UNIVERSITÉ DE NAMUR

Report on the PhD Thesis of Miłosz Martinow

The manuscript reports on two topics of investigation where high performance computing (HPC) calculations have been enacted to address questions of interest in the field of green technologies, i) hybrid organic-inorganic perovskite materials for solar cell applications and ii) bimetallic organometallic compounds for molecular photocatalysis and H_2 production. For both cases, the topic is nicely presented, highlighting the key issues and showing how HPC-based quantum chemistry calculations can be employed to address fundamental questions, in fact to go from basic knowledge to more practical aspects. This is performed by working in tandem with experiment, so that theory/simulations and experiment can improve each other.

The work is presented in the form of four publications, published in the best journals of the field, demonstrating the quality of the science. Besides the interest for the results on the different types of compounds, the PhD thesis also i) addresses more technical aspects, which are particularly important when performing quantum chemistry (DFT and TDDFT) calculations, including the choice of cut-offs and ii) deals with HPC issues since the calculations are performed on complex (large) systems.

Among these high-quality investigations, I would like to point out the way doping effects (on geometry and properties of perovskites) have been tackled by developing an iterative scheme. I have been much impressed by the elegant treatment of these different doping rates, which can go up to the understanding of phase transitions (change of space group). Then, for the bimetallic systems, the DFT/TDDFT study has highlighted how the photocatalytic first steps can be explained (excitation, charge transfer) and how the calculations can help comparing compounds (which differ by either the nature of one metal center or of the halogen atoms).

Yet, a few minor comments can be raised

- MA, methyl ammonium is not a molecule but rather a cation and its formula is $CH_3NH_3^+$ rather than CH_3NH_3.
- p. 22, it is written that, owing to the Hohenberg and Kohn theorem, all properties can be determined from the ground state electron density. I think this is only correct for ground state properties and therefore not for excitation energies.
- in Eq. (6) the sum over N should be specified, especially because the electrons can be of α or β spins
- in Eq. (20), is there any conditions (and consequence) on choosing the translation operator? An equivalent expression (with any definition of the translational vector) can certainly be written for the electron density rather than KS orbitals but for the KS orbitals, this seems to correspond to cyclic periodic conditions, which requires some precisions.
- in some figures (A1-S1), the use of logarithmic scale (for y) would have help seeing the details of the convergence of the total energy as a function of the cutoff(s).

In summary, this is an excellent piece of work and I congratulate Mr. Miłosz Martinow for it.

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Dear Rector of the Gdańsk University of Technology,

It is a honor for me writing a review on the doctoral dissertation of Mr. Miłosz Martinow. Thank you for this invitation. I appreciated a lot reading Mr. Martinow's manuscript. It is an excellent work. You will find on the next page my review, including a few comments.

Sincerely yours,

B. CHAMPAGNE

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