In Prague, May 3rd, 2019

Re: Pengbo Lyu– Evaluation of the Ph.D. Thesis "*Theoretical Investigation of Novel Two-dimensional Materials with Application Potential*"

I had a pleasure to read and evaluate the Ph.D. thesis of Pengbo Lyu (also referred to as the candidate) entitled "*Theoretical Investigation of Novel Two-dimensional Materials with Application Potential*" (in the following referred to as the thesis). The thesis summarizes candidates' efforts in the field of computer modeling of two-dimensional (2D) materials, done in a close collaboration with experimentalists. Employing state-of-the-art computational modelling approaches, the candidate not only helped the experimentalists to resolve different problems in 2D materials science but, in addition, provided deeper understanding of 2D materials to enable improvement of their properties and rational design, and predicted several novel materials with specific properties.

From the formal point of view, the thesis comprises approximately 100 pages of text which includes synopsis of 14 research articles (12 already published and attached as appendices, and two in preparation). The candidate's contribution to the presented work varies from paper to paper. Most importantly, candidate is the main author of 3 papers (one published, two in preparation) and his contribution to other articles presented therein is well documented throughout the thesis.

The thesis is well structured with the four chapters (Introduction, Methods, Results and Discussion, Conclusions) well balanced in the amount of information, except Introduction which appears relatively brief and could contain more information particularly about specialized topic of magnetic compounds.

The thesis contains surprisingly large amount of language mistakes and typos, particularly in mixing plural/singular, adverb/adjective, mixing CTF and CFT, wrong past tense, and similar. On the other hand, this may be a good sign of independent writing of the candidate. The text is in - with some exceptions now and then - relatively easy to read and the scientific argumentation is clear. The clear writing and argumentation is, in my eyes, one of the important criteria to be fulfilled by a Ph.D. candidate. The abstract in Czech also suffers from language errors, yet it reads very well.

For the future writing I recommend candidate to use larger figures wherever possible. A number of presented figures is, though still somehow readable, rather small, and could be simply enlarged as there is space for it. This would improve readability of thesis without much effort, see for example Figures 4, 10, 13, 22, 23, 37, etc.

Regarding the scientific content of the thesis, the **Introduction** section explains studied materials and their properties, and appears rather brief, in my opinion. A more detailed Introduction would improve readability of the thesis, for example explaining some relatively unknown phenomena related to Section 3.4 (Chern insulator, Dirac half-metal, etc).

The theoretical background in **Methods** is given in a sensible size and detail, though I find the chapter on DFT a bit confusing, the explanation is not very logical, which is perhaps another sign of independent work of candidate. The "dimer" on page 12 is probably "dimer method". Also it is not immediately clear what is x_1 and x_2 in on page 15, though it becomes clearer later in the thesis.

Section **Results and Discussion** present scientific results of the thesis. Generally, the science presented, particularly in attached publications is very sound; some high-impact publications are present. I appreciate synergy of experiment and theory here, and using theoretical calculations in predictive mode. I like the short summary at the end of each subsection, which concludes very clearly the new insight obtained.

Regarding particular subsections, in 3.1, there is problem with some abbreviations not explained, neither given in list of abbreviations, such as HPP and TzF. I generally recommend in writing of larger manuscripts to occasionally repeat an abbreviation with full name. The geometrical parameters in Figure 4f are hard to understand. It is not clear from context what GW on page 27 is. I was absolutely lost in discussion of Table 5. Page 38 bottom: is that really reasonable agreement? Page 40: it is not clear from context what is it and why SAED. I like the models used in section 3.1 as well the synergy between theory and experiment therein, and I think conclusion are quite interesting for experimentalists. In section 3.3, page 52: is it relevant to fix cell volume, can the system properly relax? Page 56: it is not clear to me why orbital composition is shown (Figure 33b) and why it is important. Section 3.4 is very interesting but lacks more introduction regarding the studied properties, see specific questions below. Subsection 3.2.1 on page 71 should be 3.5.1 and is hard to understand. It is not clear from context what is, e.g. turbostatic disorder, (beq), kaolinite.inp, etc. I do not understand why there two maxima in Figure 47b, as the Figure 47d is hardly readable. This should be better explained.

I find the **Conclusions** section very well written, it very nicely summarizes the main results of the thesis. The thesis are well supported by literature.

My overall impression from the presented work is positive. Despite certain problems in style and clarity here and there (in the thesis) the presented studies are methodologically and technically

sound, the supervisor's group and experimental collaborators belongs to renowned experts in the field, and the presented results are interesting chemically, and of an interest to experimentalist, material's scientists, and potentially to general public. I particularly appreciate the insight, which theoretical calculations bring into studied materials. It is not a mere reproduction of experimental numbers, but calculations give understanding and hints how to improve studied materials. Moreover, the calculations may predict new experiments and new interesting materials.

Concerning the massive amount of the work presented, I might have tens of technical questions as my expertise is in a bit different field (simulating molecules) but I tried to select a few, which would be interesting for me, and which were not clear from the thesis, and I would be happy to hear the candidates' opinion on those topics.

In summary, the presented thesis show a high-level science carried out by the candidate throughout his Ph.D. studies and therefore, I recommend it is accepted as the material for the Ph.D. defense and ultimately for awarding the Ph.D. title.

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Questions:

1/ What is the purpose of the dumping functions in eqs. 2.20 and 2.21 can you explain or show some explanatory picture? It is well-known that D3 correction is rather important to correct wrong behavior of DFT regarding dispersion, but how critical/important is the damping for the accuracy of calculations? Can you show some examples?

2/ It looks through the thesis that simple DFT, GGA and hybrid, and DFT+U work, to me surprisingly well, at least for the properties and materials studied in the thesis. I usually do not see such beautiful agreement between experiment and theory in area of small molecules, perhaps only for the compounds of the lightest elements. How much can be DFT trusted e.g. in MXenes (Chapter 3.4.1 and 3.4.2)? Molecules with high spin are usually problem in molecular calculations, does it work better in 2D materials and why?

3/ How does one assure true minima in periodic boundary conditions? I assume the hessians are not calculated in most cases? What is general strategy in searching the lowest energy structures?

4/ Can you explain general chemist what is Dirac half-metal, QAH effect, and Néel

temperature ? Explanation of these phenomena is lacking in the Introduction and would improve readability of thesis.

5/ Regarding the materials predicted during the work, e.g. those in subsections 3.3 and 3.4. Has there been an attempt to prepare them, and if they have been prepared, do they have the corresponding properties or similar ones? If not, how easy would be their preparation?

6/ Imagine that I am an investor and I can give you 5 million dollars for next five years plus lab, computer cluster, and a team of skilled scientists. The only task for you would be to do a breakthrough in 2D materials. What would you do? Which materials, properties, methods you would be chasing? And what they would be good for? Present your vision.