The tendency of oxygen to chemisorb around the vacancy, led to distortion of the plane in all the four configurations. Configuration a show the possibility of that one oxygen atom can form in-plane bond with Boron atoms near the vacancy. However, in configurations b, c and d the oxygen forms bonds with only one Boron atom. The lattice constants of defective Boron Hydride configurations varied between approximate a ~ 3.001 Å to 3.0012 Å and b ~ 5.22 Å to 5.29 Å. These lattice constant values are approximate since there is a loss of periodicity in the structure after introduction of vacancies. The lattice constants of the unit cell of relaxed 2D Boron Hydride were a = 3.002 Å and b = 5.295 Å.

5.2.5.2 Oxygen adsorption on defective Boron Hydride

The simulation results show that even when though the configuration a was initialized in the triplet state, the oxygen underwent transition to singlet state and the atomic oxygen then chemisorbed on the Boron

Hydride layer. Presence of vacancy affected the transition of oxygen molecule. However, for configuration b, we found that the oxygen did not split into singlet state, but formed a hydrogen peroxide like structure with the oxygen-oxygen bond length as 1.47 Å and bonds were formed with the hydrogen. Configurations c and d both indicate a preference to specific Boron atoms around the vacancy.

The binding energy of configuration a was the highest amongst all the configurations. In this configuration one of the oxygen atoms forms bonds with two Boron atoms near the vacancy and goes into the plane. The configuration b has a slightly higher binding energy compared to physisorbed state, but lower binding energy compared to chemisorption in singlet state. This configuration reveals a presence of a bond of intermediate strength. Further, if we compare the configurations a, c and d, with the chemisorbed configurations for Boron Hydride without defects, we can clearly see a rise in binding energy. This can be explained by the increased reactivity of Boron around vacancies for oxygen. This result shows that unlike adsorption of water molecule on Boron Hydride sheet, the vacancies play a role in adsorption of oxygen.

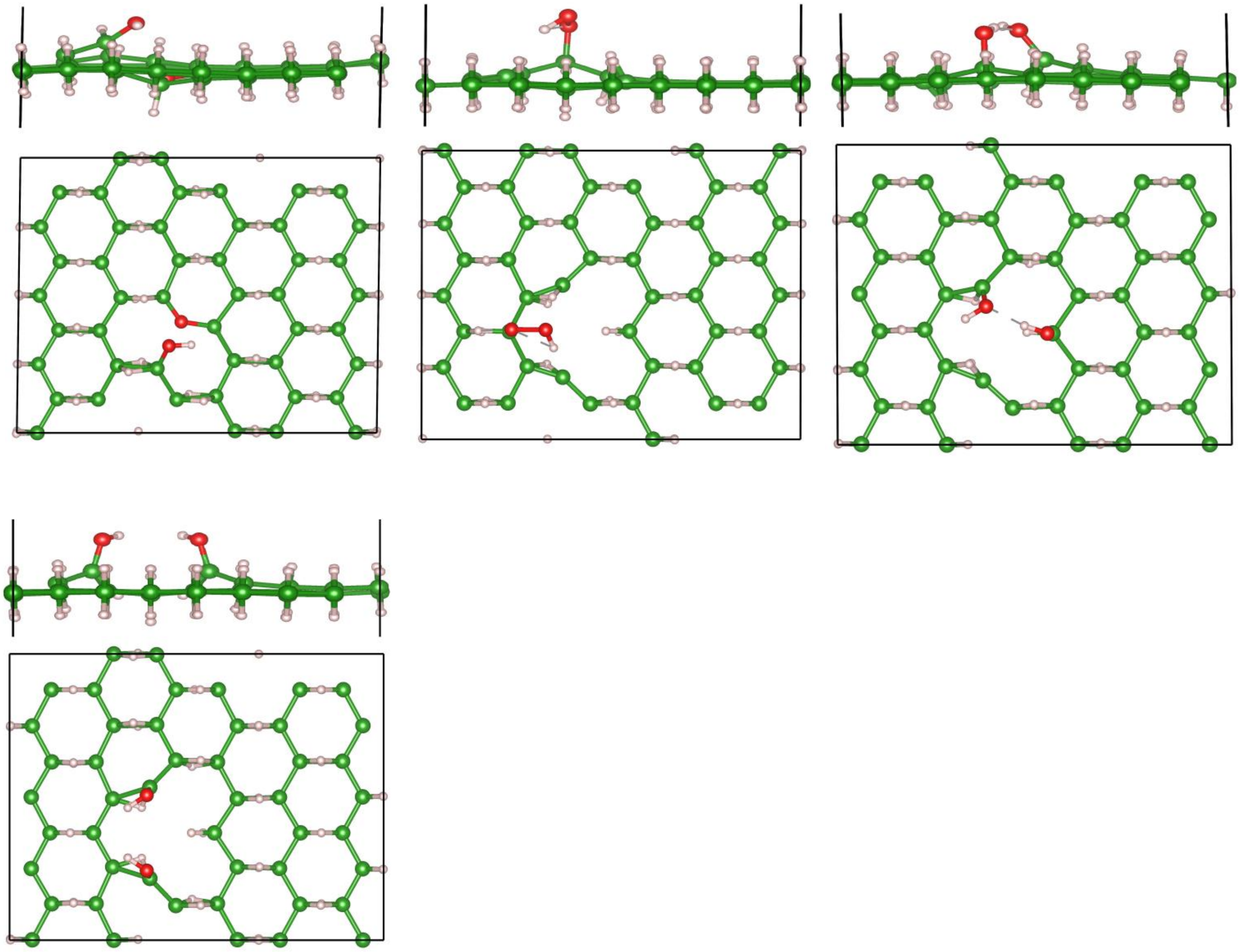

Figure 8 (left to right) Top and front view of configurations (a-d) of Boron Hydride sheet with a Boron vacancy. (Green atoms – Boron, red atoms – oxygen and pink atoms - hydrogen)

Table 6 Binding Energy of oxygen molecule at different configurations of Boron Hydride with a Boron vacancy

Configurations	Binding Energy (eV)
a	-9.5043499
b	-2.3965699
c	-7.1110099
d	-6.8495099

6 Summary

6.1 Conclusions

Calculation of binding energies through first principless calculations provided insights about the effect of interaction of oxygen with Boron-based 2D materials. Especially, the tendency of oxygen to chemisorb on the surface of Borophene sheet was evidenced by the significant energy drop in configuration C and Configuration D in Borophene sheet. Moreover, it was also observed during calculations that even with certain positions with oxygen in triplet state, the final relaxed configuration involved a triplet to singlet transition. These results are indicative of the reactivity of Borophene sheet with oxygen. This result is in line with the rapid oxidation of synthesised Borophene sheets under ambient conditions.

Passivating 2D Boron-based materials with hydrogen to increase the stability against oxidation holds credence according to the results of the simulation for both Borophane and Boron Hydride. It was found that the binding energy of oxygen on passivated structures in case of physisorption might be slightly higher due to interaction with surface hydrogen. However, a significant reduction of binding energy of oxygen is observed during chemisorption of atomic oxygen on passivated structures. The effect is more pronounced on 2D Boron Hydride compared to Borophane. Hence, indicating a higher relative stability of 2D Boron Hydride towards oxidation compared to Borophane.

Presence of oxygen, especially in the configurations involving chemisorption show severe mechanical deformations. Whereas, physisorption of oxygen for all three structures namely, Borophene, Borophane and Boron Hydride showed little to none deformation. The mechanical deformation could negatively impact the mechanical properties of the material. This further reiterates the advantage of passivating structure with hydrogen.

However, a more comprehensive picture must involve the activation barrier calculation for drawing more precise conclusions for tendencies of oxygen to chemisorb on the substrate. In order, to better compare the effect of passivation on the activation barrier.

Synthesis of Boron Hydride revealed the presence of vacancies, and the simulations were done to check if the vacancies are more stable configurations for the oxygen. Vacancies were then created in both Borophane and 2D Boron Hydride to simulate a more realistic substrate. Vacancies indeed provided configurations with higher binding energy for oxygen on both the passivated structures. However, configurations of defective Borophane in physisorbed state showed a low binding energy compared to Borophane without vacancy. This indicates that the single Boron vacancy in Borophane does not provide a stable site for physisorption of oxygen, however the site is more reactive towards chemisorption compared to pristine Borophane. Tendency of formation of hydrogen peroxide was also observed in two cases, indicating a weakening of hydrogen-Boron bond near the vacancy.

The objectives of the thesis to investigate chemical stability of Boron-based 2D materials against oxygen and the effect of vacancies on oxidation were achieved.

The results of simulations for vacancy deformation underlines the importance of including defects while performing first principles calculations on DFT framework.

Lastly, it should be noted that this calculation only includes the binding energy for one molecule of oxygen, introduction of more oxygen molecules could further lower the binding energy through steric effects.

6.2 Recommendations and Future Work

The work presented in this thesis opens up the possibility of testing variety of 2D materials for their chemical stability. Different allotropes of Borophane and Boron Hydrides can also be tested using the same methodology owing to their structural similarity.

Furthermore, different types of vacancies can be created and tested according to the likelihood of their existence as calculated from thermodynamic data or experimental results.

Moreover, the activation barrier calculations through Nudged Elastic Band (NEB) calculations can be done to provide a more holistic idea about the oxidation process.

Phonon Dispersion relations can also be used on the relaxed configurations to validate the existence of the structures obtained through DFT simulations.

A combination of all these studies can provide a thorough analysis of chemical stability of a 2D material in the operating environment. The approach hence can be used to model any reactive specie from the environment on the substrate. The wide-ranging applicability of this study and its real-world significance should not be ignored while considering development of a novel 2D material for any application.

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Appendix

A. *Binding Energy of oxygen on Defect-free Borophene for each configuration and orientation*

Configuration	Binding Energy (eV)
a-Diagonal	-1.1600399
a-Horizontal	-1.1440799
a-Vertical	-1.1246299
b-Diagonal	-1.1710199
b-Horizontal	-1.1713199
b-Vertical	-0.62226990
c-Diagonal	-1.1884399
c-Horizontal	-1.0425599
c-Vertical	-0.47959990
d-Diagonal	-0.62323990
d-Horizontal	-1.1932599
d-Vertical	-1.0566899
e-Diagonal	-1.1837199
e-Horizontal	-1.1621999
e-Vertical	-1.1553940
f	-5.2027499
g	-6.1478399

B. Binding Energy of oxygen on Defect-free Borophene for each configuration and orientation

Configurations	**Binding Energy (eV)**
a-Diagonal	-0.9144627
a-Horizontal	-0.92619990
a-Vertical	-0.903584
b-Diagonal	-0.91482350
b-Horizontal	-0.92334643
b-Vertical	-0.93367990
c-Diagonal	-1.1884399
c-Horizontal	-0.78207990
c-Vertical	-0.938258529
d-Diagonal	-1.0263899
d-Horizontal	-0.97346875
d-Vertical	-1.03494589
e	-4.7688799
f	-5.7111099