



ISSN: 0067-2904

Ab initio Study of the Electronic and Optical Properties of Stable Boron Sheet

Aqeel M. Ali^{1*}, Ali H. Al-Mowali²

¹Polymer Research Center, University of Basrah, Basrah, Iraq

²Chemistry Department-College of Science-University of Basrah-Basrah-Iraq

Received: 15/12/2020

Accepted: 5/7/2021

Abstract

Utilizing first principles calculations within PW91 exchange-correlation method, we investigated a boron sheet that exhibits related electronic properties. The 2-dimensional boron sheet is flattened and has an atomic structure where the pair cores of every three ordered hexagons within the hexagonal network are loaded up by extra atoms, which saves the triangular lattice symmetry. The boron sheet takes possession of intrinsic metal properties and the electronic bands are comparable to the π bands of the graphene that are close to the Fermi level. The real and imaginary parts of the dielectric function show a metallic or semiconductor behaviour, depending on the electric field direction.

Keywords: Borophene, DFT, Band structure, Electronic properties, Optical properties.

من المبادئ ال، ولية دراسة الخصائص الالكترونية والضوئية لشريحة بورون مستقرة

عقيل محسن علي^{1*}، علي حسين الموالي²

¹مركز أبحاث البوليمر، جامعة البصرة، البصرة، العراق

²قسم الكيمياء، كلية العلوم، جامعة البصرة، البصرة، العراق

الخلاصة

أعتامادا على حسابات المبادئ الاولية ضمن طريقة تبادل-ترايب PW91، أجرينا أستقصاء سلوك الخصائص الالكترونية المهمة لشريحة من البورون. شريحة البورون ثنائية البعد تكون مسطحة وذات هيكل ذري يمتلك زوجين من اللب ثلاثي نظام شبكة السداسية المعبئة بذرات إضافية، والتي تحافظ على التناظر الشبكي المثلي. تمتلك شريحة البورون خصائص معدنية داخلية. و ذات تركيب حزم الكترونية مقارنة لحزم في الكرافين قرب مستوي فيرمي. تظهر دالة العزل الكهربائي بفرعيها الحقيقي والخيالي سلوكا معدنيا أو شبه موصل تبعاً لاتجاه المجال الكهربائي المسلط.

*Email: aqeel.mohsin@uobasrah.edu.iq

1. Introduction

The delocalization and sp^2 hybridization of boron electrons lead to rich chemical properties that make it second to carbon as a candidate of having many crystal structures [1, 2]. The electron deficiency of this 5th element in the periodic table presents crystal structures that build up a complex bonding type, called multicenter bonds, that are significant due to their subsistence in bountiful compounds [3-5]. Theoretical and experimental researches have been carried out on boron two-dimensional (2D) sheet. Recent reports are focused on the two dimensional arrangement of boron, as in the triangular lattice [6, 7]. A completely metallic boron planar nanostructure was assembled on a silver substrate, named borophene. Boron element has the potential to be utilized to build a stable monolayer structure by mixing honeycomb and triangular units [8]. This framework consists of two atoms per the unit cell, which is called $2B:Pmmn$ crystallographic or orthorhombic crystal system (59 $Pmnm$ space group). According to the multicenter bonding design and depending on substrate types, the well-defined geometries of borophene are organized in a variety of polymorphs with commensurate cohesive energies but, however, with diverse properties. As a result of complicated bonding characteristics, the boron single layer was suggested to have Dirac points [9-11].

However, experimental studies are still lacking, while electronic structures have been explored only by theoretical researches. The borophene monolayers are metallic with significant anisotropy behaviors. Moreover, borophene has a permittivity in the range of 0-2 eV, indicating that it has a hyperbolic characteristic [12]. To attain utility of borophene as an optoelectronic substance, it is indispensable to explore its intrinsic properties [13-19]. According to studies based on the density functional theory (DFT), the band structure of borophene allotropes of different atomic geometries is metallic or semi-metallic and may have Dirac cones near or at the Fermi energy level. However, it is very important to understand the effects of the structure of borophene on its electronic properties [20-23]. Through the utilization of DFT computations, we herein theoretically analyzed possible geometry, band structure, and photo-activities of a borophene monolayer.

2. Computational methods

We have played out the computations of the all-out energies of the boron sheet utilizing the CASTEP (*Cambridge Serial Total Energy Package*) [24]. We utilized the exchange-correlation method described by Perdew and Wang (PW91) with the generalized gradient approximation (GGA). We made the plane-wave cut-off energy setting to be about 320 eV, while the force convergence criterion on every atom was set at 0.01 eV/Å. The interlayer partition was set at 9 Å, which is proper to create isolated systems. The Brillouin region was tested by using the Monkhorst-Pack sketch of K, Γ , M, and K. The minimization of the total energy was applied for the full optimization of the lattice constants and the internal atomic coordinates. The equilibrium points of the crystal structures were reached through geometry optimization in the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme. The boron flat sheet was completely relaxed through a k space mesh of $9 \times 9 \times 1$, while the mesh was expanded to $20 \times 20 \times 1$ to acquire the rigorous energies with atoms stationary after relaxations.

The unit cell, that has 32 atoms, and the hexagonal lattice vector are shown in Figure 1. The complete restful crystal structure is acquired by means of the geometry optimization with relation to lattice constants half-and-half interior atomic positions. The optical properties are determine based on the dielectric function of the atomic systems by using the Kramars–Kroing relation that depends on the real and imaginary parts of the dielectric tensor [25].

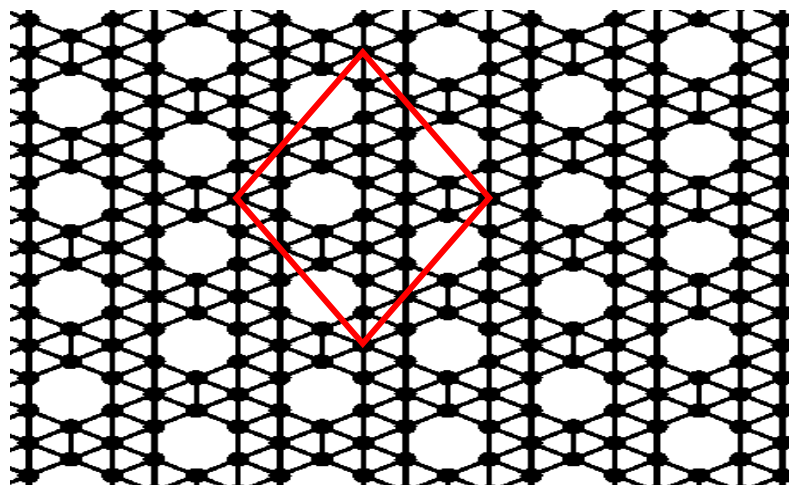


Figure 1-The structure of the studied boron sheet. The lattice vectors (red lines), $a_1 = a_2 = 8.8234 \text{ \AA}$.

3. Results and discussion

3.1 Electronic properties

Here we show an analysis for the band structure of borophene. The band structure of borophene, with geometry optimized lattice parameters, along the high symmetry directions within the first Brillouin zone is shown in Figure 2.a. The band structure is curved smoothly like the electronic π bands of the graphene sheet close to the Fermi energy level, that is degenerated at the Γ symmetry point, nearly 0.5 eV over the Fermi energy level. The Fermi level of the studied 2D boron crystal reclines at Γ point, just underneath the maximum of valence band. The occupied valence bands extend beginning from -2.7 eV and ending at the Fermi level E_F . The valence band crosses the Fermi level, creating the framework semi-metallic. The dispersive kernel of the band structure over the Γ - K orientation elucidates good electronic conveyance. The density of states has a necessary role in the interpretation of the physical properties of atomic systems. We illustrate the investigated partial density of states (PDOS) at normal pressure, as represented in Figure 2.b. The PDOS has a high value of $N(E_F)$ at the Fermi level of 1.0 states/eV per unit cell. The DOS around the Fermi level emerges predominantly at the $2p$ electronic states.

As indicated by the diagrams, at Fermi energy, there is nonzero density of states. This means that there is a significant overlapping among the valence and conduction bands. The zero energy gap indicates a metallic property that is additionally affirmed by band structure. Totally unlike numerous 2-dimensional layer materials that are either semimetal or semiconductor, borophene has a metallic property which has been described in different works [26-28]

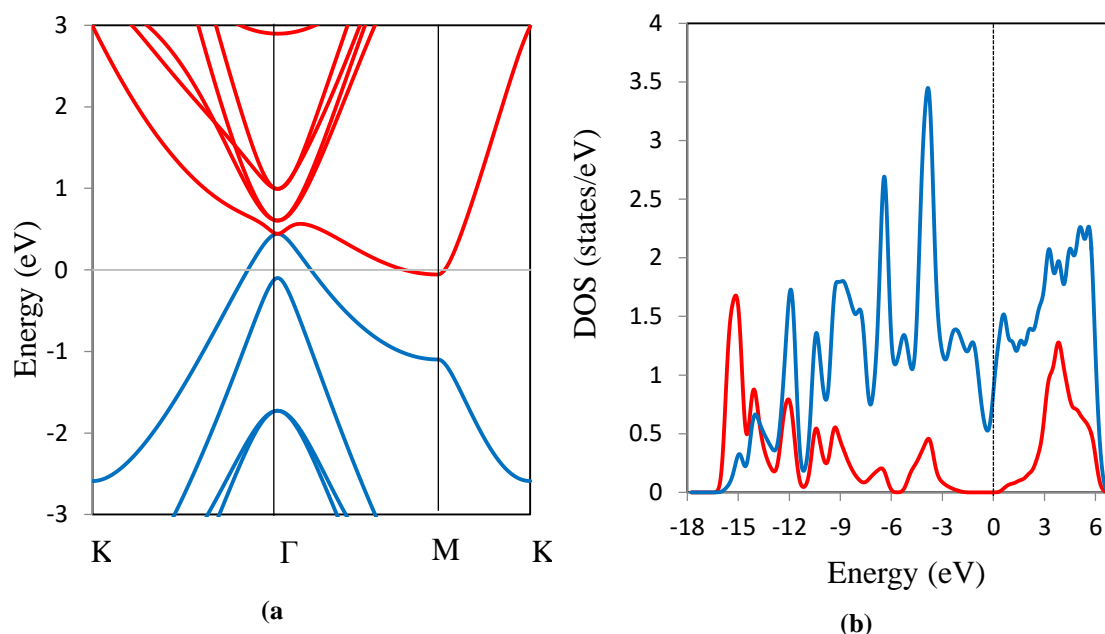


Figure 2-Electronic properties of the tested boron sheet. (a) Band structure; valance band (blue) and conduction band (red). (b) Density of states; *p*-orbital (blue) and *s*-orbital (red).

3.2 Optical Properties

Both dielectric function parts (real and imaginary) are displayed in Figure 3.a and 3.b. The two directions, *x*-axis (parallel) and *z*-axis (perpendicular), to the plane of the sheet are, respectively, utilized to show the response of the crystal under the electromagnetic field. The material response depends completely on the band structure. The dielectric function is the substance reaction toward the electromagnetic radiations, indicating energy propagation, absorption reflection, and energy dissipation. Thus, at any position where a portion of the dielectric function is negative, an absorption or a reflection happens for electromagnetic waves. The imaginary and real parts are associated by a set of equations, preferably the Kramers–Kroing equation, which are prospective to define the optical real part of the response through knowing the imaginary part function at the whole range of wave-frequencies [29]. The dielectric function comprehends two kinds of transitions; the first one is the interband transition that is a consequent process to the electronic excitation, while the second one is the intraband transition that is a consequent process to a bulk Plasmon excitation. The imaginary part is estimated via taking into account the whole probable transitions from occupied to empty states. Figures 4 and 5 show the positive static magnitude of the real part in the *x* direction, which has proceeded to the negative value over the *z*-axis of direction at 1.6 eV. Subsequently, by changing the incident angle of light with respect to the plane of structure, it is prospective to find out a nearly semiconductor action vertically to the sheet and a metallic behavior at the right side of the sheet. By means of increasing the energy of the outward photon over the *x* direction, there is an intense minimization at the limit of the visible zone with regard to the real part, which arrives to a zero value, whereas the response develops together with a temperate slope thereafter to 3.0 eV. Along these lines, the response continuity prompts a totally firm and adjusted optical response inside the referenced domain of borophene. Over the *x* and *z* directions, the optical responses next to the value of 4.5 eV are

constantly zero, thus the optical activity of borophene conducts like a vacuum space following the value of 5 eV in the two directions.

In compliance with the dielectric imaginary part (Figure 3 a and b), it may be implicated that the value of imaginary part is 2 and 1 at zero energy for z and x direction bringing to light a semiconductor behavior whereas it resorts to high positive and (8 at z direction) (4 at x direction) value representing the metallic characteristic. The imaginary part peaks confirm the transitions of interband manner. In both directions, a single peak is monitored at an energy value of 0.9 eV, clarifying the interband transitions. In fact, every peak within the characteristic of the dielectric imaginary part may be determined to the interband transition.

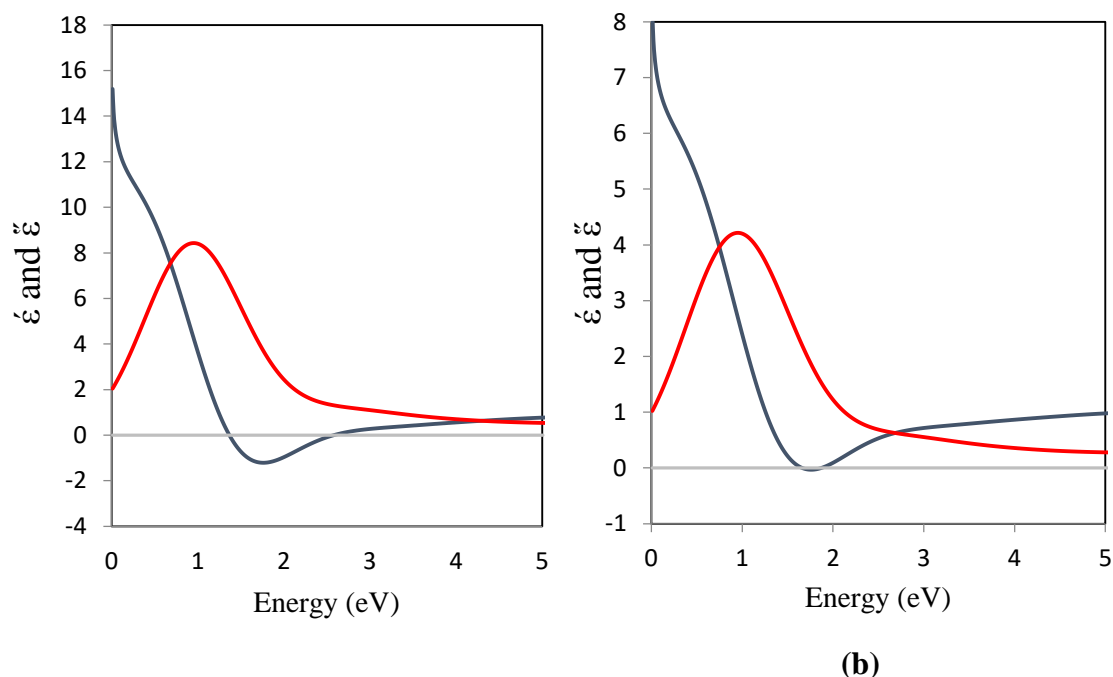


Figure 3-Dielectric functions of borophene, real (blue) and imaginary (red) (a) at z -direction (b) at x -direction.

3. Conclusions

We investigated the electronic and optical properties of a 2D boron structure (borophene). The borophene is tabular and perpetuates the triangular lattice symmetry. In compliance with the density of the electronic band structure and states, it may be very well foreseen that such substance holds the characteristics of a metal. The optical properties, thorough the dielectric function parts, were inspected and dissected in the z (perpendicular) and x -axis (parallel) directions. Moreover, the metallic and semiconductor characteristics were found with the perpendicular and parallel orientations, respectively. Whereas the optical characteristics are regularly extraordinary near lower energies for various orientations, they are nearly in accordance with one another near higher energies.

References

- [1] J. Kunstman and A. Quandt, "Broad boron sheets and boron nanotubes: An *ab initio* study of structural, electronic, and mechanical properties," *Physical Review B*, vol. 74, 035413, 2006.
- [2] K. Lau and R. Pandey, "Stability and Electronic Properties of Atomistically-Engineered 2D Boron Sheets" *Journal of Physical Chemistry C*, vol. 111, no. 7, pp.2906-2912, 2007.

- [3] H. Tang and S. Ismail-Beigi, "Novel Precursors for Boron Nanotubes: The Competition of Two-Center and Three-Center Bonding in Boron Sheets" *Physical Review Letters*, vol. 99, 115501, 10 September, 2007.
- [4] A. M. Ali and A. H. Al-Mowali, "Stability and Electronic Properties of C60Chain Polymer: DFT study" *Journal of Natural Sciences Research*, vol. 4, no. 2, p. 13-17, 2014.
- [5] X. Yang, Y. Ding and J. Ni, "Ab initio prediction of stable boron sheets and boron nanotubes: Structure, stability, and electronic properties" *Physical Review B*, vol. 77, 041402R, 2 January, 2008.
- [6] N. G. Szwacki, A. Sadrzadeh and B. I. Yakobson, "B₈₀ Fullerene: An Ab Initio Prediction of Geometry, Stability, and Electronic Structure" *Physical Review Letters*, vol. 98, 166804, 20 April 2007.
- [7] A. Lopez-Bezanilla and P. B. Littlewood, "Electronic properties of 8-Pmmn borophene" *Physical Review B*, vol. 93, 241405(R), 15 June 2016.
- [8] T. Abasi, A. Boochani and S. R. Masharian, "Metallic and intra-band investigation of optical properties for Borophene nano-sheet: a DFT study," *International Nano Letters*, vol. 10, no. 1, p.33-41, 2020.
- [9] M. Nakhaee, S. A. Ketabi and F. M. Peeters, "Tight-binding model for borophene and borophane," *Physical Review B*, vol. 97, 125424, 21 March 2018.
- [10] H. Tang and S. Ismail-Beigi, "Self-doping in boron sheets from first principles: A route to structural design of metal boride nanostructures," *Physical Review B*, vol. 80, 134113, 15 October 2009.
- [11] L. C. Xu, A. Du and L. Kou, "Hydrogenated borophene as a stable two-dimensional Dirac material with an ultrahigh Fermi velocity," *Physical Chemistry Chemical Physics*, vol. 18, p. 27284-27289, 2016.
- [12] E. S. Penev, A. Kutana and B. I. Yakobson, "Can Two-Dimensional Boron Superconduct," *Nano Letters*, vol. 16, No. 14, p. 2522–2526, 2016.
- [13] A. M. Ali, "PBC-DFT study of the electronic properties of 1,3,4-thiadiazole polymers: Substitution Linkage effects," *Iraqi Journal of Polymers*, vol. 22, no. 1, p. 43-54, 2018.
- [14] A. M. Ali and A. H. Al-Mowali, "Doping, Vacancy formation and Substitutional Effects on Semiconductor Selectivity of Rutile TiO₂ Crystal," *Chemistry and Materials Research*, vol.3, no.2, p. 22-31, 2013.
- [15] A. M. Ali, "First-principles calculations of the electronic structure of C20, electric field, and monomer interaction effects," *Canadian Journal of Physics*, vol. 91, no.1, p.81-84, 2013.
- [16] A. M. Ali, "First-Principle Investigation of The Alkali Metal Interactions With MgO Armchair - Nanotubes," *journal of kerbala university*, vol. 1, no. المؤتمر العلمي الاول لكلية العلوم, p. 135-145.
- [17] A. M. Ali, "Electron Transport in N-doped Graphene Nanoribbon," *Journal of Scientific and Engineering Research*, vol. 7, no. 1, p.179-184, 2020.
- [18] A. M. Ali and A. H. Al-Mowali, "DFT Study of Poly Furfuryl Alcohol-Rhodamine B Blend," *Advances in Chemical Engineering and Science*, vol. 4, p. 161-166, 2014.
- [19] A. M. Ali and A. H. Al-Mowali, "Ceramic Expansion by Water Layers on Magnesium Oxide: ab Initio Study," *American Journal of Materials Science and Engineering*, vol. 1, no. 3, p. 50-53, 2013.
- [20] A. M. Ali, "A Electron transport study on ultrathin armchair graphene nanoribbon," *Journal of Kufa-Physics*, vol. 11, no. 2, p. 62-72, 2019.
- [21] A. M. Ali and A. H. Al-Mowali, "Electronic Properties Of Donor-Bridge-Acceptor Molecular System," *Iraqi Journal of Polymers*, vol. 22, no. 1, p. 106-112, 2018.
- [22] A. M. Jassem, A. H. Raheemah, W.A. Radhi, A. M. Ali and H. A. Jaber, "Highly Diastereoselective Metal-Free Catalytic Synthesis of Drug-Like Spiroimidazolidinone," *Russian Journal of Organic Chemistry*, vol. 5, no. 10, p.1598-1603, 2019.
- [23] A. M. Ali, "Theoretical Investigation for Neon Doping Effect on the Electronic Structure and Optical Properties of Rutile TiO₂ for Photocatalytic Applications by Ab Initio Calculations," *Journal of Physical Science*, vol. 23, no. 2, p. 85–90, 2012.
- [24] Clark S J Segall M D Pickard C J Hasnip P J Probert M J Refson K & Payne M C "First principles methods using CASTEP", *Zeitschrift fuer Kristallographie*, 220 (5-6) (2005) 567-570. 25 Mannix A J, *Science*, 350 (2015) 1513.

- [25] A. A. Al-Jobory, W. I. Ahmed and J. A. Ibrahim, "Electronic Structure and Optical Properties of GaAs_{1-x}P_x: A First-Principles Study" *Iraqi Journal of Science*, vol. 61, no.1, p. 77-82, 2020.
- [26] A. J. Mannix, "Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs," *Science*, vol. 350, no. 6267, p. 1513-1516, 2015.
- [27] B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen and K. Wu, "Experimental realization of two-dimensional boron sheets," *Nature Chemistry*, vol. 8, no. 6, p. 563-568, 2016.
- [28] B. Peng, H. Zhang, H. Shao, Z. Ning, Y. Xu, G. Ni, H. Lu, D. W. Zhang and H. Zhu, "Stability and strength of atomically thin borophene from first principles calculations," *Materials Research Letters*, vol. 5, no. 6, p. 1-9, 2017.
- [29] I. M. Ibrahim, A. S. Mohammed and A. Ramizy, "Energy Band Diagram of NiO: Lu₂ O₃/n-Si heterojunction" *Iraqi Journal of Science*, vol. 59, no.1B, p. 287-293, 2018.