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Studijní oddělení
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To whom it may concern,
I report here on the doctoral thesis of Mr. Narendra Prabhakar Arasu, who submitted the thesis in order to apply for the doctoral degree awarded by the Charles University.

Significance: The thesis applies the methods of theoretical condensed matter physics to actual problems in the field of electron transport through molecular bridges ("molecular electronics"). The results accompany the measurements of affiliated experimentalists from laboratories which are well established in the field.

Chapter 1: The introduction describes well the context of the work, it introduces some simple models and describes the computational techniques. It is complete and pedagogical. In this thesis, two theoretical techniques are employed: (1) *ab-initio* density-functional theory for equilibrium properties and (2) NEGF method for the calculation of molecular conductance. Given the complexity of the researched systems (molecules in contact with bulky metals), the techniques are adequate. However, the theoretical tools are not critically evaluated. For example, the author writes that results with the GGA functional have a "reasonable accuracy". I see that there is a plenty of room for developing a more critical attitude towards his numbers.

Chapters 2-4 embed the candidate's publications along with accompanying texts, which introduce the problem and indicate candidate's contribution to the published articles. The candidate himself describes too many experimental details and recipes of synthetic chemistry, many of them unrelated to his calculations (*e.g.* NMR measurement or toxicity of the precursors of a molecule). His motivation could have been to give the reader a broad background, but this came at the expenses of promoting his own creative contributions and defending the quality of his theoretical results. How do the results depend on the basis set, supercell approximation, the at times *ad hoc* geometry and parametrization of the functional? These questions are almost nowhere addressed and this is a critical omission, given that this is a theoretical thesis in the field of Condensed Matter Physics and Materials Research.

Chapter 5 establishes general rules that relate the conductance of aromatic and anti-aromatic molecules. The conductance can be affected by destructive quantum interference and this phenomenon is discussed in the state-of-the-art formalism of so called connectivity rules. In other terms, it establishes a general relation between a chemical structure and a physical property. It is a pity that the connectivity rules were not discussed at length in the thesis, for example, in the Introduction.

Conclusion: The thesis of the candidate presents new results in the field of molecular electronics. All results were published in peer-reviewed journals and therefore they are an advance in the field. Undoubtedly, the collaborations secure the high impact of the thesis. The drawback of the thesis is, that it nowhere goes beyond the application of established techniques, which are implemented in third-party computer applications. Specifically, it does not advance the theoretical methods. Furthermore, the physical phenomena that are presented in Chapters 1-4 are tied with the specific systems (molecule A, substrate

B), and it is hard for me to judge (from the level of the presentation) if they could have broader applicability. This makes the significance of the thesis perhaps a bit narrow in my opinion. The candidate can make an improvement in this direction by responding the questions below at the defense. Nevertheless, the skills of the candidate, reflected in his thesis, enable him to pursue an independent research.

Questions to be addressed in the defense:

1. I would appreciate if the author included a critical assessment of the theoretical methods, since they involve a plenty of approximations. What are the approximations (both in the *ab-initio* and the transport problem)? Is there a limit/regime, when they are more precise? Which transport phenomena are captured or not captured by these techniques? Can one take the resulting numbers literally?
2. In Chapter 2, both donor and acceptor levels acquire a broadening due to the platinum surface. Thus, the photo-generated electron-hole pair would leak to the substrate as a whole and recombine. Can one infer some design principles for the molecular device to actually generate a photo-current?
3. In figure 3(b,c), page 66, there is a comparison between a simmulated and measured AFM images. The two differ qualitatively, *e.g* the calculated image is much more blurred and it has a deep valley along the diagonal. The latter feature is absent in the experiment (even if we smear it). The simmulated AFM images of the original reference of the method also seem sharper (Hapala *et al.*, PRB 2014). Please, explain the theoretical blur and the difference along the diagonal. Could the discrepancy be due to artifacts in the van der Waals parametrization?
4. In Chapter 4, the transmission functions are interpreted as showing the frontier orbital peaks, HOMO and LUMO, with the Fermi level located in the gap between them. Depending on the position of the Fermi level, the conductance is said to be either HOMO- or LUMO-dominated. However, there is a broad blob like feature in the middle of the gap (p. 92, Fig. 4), visible for all terminations. This could indicate either a so called molecular *gateway* state, or an artifact of the metal cluster. What does the feature represent?

Sincerely,

Ing. Richard Korytár, Ph.D.