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Review of Ph.D. thesis entitled "Correlation Effects in Hybrid Kohn-Sham Density Functionals: A Critical Evaluation of Existing Approximations and the New UMK26 Functional"

The Ph.D. Thesis I received to review has been prepared by Mr. Vignesh Balaji Kumar, M.Sc.. The Thesis is written in English and entitled "Correlation Effects in Hybrid Kohn-Sham Density Functionals: A Critical Evaluation of Existing Approximations and the New UMK26 Functional". The Ph.D. project was realized under the supervision of Professor Ireneusz Grabowski (supervisor) and Dr. Szymon Śmiga (auxiliary supervisor) and prepared in the Institute of Physics of Nicolaus Copernicus University in Toruń.

The research, which is a basis of the application for the Ph.D. degree, is devoted to the density functional theory (DFT), the computational method which in the last decades has dominated the quantum chemistry. There are thousands of articles related to the development and applications of the DFT approach. In spite of this there is still room for novel ideas and new routes for the search of ideal functional applicable to the variety of unsolved chemical problems.

One of the open fields in the DFT theory is its relation to the *ab initio* schemes based on the wave function theory (WFT). The advantage of the WFT approach is its capability to provide a solution of the Schroedinger equation up to desired accuracy on condition that the investigated system is sufficiently small. The DFT and WFT schemes can be confronted in many ways, the most natural is a comparison of, e.g., energy related properties, in other words, generally understood atomic and molecular properties. One

of the interesting options would be a comparison of the basic quantity of the DFT approach, i.e. electron density, with that obtained via the *ab initio* schemes, it is, the WFT based methods.

A very attractive possibility has emerged in recent years via so called Kohn-Sham (KS) inversion procedure, introduced by the Wu-Yang (WY) scheme, which makes it possible to construct the KS potential on the basis of the supplied electron density. This opens the way to construct the KS potential on the basis of very accurate *ab initio* densities, obtained, e.g. with the FCI (full configuration interaction) approach or with the other high-accuracy WFT methods, like e.g. CCSD(T) (coupled cluster singles and doubles with perturbative triples). Of course, the high-level WFT results can be obtained for the relatively small systems, but a comparison of the WFT-based potential, e.g. obtained with the WY scheme versus original DFT one, can provide a lot of useful indications to improve the existing DFT functionals. An analysis of the existing functionals as well as a construction of the novel ones are the subject of the reviewed Thesis.

The core of the dissertation is a set of two published and thematically related scientific articles, containing the results of the Ph.D. research, published in the renowned journals: the first one in *The Journal of Physical Chemistry Letters* (JPCL) and the second one in *Journal of Chemical Theory and Computation* (JCTC). The former is authored by the Ph.D. candidate and both supervisors while the latter includes additional three coauthors cooperating with the candidate. It should be noted that Mr. Kumar is the first author in both of them which indicates his meaningful contribution to the papers.

There are two principal goals of the Ph.D. research presented in the published papers and forming the essence of the dissertation. The first one is discussed in chapter II of the dissertation and in the JCPL paper and is devoted to the critical evaluation of a number of hybrid functionals available in the LIBXC library. The functionals were analysed from the viewpoint of the total energies, ionization potentials (IP), electronic densities and exchange-correlation (XC) potentials. These quantities were calculated with the tested potentials and compared to the reference values obtained with the methods based on the WFT approach, namely the FCI and CCSD(T) schemes. One may note that the confrontation of the DFT and WFT results can be seen as pretty straightforward in the case of the first three quantities (energy, IP, densities) but is more demanding when comparing the XC potential used in the DFT calculations with the *ab initio* XC one. The latter can be done on the basis of the mentioned earlier Wu-Yang inversion scheme. The detailed

analysis of the errors in the large number (155 items) of hybrid functionals required exceptional work and I consider this as outstanding achievements. The research made it possible to establish a hierarchy of the hybrid functionals based on the respective errors and to emphasize the role of the long-range Hartree-Fock coefficient in shaping the exchange correlation potential. I am impressed by the performed work and the findings reported in this part of the dissertation.

An important observation made in the above study is that the quality of correlational effects in the hybrid functionals are dependent to a significant degree on the difference between the semilocal exchange and exact-exchange contributions. This is a non trivial conclusion and it creates a strategy to develop a new exchange-correlation functional. This issue is a subject of a chapter III and the JCTC paper which are devoted to the development and the validation of the novel hybrid XC functional named UMK26.

The UMK26 has been put together by forming the exchange part as a combination of the Hartree-Fock exchange and Becke88 component while the correlation part has been taken from the LYP scheme. It is surprising that the functional based on this rather straightforward formula (see Eq. 3.4 in the dissertation) demonstrates a very satisfactory performance. It was shown that the UMK26 provides an evident improvement in quantities such as correlation potential and correlated electron densities. The same refers to the potential energy curves for charged systems. Another example of a good behaviour of the new functional is much smaller value of so called self-interaction error (SIE) as it has been demonstrated for the benchmark data set known as SIE4x4.

A summary of the most important findings is presented in chapter IV, and the final part of the dissertation includes a list of cited references (106 items). The dissertation, written in correct English, is 113 pages long. The editorial work was prepared with due care, I did not encounter any noticeable errors.

The research conducted by the doctoral candidate deserves recognition. It requires an excellent understanding of the broad spectrum of quantum chemical methods currently available in the literature and a good knowledge of modern quantum chemistry and physics. The analysis and calculations performed are by no means trivial, and their successful implementation demonstrates proficiency in using theoretical tools in research based on the wave function methods and on the DFT. It should be mentioned that this research relied not only on the straightforward calculations but it required

also a lot of programmer's work on developing and putting together many modules available within the quantum chemistry resources.

It should be noted that besides the papers constituting the core of the current dissertation Mr. Kumar is a coauthor of additional four papers devoted to the DFT theory.

I have to mention that the current research has been carried out within the scientific team which has unquestionable achievements in the field of a development of the density functional theory. The research group, lead by prof. Ireneusz Grabowski at the Nicolaus Copernicus University, has a prominent position in Poland and is also appreciated at the international level. This is an additional factor contributing to the high quality science performed also at the doctoral level.

In summary: I believe that Mr. Vignesh Balaji Kumar, M.Sc., performed valuable research that allowed for the analysis of the usefulness of an interpretable construction principle for hybrid functionals. He handled the undoubtedly complex calculations brilliantly and the findings of the Ph.D. Thesis are valuable tools in pushing the limits of KS DFT.

In conclusion, I declare that the doctoral dissertation of Mr. Vignesh Balaji Kumar, M.Sc., meets both the requirements typically set for doctoral dissertations and the currently applicable statutory requirements, so he fulfills all formal and substantive requirements and therefore I strongly support his application for the Doctor of Philosophy in Physics degree. Thus, I request the Council for the Discipline of Physical Sciences of the Nicolaus Copernicus University in Toruń to admit Mr. Vignesh Balaji Kumar, M.Sc., to the further stages of the doctoral process. Bearing in mind both the great deal of effort as well as the scientific significance of the presented results I recommend to award the doctoral degree with distinction.