Referee Report on Mgr. Maximilián Lamanec's Doctoral Thesis

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Reviewing Mgr. Lamanec's doctoral thesis was both a pleasure and a challenge: enjoyable at the beginning and demanding towards the end. The easy part was assessing the high quality of the thesis and the work accomplished during his Ph.D. in Professor Hobza's group. It is exceptional, to say the least, to complete a Ph.D. with eight publications, especially in prestigious journals such as Science, JACS, Angewandte Chemie, and Nature Communications. The challenging part was providing constructive criticism, as is customary, or posing relevant questions that were not addressed during the rigorous peer-review process.

Thesis Overview

The thesis, as indicated by its title, focuses on the synergy between theory and experiment in dative and non-covalent bonding, specifically in three distinct and highly topical areas: dative bonding in fullerenes (and other p-group element-containing model systems), hydridic hydrogen bonds, and computational support (primarily visualization) for Kelvin Probe Force Microscopy measurements of σ- and π-holes. This synergy is a distinguishing feature of this work, which, I believe, partially facilitated its publication in such high-ranking journals. I strongly resonate with the author's assertion in the Introduction advocating the plausibility of basic research over the current trend of favoring applied research. Proper understanding of these relatively unknown interaction motifs is undoubtedly essential for any future technological or other applications.

Thesis Structure and Content

The thesis follows a standard structure: the Introduction is followed by a chapter that briefly introduces the theoretical concepts of dative bonding, charge-inverted halogen bonding, and non-covalent interaction motifs attributable to the presence of σ- and/or π-holes in molecules. The next chapter presents an overview of the computational chemistry methods used. The subsequent three chapters are dedicated to each of the main topics, where the author first elaborates on the concepts and then briefly summarizes key findings and conclusions, with proper references to published work. While the thesis is well-written, some typographical errors remain, such as:

- Hyphens/spaces in words (e.g., p. 6 "va-rious"; p. 40 "the ir")
- Missing words (e.g., p. 5 "anomaly of water"; p. 19 "Computational Modeling Non-Covalent Interactions"; p. 21 "...yields approximately 50%.")
- Incorrect letter capitalization (e.g., p. 28 "a site"; p. 31 "motifs a")
- Incorrect chemical formulas (e.g., p. 39 "$Me_3SiH...CH_3(CN)_3$" and "$Me_3SiH...C(CN)_6$")
- Ordering of figures and tables (e.g., Figure 5.2 precedes Table 5.2, although Table 5.2 is mentioned first in the text)
- Notation errors (e.g., p. 43 Δv instead of ΔI)
- Notation inconsistencies (e.g., noncovalent vs. non-covalent).

Some formulations could be more precise, such as using "iterative" instead of "variational" treatment of excitations in the Coupled Clusters method. Additionally, some sections, like Section 3.3.3 on Explicitly Correlated Methods, cover topics somewhat unsystematically, lacking discussion on F12's predecessor, R12. However, the inspection of computational details in the respective sections and attached publications leaves no doubt about the correct application of these methods.

Conclusion

In conclusion, Mgr. Lamanec's thesis meets the highest standards. The candidate has demonstrated comprehensive understanding and knowledge, and the presented research is not only original but cutting-edge. Therefore, after a successful defense, I recommend awarding Mgr. Lamanec the Doctor of Philosophy (Ph.D.) degree.

Questions for Discussion During the Defense

1. CCSD(T) ground state predictions tend to be quite reliable, presuming the strong dominance of a single reference/determinant in the reference wave function. Did you analyze the magnitude of the multi-reference character of the reference wave function for potentially problematic species, such as C_{20}, C_{60}, or C_{70}?
2. The interaction of C_{60} and C_{70} with one and two piperidine molecules is discussed, showing notable differences. Can you extrapolate the impact of interaction with "n" piperidine molecules?
3. In Table 4.2, MP2 intrinsic interaction energies of C_{60}...piperidine are overestimated in all complexes except for "DB." Do you have any explanation for this?
4. Figure 6.8 compares calculated ESP with results from KPFM. From my naive perspective, anthracene compares very well, but for 9,10-dichlorooctafluoranthracene KPFM results resemble two (almost separated) round areas of positive charge. Can you comment on this observation?

In Bratislava, 4th of June 2024

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