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Prof. dr hab. Tatiana Korona
Faculty of Chemistry
University of Warsaw
ul. Pasteura 1
02-093 Warsaw, Poland

Review of Mr. Vignesh Balaji Kumar's Doctoral Dissertation, entitled "Correlation Effects in Hybrid Kohn-Sham Density Functionals: A Critical Evaluation of Existing Approximations and the New UMK26 Functional"

The dissertation of Mr. Vignesh Balaji Kumar has been prepared under the supervision of Prof. Dr. hab. Ireneusz Grabowski and Dr. Szymon Śmiga (as auxiliary supervisor) at the Department of Quantum Physics of the Institute of Physics, Nicolaus Copernicus University in Toruń.

The scope of the dissertation includes topics related to the development of density functional theory (DFT). DFT is very popular among molecular scientists because of a good trade-off between the accuracy and computational costs. However, the large number of available functionals can make it difficult to plan the application of DFT to practical problems: the variety of functionals can be confusing for novice users, but it can be also uncomfortable for more experienced computational chemists and physicists. Therefore, studies aiming to answer the questions: how to find out which functionals work better than other and why it is so, plus how to design new functionals in a more systematic way, are of great value to the academic community of computational scientists. The dissertation of Mr. V. B. Kumar, which critically examines existing hybrid functionals and proposes a new hybrid functional based on the outcome of this examination, fits well into the current trend of research aimed at improving our understanding of the theoretical foundations of DFT.

The dissertation, written in English, is based on two published papers accompanied by a general introduction and conclusions. The thesis is composed of 4 chapters and contains 124 pages and 106 references (not counting references from both publications). Such a form for the thesis is quite popular, but since both included papers are the result of joint efforts of several authors, it may be difficult for a reviewer to evaluate the level of individual work of the doctoral candidate. Luckily, in this case a detailed list of Mr. Kumar's activities is available in the final chapter, from which it becomes clear that he played a key role in all stages of the presented research.



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Chapter 1 presents a recapitulation of theoretical developments relevant to the study. It starts with the very beginnings of quantum theory, followed by an introduction of DFT and various types of density functionals, including hybrid ones, which will be examined in detail in this work. Afterwards, the author discusses the role of the exchange-correlation (XC) potential in DFT and presents, among others, several methods allowing to obtain this potential, like e.g. the Wu-Yang (WY) approach. This part is followed by the short discussion about the correlation potential and correlated density. Finally, Mr. Kumar presents the objectives of the thesis, which may be briefly described as a list of the following tasks: (i) a critical analysis and improvement of tools for computing Kohn-Sham (KS) XC potentials; (ii) an evaluation of existing hybrid functionals against accurate ab initio benchmarks, by utilizing not just energy benchmarks, but quantities like the electron density, exchange-correlation potential, and the ionization potential; (iii) an evaluation and critical examination of the correlation part of the global hybrid potentials; (iv) a construction of a new global hybrid, single-parameter functional, optimized against the accurate ionization-potential (IP) benchmark.

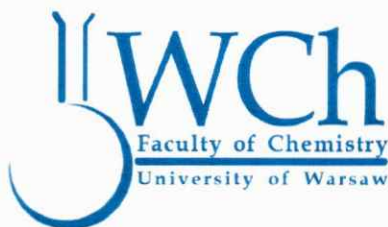
Chapters 2 and 3 represent the core of the thesis. Both chapters consist of three parts, with the middle part being the actual publication, the first part containing the introduction and recapitulation of the main findings of the paper, and the third part representing the supplementary information.

Chapter 2 is composed around the paper entitled "A Critical Evaluation of the Hybrid KS DFT Functionals Based on the KS Exchange-Correlation Potentials", published in *Journal of Physical Chemistry Letters* (JPCL). In this study, the doctoral candidate, with both supervisors as coauthors, develops a methodology to critically evaluate the quality of hybrid XC density functional approximations. Differently from many other developments in the field, this methodology is not focused on energy parameters only, but extends the examination to KS XC potentials, electron densities, and ionization potentials, using the inversion procedure to obtain the XC potentials from the KS electron densities for hybrid potentials and proposing appropriate error estimators. The methodology is then used to test 155 common hybrid functionals from the libxc library with accurate FCI or CCSD(T) benchmarks as references. Errors of densities and XC potentials are measured using the L_2 norm, and for the XC potential an additional error indicator is proposed, where the potential value at each point is weighted with the value of the reference density, which effectively eliminates the long-range region and allows to take care of core and valence regions only. A simultaneous comparison of errors of the total energies and electron densities reveals that some of these functionals have small errors for both of these quantities, and that the functional-driven (FD) error is more significant than the density-driven (DD) error, what gives a recipe of how to find a better-performing hybrid functional: one should look for a functional with a reduced FD error. These findings are accompanied by computational details presented in the supporting information, where the full list of functionals, the short reminder of the WY method and details on packages used for the calculations, as well as the numerical proof of the grid convergence and basis set convergence have



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been presented, followed by the derivation of the asymptotic behavior of the XC potential error in the case of hybrid potentials.

Similarly, Chapter 3 contains the paper "On the Primary Role of Semi-Local and Exact-Exchange Difference in the Description of Correlation Effects in Hybrid Functionals", accepted to Journal of Chemical Theory and Computation (JCTC) at the time when this thesis was submitted (the paper has been published in the meantime). The important discovery of this work is that the correlation in hybrid density-functional approximations (DFAs) arise mostly from the difference between the semilocal exchange and exact-exchange contributions instead of the semilocal correlation functional itself. The nontrivial finding that the exchange-difference is pivotal for restoring the correct behavior of the C component in the XC functional, has lead the authors to the proposal of a new methodology of the construction of global hybrid functionals. Finally, in order to proof this concept, a new functional, denoted as UMK26, has been proposed and tested on several benchmarks.

Finally, Chapter 4 recapitulates the main findings of the thesis and sets plans for future developments of the UMK26 functional. Additionally, this chapter contains an important information for judging the contribution of Mr. Kumar in the multiauthor publications included into this thesis, as well as the list of his remaining publications and other proofs of his scientific activities, like the active participation in scientific conferences.

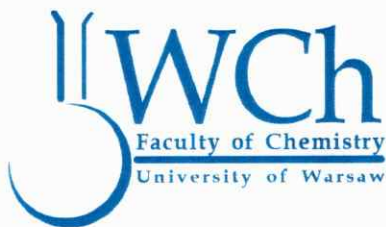
Since the major parts of Chapters 2 and 3 represent peer-reviewed publications, the analysis of Chapter 1 and of the introductory parts of Chapters 2 and 3 is especially important to assess the ability of Mr. V. B. Kumar to write independently scientific texts, in particular - to explain the major approaches utilized by him in the study and to present the conclusions obtained from the analysis of the generated data. Overall, these parts of the thesis show the abilities of the doctoral candidate to perform these tasks. However, I have several critical remarks regarding the presentation of the theoretical part, which are listed below.

First of all, there are many inaccuracies in the introductory chapter, which probably arose from haste to finish the dissertation. For instance, in subchapter 1.1.1 Mr. Kumar gives an overview of quantum theory of many-electron systems (according to the title), but since he (unnecessarily in my opinion) starts from the early history of quantum mechanics, he should follow in that vein and should begin with a general form of the time-dependent Schrödinger equation in place of eq. 1.1, which represents the time-independent Schrödinger equation for N electrons. In order to arrive at eq. 1.1, one should go through the separation of nuclear and electronic motions first, which is not mentioned here. Mr. Kumar also writes that this equation allows to "accurately calculate the states of any chemical systems", which is only true if the relativistic etc. effects are neglected and - for eq. 1.1 - it is true for the electronic part of the system under study. Next, Mr. Kumar mentions some old and several more recent approaches devised to deal with many-electron problems. In my opinion, this



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part of the thesis is too superficial. A reader would benefit more with a more precise description of the methods and their relationships among each other than from historical curiosities, regarding who, when and where proposed a particular method. I also disagree with the analogy, which Mr. Kumar makes between the post-HF methods, which he has just listed as methods evaluating electron correlation in the ground state (MP, CCSD etc.) and the methods denoted by him as post-DFT, where he lists a method like TD-DFT. The latter method extends DFT to obtain electron excitation properties, while the post-HF methods extend HF to calculate electron correlation (rather than excitations).

In the next subchapter (1.1.2) about the KS theory several inaccuracies can be found. For instance in eq. 1.3 the integration (summation) over spins is missing. It should be noted that the bold $\mathbf{r}$ is explicitly identified as the spatial coordinate only (see top of p. 5), while in eq. 1.1 a general bold $\mathbf{x}$ set of coordinates is introduced, encompassing both spatial and spin coordinates. Next, in eq. 1.6 there is an inconsistency in notation in the integral in comparison to eq. 1.3 ($d\mathbf{r}(\text{bold})$ versus d^3r'). In Figure 1.1 the symbol Δ should be replaced by ∇ . In subchapter 1.1.4 (top of p. 8) Mr. Kumar mentions the self-interaction error, but this concept has not been introduced earlier, which would be a good idea in view of its usage in the following pages. Similarly, in subchapter 1.1.7 a more detailed explanation of how eq. 1.16 is used to build range-separated hybrid functionals, instead of short "based on this", would be welcome. In the same subchapter a dispersion correction is mentioned, but only in the context of spin-component scaled double hybrid DFT, while this correction is also used for other functional types (see e.g. S. Grimme, J. Comput. Chem. 25, 1463, 2004).

In the subchapter 1.2 the doctoral candidate collects necessary developments, which he will need in the main part of his study. This part is very difficult to read, especially the derivations are hard to follow, partly because some parameters are either not defined or defined implicitly. Starting from very beginning, the missing definitions include $a_{i\sigma}$ and $a_{i\sigma}^\dagger$ operators, and the ψ_i function (annihilation and creation spinorbital operators and probably HF spinorbitals (eqs. 1.20-1.22)); then no explanation for the rightmost symbol of eq. 1.24 has been given, similarly to τ_{KS}^p (p. 13). The author also writes that he subtracts eq. 1.26 from 1.27, which is not possible, since eq. 1.27 represents an eigenequation. Only after looking into the original papers or Chapters 2 or 3 some of these formulas become clear for a reader. In subchapter 1.3, where the correlated density is introduced, there is a problem with eqs. 1.37 and 1.38: either all three ρ 's are probability densities, what eq. 1.37 implies, or one of them is a radial probability density. In the second paper of this thesis, which uses the difference radial distribution concept, the functions $\rho(r)$ and $RDR(r)$ have been used instead (see p. 65, below eq. 8). In subchapter 2.2, which precedes the JPCL paper, the definition of the $\Delta\rho^{\text{ref}}_{V_{xc}}$ error is missing (p. 29). The meaning of this error becomes clear only after reading this paper (p. 32).



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There are also some minor issues:

- a) it is generally accepted that "e" is used to denote the elementary electric charge, while the electron charge is -e, not e (p. 2);
- b) a misprint: "rho" instead of "p" in p. 29;
- c) all publications' titles in the bibliography lack capital letters where they are expected (i.e. in the names of methods and in papers written in German, where all words are capitalized);
- d) refs. 24 and 27 are incomplete (either the journal name, volume, and pages, or the author(s) are missing).

Despite these critical remarks, I consider Mr. Kumar's work to be a valuable contribution enhancing our understanding of how DFAs work and how they can be systematically improved. The findings of the dissertation have been published in two top journals available for the community of quantum chemists: *Journal of Physical Chemistry Letters* and *Journal of Chemical Theory and Computation*. In both publication Mr. V. B. Kumar is the first author.

I also have several questions to Mr. Kumar to be discussed during the defence:

- 1) Has the standard contracted aug-cc-pVTZ basis been tested when utilizing the WY method? If yes, what is the quality of the results in comparison to the uncontracted version?
- 2) How the appearance of numerical instabilities in the Wu-Yang inversion method can be explained? How the reliability of the results has been estimated, in view of possible instabilities? How these numerical problems limit the size of studied molecules?
- 3) What is the distance between He nuclei for the results presented in p. 48?

Summarizing, I conclude that the presented doctoral thesis represents a solution of the original scientific problem, shows the candidate's ability to perform an independent scientific research and his knowledge in the field of quantum mechanics, and in particular in electronic structure theory. Therefore, the dissertation meets the requirements set in Article 187 of the Law on Higher Education and Science of July 20, 2018, as amended [art. 187 ustawa *Prawo o szkolnictwie wyższym i nauce* z dnia 20 lipca 2018 r. (z późn. zm.)] and in Resolution 38 of the Senate of Nicolaus Copernicus University in Toruń of Sept. 26, 2023, regarding the procedure for awarding the doctoral degree. Therefore, I recommend that Mr. Vignesh Balaji Kumar be admitted to the subsequent stages of the doctoral dissertation process.