8 February 2024

Report on the dissertation "Electronic Structure Effects in Molecular Junctions" written by Mr. Štěpán Marek for obtaining the doctoral degree at the Dept. of Condensed Matter Physics at Faculty of Mathematics and Physics, Charles University.

The dissertation describes the work in the field of electronic structure calculations of Mr. Marek as part of his work towards obtaining the doctoral degree. The thesis summarizes his research on the calculation of the electronic properties of molecular junctions using DFT and other methods. The work is timely and of quality, the findings relevant and I believe this study advances the description of electronic structure in molecular systems.

The thesis starts with a short chapter which introduces the systems and outlines the main results. Then, the equations for electron transport are derived using Green's functions. In chapter 3, the computational methods used to compute the different molecular junctions studied are presented, in particular the description of semi-infinite electrodes using self-energies, and the corrections introduced by the GW methodology using DFT as a starting point. Chapter 4 summarizes the results on the molecular systems investigated in this thesis: ferrocene junctions, "Geländer" molecules exhibiting helical molecular orbitals, and sodium clusters studied using the GW approximation. Finally, the last chapter outlines some future directions of this work.

The dissertation is clearly written and easy to follow. The methodologies are described thoroughly and the implications of the present work for electronic structure and transport calculations are clear. The dissertation and associated papers demonstrate that the candidate can perform and analyze electronic structure calculations at a high level.

In my opinion, Mr. Marek has demonstrated his ability to carry out creative scientific work, and fulfils the conditions for a doctoral degree. I also have some questions, which will serve as discussion points during the oral examination.

- In the ferrocene junctions, the thesis highlights the LUMO in determining conductance due to its proximity to the Fermi level. I agree with this. However, the calculated transmission spectra show, both for the parallel and perpendicular geometries, that transmission at the LUMO energy is higher than unity (Figs. 4.4, 4.5). This indicates the presence of another molecular orbital, or transmission through several conductance channels. To be sure, Fig. 4.7 compares the total transmission with the contribution of the LUMO and differences in peak height are visible. Can you discuss and extend the material in the dissertation related to this?

- The section on helical orbitals in the "Geländer" molecule shows compelling evidence of the angular momentum acquired by electrons tunneling across this system. The angular momentum plot of Fig. 4.11 shows high values but also a large gap around the Fermi energy, suggesting that these effects will not be prominent at low bias voltages. How does this compare with the

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experimental results mentioned in this section? Also, can you speculate and propose a new molecular system where these effects are more prominent near the Fermi level?

- Efforts in correcting DFT electronic structure using GW-based approaches have been pursued in the literature. A popular approach is the DFT+Σ method, which introduces GW-like corrections in the subspace of the junction Hamiltonian associated to the molecule. Can you compare this kind of approaches with the evGW you studied? Are there any quantitative comparisons in the literature that may help evaluate the performance of evGW compared to other GW-based methodologies?

- The methanethiol/Na clusters of Fig. 4.25 are calculated using DFT, HF and evGW. The PDOS on the carbon atom shows clear differences in molecular peak positions depending on the approximation used. Can you comment or speculate on the effect of GW vertex corrections on the molecule for very large metal clusters? How would they compare to the other approaches which focus on corrections only on the molecular spectrum?

In summary, the candidate has undertaken ambitious and timely problems. His work has advanced the understanding of the field of electronic structure calculations of molecular junctions. I believe this work establishes that Mr. Marek can carry out independent research. I look forward to discussing these topics with the candidate in the oral examination.

Sincerely,

Héctor Vázquez

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