

The review on Ph.D. thesis

Development of methods for an accurate description of cohesive properties of molecular solids

by Khanh Ngoc Pham

Report on the content of the thesis

The dissertation thesis is a nice contribution to understanding interactions in molecular crystals focused on state-of-the-art methods. As several important computational methods are not implemented in periodic boundary conditions (PBC) or are almost intractable because of computational cost, the author also uses many-body expansion (MBE), which decomposes the binding energy into the energy contributions from dimers, trimers, tetramers, etc. The MBE approach enables the obtaining of benchmark binding energies from correlated methods as coupled clusters with single, double, and perturbative triple excitations (CCSD(T)), the golden standard in quantum chemistry. The central property, the binding energy of the molecular crystal, is, however, slowly converging with respect to the internal numerical parameters in both PBC and MBE approaches. Therefore, the first part of the thesis results is focused on convergence tests, and deep insight into the sources of errors is provided for investigated methods and their components. In the second part of the thesis results, random phase approximation (RPA) and Møller-Plesset (MP) perturbation theory were carefully evaluated. I understand it as a main methodologic goal and, in my opinion, the development of approximate medium-computationally-cost methods is essential for the progress in the field of (weak dispersive) interactions in molecular crystals. Only very small systems can be achieved by benchmark correlated methods and mean-field theories based on density functional (DFT) are not accurate enough, i.e., systematic method development is needed.

The thesis length is 113 pages including references, plus 17 tables containing data in the appendix to the thesis. I appreciate the very good presentation style, graphs, figures, and tables and there is only a small number of language errors, in my opinion. Overall, it leaves a very good impression. However, some figures and their discussion in the text seem to me not very compatible, and it was difficult to understand what the author described (see details below). The results are detailed, systematic, and of very high quality. Only their description is sometimes a little bit boring (convergence, convergence, ...), as the reader can see the same in the tables. However, I understand that the accuracy of the investigated methods and their components is of extreme importance in this thesis.

Formal comments

The official topic/thesis assignment is missing, and the definitions of goals are rather vague on page 3. Therefore, it was difficult to perform traditional analysis, how original goals were fulfilled, etc. Fortunately, the deep-insight topic, detailed results, and two referenced papers

in well-recognized international journals corresponding to the thesis (first authorships of the Ph.D. applicant) clearly confirm the high quality of work and fulfillment of the Ph.D. level.

Core journal articles corresponding to the thesis (Page 121, "List of Publications") were not enclosed in the Ph.D. thesis (at least in the pdf version I obtained). While published articles P1 and P2 I could download from the journal's web page, I do not understand why P3 (article in preparation) is mentioned if the content is not available.

The contribution of the Ph.D. applicant is not mentioned. Fortunately, the authorship of both articles guarantees essential contributions (the Ph.D. applicant is the first author; the supervisor is the corresponding author). However, I prefer to mention explicitly the roles of all three authors of publications concerning the thesis or statement of what data were obtained and analyzed by the Ph.D. applicant (all?). In addition, it is not clear to me, if an efficient scheme for obtaining reference binding energies from MBE is completely developed in the thesis, or if this is an extension of previous results/algorithms achieved in the author's group.

Comments and questions on the scientific contents

Abstract: "... RPA ... the proposed correction scheme ..., which can be used to obtain reference binding energies of the considered systems at a lower cost than the CCSD(T) method." Is it relevant to compare the corrected RPA method with the CCSD(T) method concerning computational cost, if different computational technique was used (PBC vs. MBE, respectively)?

Page 3 "... coupled cluster (CC), cannot be directly used in this scheme due to their high computational requirements, except for very small systems [29]": What is your opinion on the CCSD(cT) method used for calculation of CO adsorption on Pt(111) represented by 2x2 surface slab? (recent Faraday Discussion 2024, DOI 10.1039/D4FD00085D)

Page 41 "... we divided dimers into two groups: a proximate group ($r < 10 \text{ \AA}$) and a distant group ($10 < r < r_{\text{cut}}$). It is evident from Fig. 3.1 that the differences between AVQZ and AVTZ arise primarily at the proximate dimers, while these differences are close to zero for the distant dimers.": I cannot see any change of lines at 10 \AA in Fig. 3.1 and I cannot identify any dimer/dimer distance. In addition, the x-axis label "Cut-off distance" refers to the different quantity. Please clarify, what you like to show in Figure 3.1.

Page 45 "This can be seen in Fig. 3.2 as an example, where the difference in the 3-body DFT (KS/PBE) energy is nearly zero at short distances but begins to increase at larger distances.": I cannot see the mentioned change, in the opposite, I see a black line DFT(KS/PBE), which is almost constant (parallel to the x-axis). In addition, the x-axis label "Cut-off distance" refers to the quantity introduced later in Section 3.1.2 on page 47. Please clarify, what you like to show in Figure 3.2.

I could not find information on the electronic structure of described molecular crystals. It is generally known that some methods are not useful/reliable for metallic systems. Please, show

band structures for your systems and comment more generally on the performance/suitability of all your tested methods for large gap/small gap/gapless systems.

Correlation-consistent basis sets developed by Dunning et al. were designed to systematically converge post-HF calculations to complete the basis set limit. In the thesis, the statements of convergence of various contributions are based on the behavior of energy difference obtained from two subsequent correlation-consistent basis sets (aug-cc-pVTZ and aug-cc-pVQZ or others, see e.g. Figures 3.1 and 3.2., Tables 3.4. and 3.5). Is systematic convergence guaranteed also for DFT methods? (in other words, is the DFT/aug-cc-pVQZ energy necessarily better than DFT/aug-cc-pVTZ?) And what about RPA@DFT methods? To this end, were basis set superposition errors (BSSE) accounted for?

As the target property is the binding energy of the whole crystal (Section 6.4), is the testing of the changes of such (total) binding energy with respect to the change of local basis set used in the MBE equivalent to the testing of each energy component separately (as done in chapter 3.1)? In this direction, could you list a total number of two-body, three-body, and four-body terms in MBE corresponding to some typical calculation? Could you guess the uncertainty of a particular method (e.g. CCSD(T)) in predicting the binding energy of the whole crystal (your systematical MBE error)?

The CCSD(T) data for the solids studied in the thesis were recommended as benchmark data. Are available other independent many-body calculations (such as QMC) or experiments?

Conclusions

The dissertation thesis is well done, with few imprecisions. The author carefully analyzed various convergence issues of many-electron methods in periodic boundary conditions and many-body expansion. He applied tested methods to obtain high-quality binding energies of several molecular crystals, namely crystalline hydrocarbons. The work brings reference data on the molecular crystals and carefully analyses convergence issues. Random phase approximation with additional corrections was found as a promising alternative method to extremely computationally demanding reference methods. The work contains new findings which substantially contribute to the understanding of interactions in molecular crystals. I for sure recommend the thesis for the defense and the award of a PhD title.

František Karlický

Department of Physics, Faculty of Science, University of Ostrava
Chittussiho 10, 710 00 Ostrava, Czech Republic