Anonymous IJQC Reviewer[1]

[1]Affiliation not available

June 15, 2020

Abstract

In this manuscript, the authors present, discuss, and assess several criteria to evaluate the transferability of approximations to the exchange-correlation functional of density functional theory (DFT). In the first part of the paper they demonstrate that one criteria often used to assess such transferability - the number of parameters in a given functional - is clearly inadequate for the task. In the second part of the paper, the authors introduce three statistical criteria with roots in statistics and machine learning and apply them to a selection of existing density functional approximations.

Considering that the choice of the functional can have a profound impact on the quality and computational cost of DFT calculations and that there are hundreds of functionals available in the literature, this is clearly a topic of importance for a large number of researchers.

The work presented here is, to the best of my knowledge, scientifically sound and original. I therefore recommend that the manuscript be accepted for publication in IJQC after the authors have taken the comments bellow under consideration.

1 Referee Report

I would like to thank the authors for this well written, thought-provoking manuscript. It made for a very enjoyable read and I believe it is an important addition to the literature on the design and benchmarking of exchange-correlation functionals of DFT. I would also like to congratulate IJQC for this new article format where the computer code and the data used to generate plots are only a few clicks away. This is definitely a step forward in ensuring that scientific results are readily available and reproducible.

For the last 15 years I have followed closely, albeit mainly as an outsider, what the authors call the "*two philosophies at war in the world of functional development*". It's good to see that there is nowadays a greater focus on the issue of how to properly assess the transferability of functional approximations. In the end, regardless of how they are constructed, functionals should be assessed against the same data using sound and well justified criteria. From this point of view, the work presented in this manuscript is a clear step forward. I believe the manuscript could be published as is, but the authors might want to take into account the following comments first.

1. In the first part of the manuscript the authors present their one-parameter fit of exchange-correlation functionals. Although I appreciate the point the authors are trying to make, the fact that Eq. 5 cannot be used in practice to evaluate the functional for arbitrary values of the density seems problematic to me. A functional cannot be reduced to a finite set of points. As a simple example, one can look at the existing approximations to the LDA correlation, as most of them are fits to the same set of points (the Monte Carlo data of Ceperley-Alder). These functionals are clearly not equivalent, as they give close, but different results. The authors do point out that a spline interpolation can be used, but in that case it's hard to argue that such interpolation is a one parameter fit. I guess one could instead make the point that in the limit of infinite number of points (and infinite number of significant digits in the parameter), Eq. 5 is able to represent a given functional for arbitrary densities. Would this be correct? Maybe the authors could comment further on this?

2. Another question that is not entirely clear to me regarding the one-parameter fit is if or how such procedure could be carried over to hybrid functionals and in particular to range-separated hybrids. I understand that this goes beyond the scope of the paper, but considering the popularity and importance of such functionals, I would appreciate if the authors could share any ideas they might have on this subject.

3. Looking at Table 3, there's a somewhat obvious connection that could be made between Sections 2 and 3. At first glance, there seems to be no correlation between the ranking of the functionals and the number of degrees of freedom. This would be further proof of the inadequacy of counting parameters as a proxy for functional transferability.

4. I couldn't find the ASCDB_UE_C.csv file that is used in the Jupyter notebook to generate Table 1 in the associated data. Also, it seems that the weights defined in Eq. 11 are hard-coded in the notebook. The manuscript explains how they should be calculated, but it is not possible to check the values without further data.

5.Finally, a very minor point. Although it has become customary to cite Ref. 53 of the manuscript when referring to the PW91 GGA, the functional was first described in (Perdew, 1991). I mention this because I've seen a few times people mixing up the PW91 GGA with the PW92 LDA as they assume (correctly!) that the year appearing in the functional abbreviation corresponds to the year in which the corresponding paper was first published.

References

Ziesche, P., & Eschrig, H. (Eds.). (1991). . In *Proceedings of the 75. WE-Heraeus-Seminar and 21st Annual International Symposium on Electronic Structure of Solids* (p. 11). Akademie Verlag.