Review of the thesis of Mgr. Adam Jaroš with the title "Endohedral fullerenes: From exotic chemical bonding to molecular electronics"

I have been tasked to review this thesis for defence. I declare, that I have no bias or conflict of interest. I would like to start by pointing out that this task was a pleasurable one, due to the content but also the style of the thesis. The work is well written, and the author has a very enjoyable writing-style, something that is important for future publications. The language is very good. The figures are well prepared and easy to understand. The list of abbreviations seems to be complete, which is always good for potential readers. The thesis includes six papers, two of which have not been submitted. This is a good number especially seeing the quality of the published work and the very advanced state of the two last publications. I am impressed by the scientific outcome of this research work.

The introduction to the thesis is entertaining and to the point. Already here the candidate shows a good knowledge of the pertinent literature. This holds also for the rest of the thesis. With 325 cited references this thesis contains probably the most complete reference list of any thesis I have read so far. The introduction contains a description of fullerenes their derivatives and their chemistry. This is an important part of the thesis as it demonstrates the candidates ability to discuss with experimental scientists. This is of high importance seeing how science continues to specialize. The chemistry of fullerenes has evolved and experimentalists have been able to include many metals and even small molecules into fullerenes. It is also possible to get several metal atoms inside the fullerene. This is where it gets especially interesting for the theoretician, as the bonding between metal atoms, ions or molecules in a carbon cage must be rather special and could possibly be tuned by the size of the fullerene. This is a well-chosen subject of study, but it is not for the faint of heart as it will be computationally demanding. The supervisor must be given credit here for picking a good subject and the candidate for investing a lot of effort and hard work into this project.

So far one could think that the topic of endohedral bonding of metals is a rather obscure one, but the candidate shows how this can be connected to the important field of molecular electronics, the ultimate miniaturization step in electronics. In this part of the thesis the candidate shows a proper grasp of the workings of devices like memristors and how to build them using molecular electronics. The candidate then touches upon the theory of chemical bonding and demonstrates, that he has understood the challenges and interesting points yielded by the subject of this study. In the final part of the introduction one could have wished for an additional discussion on how the proposed endohedral bonding could be detected by spectroscopical methods, but this was outside the scope of this work.

The computational part starts with a solid introduction into wave-function based methods. This part seems quite complete to me, from Hartree-Fock to configuration interaction methods, onto perturbation theory and coupled cluster theory every method is briefly described. The multireference part could have been slightly longer, as these methods are used and may contain some pitfalls that would have been worth mentioning, like intruder states or the proper choice of the active space and methods to aid therein. But the thesis is not meant as a textbook and this part still serves as a good introduction. This part continues with a quite thorough introduction to DFT, following standard textbook ideas. It is very well written and avoids ambiguities, errors and misunderstandings sometimes found in such introductions. The problem of dispersion in DFT is properly addressed. The author shows his understanding of the required molecular basis sets. A short introduction to relativistic effects follows and the author should be commended for quoting the 1916 Sommerfeld paper as the origin of relativistic quantum chemistry. The concept of non-equilibrium Greens functions is introduced. There follows an introduction into population and bonding analysis. The author explains Mulliken and Löwdin analyses in some detail, although they are not really used anymore, but this is probably meant to show the history and development of such methods. NBO and QTAIM methods are very briefly explained, here a bit more explanation could have been in order, e.g. for the definition of the DI. The presentation of the used software shows the many different methods the author has used to properly investigate the systems of interest and this finishes the very readable introduction.

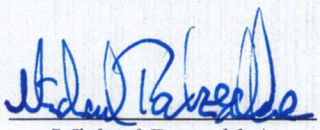
The rest of the thesis introduces the reader to the results of the research work. The articles are very well summarized. The importance of being able to summarize the results of a long study in a couple of

sentences cannot be overestimated and the candidate does a very good job here. This part starts with the exotic bonding in fullerenes. The example of HF-H_2O interaction inside a fullerene is discussed, the author shows his thoroughness by comparing the DFT results with wave-function based methods. Very new concepts like charge-shift bonding are explored and the explanation for the observed change in bonding inside the fullerene based on DI's and electron-deformation densities is a very good one. There follows the part of the thesis that is closest to my heart, the trend in An-An bonding. This is of profound interest in the actinide community and it is a notoriously difficult subject to tackle, as can be seen by the many publications on U_2 in vacuum. Here different lighter actinides (Ac-Cm) are used and they are not in vacuum but inside a fullerene! The bonding to the cage is discussed, this is very important as it will have a huge influence on the An-An part of the bonding interaction. The important aspect of d and f contribution for different actinides is evaluated. The results are presented very clearly Figure 3.5 is really beautiful and packed with information. The part on the methodology for An-An interaction (paper V) is equally impressive and I wish it speedy publication. The problem of spin-state ordering is addressed. Many DFT functionals are compared to CASSCF and CASPT2 results. With an active space of 6 electrons in 14 orbitals for U_2 the calculations are already extremely demanding. If this was a complete state averaged calculation, it has to include 3003 septets, 25025 quintets, 63063 triplets and 41405 singlets. As I stated earlier a calculation not for the faint of heart! This chapter then discusses the memristor results from papers II and IV and finishes with the spinristor paper VI. The memristor is supposed to work with a metal-halide or chalcogenide inside a fullerene, by rotating this molecule. Without an electric field, the two rotamers 0° and 180° are of the same energy with a transition state at 90°, with an electric field this changes as the rotamers are no longer of the same energy. To test the efficacy of such a system six different substances were tested inside C_{70}. Thermodynamic data was produced to check whether the envisioned systems are chemically feasible and switching field strengths were calculated. This paper serves as a good proof of concept. Paper IV takes this even further, a large number of computational methods are brought to bear on the problem giving us a good understanding of the energetics involved in the switching. Even more encapsulated molecules are considered. This leads to an impressive amount of data for the rotational barriers as a function of field strength. Interesting correlations between the switching barrier and M-X distances as well encapsulation energies are found and discussed. The final paper in the thesis deals with a simplification of such memristors, where the preference of a single metal for certain binding sites inside the fullerene is used. As spin-state ordering might be an issue, the author correctly uses multi-reference methods to check the DFT results. This paper is a proof of concept and deals with two systems Ti@C_{70} and Zr@C_{70}. This is an interesting idea and the results show that such a system might indeed be used as a spinristor. I am looking forward to further publication in this field.

While reading the thesis a number of questions for scientific discussions came to my mind. During the defence, I would like the candidate to answer the following selection of questions:

1) Could you briefly discuss the impact of endohedral bonding on such spectroscopical results as IR, NMR, TRLFS?
2) Could you explain the physicists definition of correlation and, with that in mind, comment on spin scaled methods?
3) Would you comment on the usefulness of double hybrids for your systems. Further, can you please comment on the possible problem of dispersion double counting in double hybrids.
4) Briefly on relativistic effects: Why is $p_{1/2}$ contracted and $p_{3/2}$ more diffuse?
5) What is IQA and why was it not used in your studies?
6) On the properties of actinides: What is the actinide break and did you observe it in your studies?

In conclusion, this thesis is very well written and contains state of the art research on interesting topics. It fulfills in my opinion all requirements for a PhD thesis and I recommend the dissertation of Mgr. Adam Jaroš for defence and after its successful defence I recommend to award the candidate the academic degree of Ph.D.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(Michael Patzschke)