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Review of Ph.D. thesis entitled
“Development of methods for an accurate description
of cohesive properties of molecular solids”

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Reviewer: RNDr. Petr Toman, Ph.D.

This thesis is focused on development of methods for prediction of the molecular structures and stability of organic molecular crystals with emphasis on reliable calculations of the solid-state binding energies. The work has the usual structure. The introductory section with a brief explanation of the scientific importance of the performed research is followed by a description of the used quantum chemical methods and computational techniques and definition of the investigated energy components. Next chapter is devoted to the study of the convergence of particular energy components calculated from the many body expansion (MBE) and periodic boundary condition (PBC) approaches. Special attention is paid to finding the optimal parameters of the methods with respect to reliable but simultaneously computationally feasible calculation of the energy components. Then, the results of both MBE and PBC approaches are compared. After that, effect of using of different types of orbitals in the random phase approximation calculations is analyzed. Finally, the accuracy of the energy components calculated by approximate methods is determined and the conclusions are concisely summarized. The thesis includes also an extensive list of literature references. Overall, the thesis is well formatted and the language level is at high standards. Nevertheless, some minor corrections related to formatting and grammar are given below. The scientific importance of the subject matter lies in the fact that, depending on the preparation procedure, many molecular solids can be found in several polymorphs with different physical and chemical properties important for their potential use in practical applications. Computational chemistry is then among key tools for optimizing the synthesis and sample preparation procedures to obtain materials with desired properties. The methodology used by the author corresponds to both the current state of the art in the field of the quantum chemistry and the computing power of current

computers. While the calculations are limited only to a set of four molecular solids, the number of the applied and compared methods is very large. Achieved results, such as the many-body-resolved binding energies, allow identification of sources of errors for the studied methods in more details than simple comparison of the total binding energies with experimental or other reference data. In this way, the thesis contributes to the future development of novel low-scaling methods and computational approaches. Part of the results has already been published in two papers in the Journal of Chemical Physics (K.N. Pham is first author, current IF = 3.1), preparation of another publication is announced.

Questions and notes

1)

Could you explain difference between the size-consistency (mentioned on pp. 10 and 14) and size-extensivity of the quantum chemical methods (p. 12)?

2)

Page 53, Figure 3.6

Uncertainty of the energy contributions is estimated as the largest variation, which depends on one point only. Would not it be better to consider the root mean square deviation, which depends on all data in the selected cut-off interval?

3)

The calculations are focused on relatively small hydrocarbons. Can the knowledge gained be used to study larger molecules containing, for example, more extensive conjugation, heteroatoms, or possibly even transition metals?

4)

In addition to the electron energy, the structure and stability of molecules and their chemical reactions are also influenced by the zero-point energy and non-zero temperature and pressure. Consequently, from a practical point of view, the Gibbs free energy is more important than the electron energy itself. Is it possible to use the obtained results also for a more accurate prediction of the Gibbs free energy?

5)

Page 55, sentence *“Furthermore, the basis set convergence of the energy components depends on distance, and large basis sets are mainly required for interactions at short distances, while small basis sets can be used for interactions at large distances to save computational cost.”*

There should be a more detailed classification of basis sets than just small and large to avoid misunderstanding. Note that the presence of diffuse functions in the basis set is important for a meaningful description of interactions at large distances.

Formal comments

1)

The name Hartree-Fock is misspelled on several places including the chapter titles and List of Abbreviations.

2)

Page 36

There should be written “the cubic and orthorhombic forms, respectively” instead of “the orthorhombic and cubic forms, respectively”.

3)

On page 28, the basis sets aug-cc-pVXZ are explained. However, these basis sets are denoted as AVXZ on p. 37 and following.

4)

On pages 41, 49, 77, and 117: There is a missing unit Å in the expression $10 < r < r_{\text{cut}}$. It can be misunderstood as 10 bohr.

5)

On page 56, Figure 3.7: Shortcut HFRCUT is not explained.

6)

List of Abbreviations should be in alphabetical order.

7)

Page iv

There should be written “Vedoucí doktorské práce” instead of “Vedoucí bakalářské práce”.

Conclusion

This doctoral thesis represents a valuable contribution to the development of the quantum chemical methods and computational approaches in molecular modeling and meets the standard requirements for doctoral dissertations in the field of quantum chemical calculations. The author has demonstrated his knowledge of a wide range of quantum chemical methods and his capability of independent creative scientific work, which can bring original results interesting to international scientific audience. Therefore, I highly recommend awarding the Ph.D. degree to Mgr. Khanh Ngoc Pham.

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