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A review of the PhD thesis entitled:

"Correlation Effects in Hybrid Kohn-Sham Density Functionals: A Critical Evaluation of Existing Approximations and the New UMK26 Functional" by Vignesh Balaji Kumar

General remarks

The PhD thesis is devoted to one of the most important and longstanding challenges of modern quantum chemistry, namely the understanding and improvement of exchange-correlation (XC) approximations within Kohn-Sham Density Functional Theory (DFT). Since the predictive power of DFT is fundamentally limited by the quality of the XC functional, any effort leading to a deeper understanding of exchange and correlation effects as well as to the development of more robust density functionals is of high scientific significance.

The candidate performed a systematic assessment of 155 hybrid density functionals using quantities usually neglected during functional development, including exchange-correlation potentials, correlation potentials, densities and ionization potentials. Based on these studies, he proposed the new UMK26 hybrid density functional. The results were published in high-quality international journals; the candidate demonstrates scientific maturity, methodological independence and advanced computational skills.

Vignesh Balaji Kumar is enable to solve quantum chemical problems related to both methods/numerical algorithms developments and their practical implementations. Such skills are especially valuable nowadays since the market becomes more and more dominated by “pure” applicative works – without the priceless methodological efforts, which are very often very long-term investments and often not-enough appreciated, it would be impossible to reach the current stage of quantum chemistry, where various multiscale chemical problems can be understood by computations/modelling. From this respect the objectives of the thesis are very timing.

Detailed comments

The dissertation is organized into four short chapters comprising theoretical introduction, two scientific chapters directly corresponding to the publications constituting the PhD thesis and a

final summary chapter. The thesis is written in good English, the scientific reasoning is coherent and the graphical material is carefully prepared. The structure is logical and allows the reader to follow the evolution of the scientific ideas leading from methodological considerations to the final development of the UMK26 functional.

The first chapter provides a broad introduction to modern electronic-structure theory, starting from the many-electron Schrödinger equation and proceeding through Hartree-Fock theory, post-Hartree-Fock methods and various generations of density-functional approximations. In general, this part is scholarly written and demonstrates that the candidate possesses a sound understanding of both wavefunction and density-based approaches. Particularly valuable is the extensive discussion of exchange-correlation potentials and inverse Kohn-Sham methodologies. The sections devoted to MRKS and Wu-Yang inversion procedures are especially important because they constitute the methodological foundation of the subsequent chapters. The candidate carefully discusses practical difficulties related to finite-basis-set representations, regularization schemes and oscillatory artifacts in reconstructed potentials. Such aspects are usually omitted in standard quantum-chemical textbooks and therefore provide additional scientific value for readers interested in this area.

An especially interesting aspect of the introductory chapter is the discussion of correlation potentials and correlated densities. These quantities play a central role throughout the dissertation and are subsequently transformed from rather abstract formal objects into practical tools for evaluating exchange-correlation approximations. In this regard the thesis offers a deep and parallel perspective compared with traditional DFT literature, where total energies often dominate the discussion.

The second chapter presents the first publication underlying the dissertation and contains a comprehensive assessment of 155 hybrid density functionals. This part constitutes, in my opinion, one of the strongest components of the thesis. Historically, density functionals have been developed and optimized predominantly using energetic criteria. The candidate convincingly demonstrates that such an approach may conceal important deficiencies when other physically relevant properties are considered. Particularly striking is the discovery of a hierarchy of errors of various chemical quantities: $\Delta v_{xc} > \Delta IP > \Delta \rho_{v_{xc}}^{ref} > \Delta \rho > \Delta E_t$ which clearly reveals that exchange-correlation potentials and ionization potentials are significantly more demanding quantities than total energies. This observation is scientifically important because it exposes limitations that remain largely invisible within traditional thermochemical benchmark strategies. An equally important outcome is the demonstrated correlation between the quality of exchange-correlation potentials and the accuracy of ionization potentials. This result naturally connects the presented work with Bartlett's correlated orbital theory and provides an elegant physical

justification for employing ionization-potential-based optimization strategies in future density-functional developments. The extensive comparison with wavefunction-based methods is also valuable. It is instructive that many modern hybrid functionals can compete with sophisticated correlated methods in energetic predictions while remaining significantly inferior regarding densities and exchange-correlation potentials. Such observations remind us that excellent energetic performance alone does not necessarily imply satisfactory physical realism of a functional for other properties. A question naturally arising from this chapter concerns the transferability of the conclusions to systems possessing pronounced multireference character. Since most reference data originate from FCI or CCSD(T)-quality calculations, one may wonder whether the observed performance trends would remain unchanged for cases where static correlation becomes dominant and single-reference treatments become less reliable.

The third chapter presents the second publication and contains the most original scientific contribution of the dissertation. The candidate argues that the dominant qualitative features of correlation effects observed in hybrid functionals originate not primarily from semilocal correlation functionals but from the difference between semilocal and exact Hartree-Fock exchange contributions. The corresponding analyses of correlation potentials and correlated densities are convincing and reveal an important role of exchange-only contributions in generating physically meaningful correlation effects. Such results contribute to a deeper understanding of why hybrid functionals work and constitute one of the most interesting theoretical findings of the dissertation. The proposed interpretation subsequently leads to the development of the UMK26 functional. The obtained results for UMK26 are promising. The functional demonstrates improved performance for several challenging properties including ionization potentials, charge-transfer excitations, self-interaction-sensitive systems and dissociation curves of charged species.

Several scientific questions nevertheless emerge from this chapter:

1. Considering that the UMK26 mixing parameter was optimized using only 16 relatively small systems, how transferable do you expect the optimal γ -value, and, more generally, the proposed exchange-difference construction principle to be to chemically more diverse systems, such as larger molecules, open-shell species, or transition-metal complexes?
2. Since UMK26 was optimized primarily using ionization-potential criteria, would a simultaneous optimization involving correlation potentials or/and correlated densities lead to better outcomes ?
3. Do you expect the exchange-difference picture proposed here to remain meaningful in systems with substantial static or multireference correlation, where a single-determinant exact-exchange reference itself becomes qualitatively inadequate? (bond elongation?). It seems that further progress toward the strong-correlation regime may require replacing the

fixed global scaling of the XDiff contribution by a suitably constructed local mixing parameter $\gamma(r)$, capable of responding to the near-degeneracy and improving fractional spin-behavior.

4. Have you analyzed the individual kinetic and interaction contributions to the correlation energy (T_c , U_c) for the systems used in the UMK26 optimization? Since the central result of the thesis is that the semilocal–HF exchange difference reproduces important qualitative features of correlation, it would be particularly interesting to determine whether this exchange-difference term correlates with U_c or T_c or with some combination of both. Such a decomposition could provide a deeper physical interpretation of the exchange-driven correlation picture, especially in view of earlier DFT studies demonstrating the nontrivial and, in some situations, crucial role of kinetic correlation in correlation energies, potentials, and densities, e.g. Gritsenko, van Leeuwen and Baerends, J. Chem. Phys. 104, 8535 (1996); Gritsenko and Baerends, Phys. Rev. A 54, 1957 (1996), as well as subsequent analyses of kinetic and strong correlation, including B13 and KP16/B13-type approaches.
5. Since the local KS potential is explicitly reconstructed by inversion of the GKS density, why were the ionization potentials taken from the original GKS HOMO eigenvalues rather than from the eigenvalues of the inverted KS system?

These comments should not be regarded as criticism. On the contrary, they reflect the fact that the dissertation addresses scientifically ambitious questions and can open some promising research directions that could form the basis of future developments in DFT. The above points could be further discussed during the defense procedure.

Recommendation

To summarize, the PhD thesis addresses important and contemporary problems of DFT. The candidate developed and applied novel methodologies for assessing density functionals and proposed a new physically motivated hybrid approximation.

In my opinion all objectives of the thesis have been successfully accomplished. I therefore conclude that the dissertation fulfills all formal and scientific requirements required for the PhD degree in the discipline of physical sciences.

Accordingly, I strongly recommend admission of Mr. Vignesh Balaji Kumar to the further stages of the doctoral procedure.

Yours Sincerely,

Dr hab. Mariusz Paweł Mitoraj, prof. UJ, 08.10.2026