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Review of the doctoral dissertation of Isabel Maria Arias-Camacho, M.Sc., entitled: "Effects of the adsorption of harmful gas molecules on boron-based materials"

The doctoral dissertation of Isabel Maria Arias-Camacho, entitled: "**Effects of the adsorption of harmful gas molecules on boron-based materials**" was submitted at the University of Warsaw (UW) under the supervision of Dr. hab. Nevill Gonzalez Szwacki. The student conducted this study mainly Institute of Experimental Physics, Faculty of Physics

The dissertation is in the form of a collection of papers with 4 manuscripts; all these manuscripts have been published in international peer-reviewed journals. The impact factor of the papers is 3.2, 4.3. 6.3 and 2.4, respectively. Other two papers published in international peer-reviewed journals are mentioned but not included in the collection of paper. The student is the first author of all four papers. The student is the corresponding author for the first and third paper, while the supervisor is he corresponding author for the other two. The papers included in this Ph.D. thesis have garnered 8 citations on Scopus https://www.scopus.com/authid/detail.uri?authorId=58513579400 at the present date; the number is low because all papers were published in the last 2 years.
Arias-Camacho's dissertation takes 112 pages. The thesis is composed by an Introduction; the second chapter is devoted to the methodology. The third chapter contains the 4 manuscripts, while in the fourth and last chapter there is a short summary of the published results.

Chapter 1 is an introduction on the field of the Borophene, borophene polymorphs, two-dimensional materials Mbenes relevant for the PhD thesis and an introduction to the harmful gases. The author wrote about the role of the sensors and how the two-dimensional materials learning can be used in the context of the density functional theory.

Chapter 2 is devoted to the methodology. The Ph.D. candidate described how the Schrödinger equation governs quantum systems. For larger systems, approximations like the Born–Oppenheimer method separate slow-moving nuclei from electrons. The Hartree–Fock approach models electrons as independent particles interacting via an average potential. It uses spin orbitals combined in a Slater determinant to satisfy antisymmetry and the Pauli principle. Hartree–Fock neglects full electron correlation, so post-Hartree–Fock methods are employed to improve accuracy. It was shown that Density Functional Theory (DFT) instead focuses on electron density rather than many-body wave functions. The Kohn–Hohenberg theorems establish that ground-state properties are uniquely determined by the electron density. The author described how, within the Kohn–Sham equations, the electron density is computed iteratively until self-consistency is achieved. Approximations such as LDA, GGA, and hybrid functionals were used in the thesis. Finally, there is a description of phonons, linear-response methods to determine the Hubbard correction, the electronic conductivity and approaches to evaluate the charge. The chapter is extensive and accurately describes the main features of all these methods.

Chapter 3 is the core of the thesis. It consists of 5 subsections, the first serves as an introduction to the main results where in the other 4 subsection the 4 manuscripts were reported. Paper I studies the Borophene sheets as potential candidates for the detection and removal of harmful gas molecules, paper II

describes Exploring the Structural, Electronic, Magnetic, and Transport Properties of 2D Cr, Fe, and Zr Monoborides. Paper III investigates the Influence of the Hubbard U Parameter on the Structural, Electronic, Magnetic, and Transport Properties of Cr/Fe/Zr-Based MBenes. Finally, paper 4 focuses on Exposure of MBenes to environmentally hazardous molecules.

Subsection 3.2 reports The discovery of graphene initiated the exploration of two-dimensional materials with exceptional properties. Borophene, a mono-elemental member of the Xenes family, exhibits unique bonding and multiple polymorphs. This work examines three borophene structures: buckled hexagonal, α-sheet, and honeycomb-like forms. Their interactions with five hazardous gases (CO, CO_2, NO, NO_2, NH_3) are systematically studied. The α-sheet and honeycomb structures are analyzed in detail, with the buckled form as a reference. Findings suggest borophene's strong potential for toxic gas sensing and capture applications.

Subsection 3.3 reports the MBenes are a newer class of 2D materials with diverse structures and properties. This study uses density functional theory to analyze orthorhombic and hexagonal M_2B_2 (Cr, Fe, Zr). Both symmetries exhibit metallic behavior and dynamic stability, suggesting feasible synthesis. Some ferromagnetic forms show magnetic moments above 2.5 $\mu B/M_2B_2$, indicating strong 2D magnetism. These findings advance MBene research with potential applications in energy, sensing, and catalysis.

Subsection 3.4 is devoted to a paper where the candidate show how MBenes are exceptional mechanical, electronic, magnetic, and chemical properties, making them promising for catalysis and 2D magnetism. A density-functional theory study analyzed their orthorhombic and hexagonal phases. Results reveal metallic behavior, energetic stability, and strong dependence on initial theoretical conditions. Certain phases, like orthorhombic Cr_2B_2, exhibit very high magnetic moments, enabling room-temperature magnetism. These characteristics highlight their potential in energy, sensing, catalysis, biotechnology, and spintronics.

Subsection 3.5 includes a paper published where the author show why 2D materials are promising for gas sensing due to their stability and large surface area. MBenes (Cr_2B_2, Fe_2B_2, Zr_2B_2) exhibit strong electronic and physicochemical properties favorable for molecule adsorption. This study used first-principles calculations to analyze their interactions with CO, CO_2, H_2O, NH_3, NO_2, SO_2, O_2, and N_2. Adsorption sites, charge transfer, electronic structure, and magnetism were systematically examined. Results show these MBenes are suitable for gas detection and nanotechnology-based sensor applications.

In **Section 4**, the author provides a three pages summary about the presented papers, highlighting the main results of the research.

After analyzing the above result, I have some questions and remarks which are reported below with the latter Q and R in addition to their number:

Q1) In the paper 1, you showed how Borophene sheets as potential candidates for the detection and capture of harmful gas molecules such as CO, CO_2, NO, NO_2, and NH_3. However, do we need to check if Borophene captures also non-harmful molecules as O_2 and N_2?? Indeed, this was done in paper 4.

Q2) In the paper 1, what is the need to calculate the conductivity relative to the interaction with the gas? Because the change in the conductivity will work as sensor?

Q3) Regarding the magnetism in paper I, are the magnetic moment localized on some atoms? Which one? the nitrogen?

Q4) Related to manuscript 2 and 3, I do not think that sigma_zz make sense for 2D systems. Is this why it is always zero?? Are sigma_xx and sigma_yy equal by symmetry in the P6/mmm crystal structure?

Q5) In the Figure 2 of paper 4 (and also in similar magnetic configuration), there are several possible magnetic configurations with 8 atoms, why did you choose that ones in Figure B12? Any special reason?

Q6) Have you tested the ground state for altermagnetism? The magnetic configuration of Fe2B2 in figure 2 of paper 4 looks a potential candidate for altermagnetism.

R) Sometimes the captions of figures where extremely short as Figure 3 of paper 4 or Figure 6 of paper 3.

In summary, the motivation for this research is presented clearly and with precision. The thesis is well-edited, and the text is legible and grammatically accurate, making it easier to analyze and evaluate the results. The candidate performed an enormous number of calculations considering different crystal structures, different molecules and different Coulomb repulsions. All the theoretical figures (most of them are likely obtained from the Ph.D. candidate) in the four papers are very detailed, striking and well-structured.

The research conducted by the Ph.D. candidate is on the field of the detection and capturing of harmful gases. This research trend is very interesting from the scientific and applicative point of view. Despite some secondary questions, the doctoral dissertation of Isabel Maria Arias-Camacho, M.Sc., in my opinion, meets all the quantitative and qualitative criteria for doctoral dissertations in the field of Natural sciences in the discipline of physical sciences. The doctoral dissertation presents the candidate's general theoretical knowledge in physics as well as the ability to independently conduct scientific work. The subject of the doctoral dissertation is an original solution to a scientific problem. I conclude that my evaluation of the PhD thesis is POSITIVE. In connection with the above, I request that Isabel Maria Arias-Camacho, M.Sc., be admitted to the next stages of the doctoral procedure.

Signature 27 July 2025