FACULTY OF SCIENCES

DEPARTMENT OF CHEMISTRY
GHENT QUANTUM CHEMISTRY GROUP

Patrick Bultinck
Professor

E   Patrick.Bultinck@UGent.be
T   +32 9 264 44 23

Campus Sterre, S3
Krijgslaan 281
B-9000 Ghent
Belgium

www.quantum.ugent.be

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Dear Prof. Dr. Corminboeuf,

I am pleased to resubmit our manuscript entitled, "Quantifying delocalization and static correlation errors by imposing (spin-)population redistributions through constraints on atomic domains" for consideration as a Journal of Chemical Theory and Computation research article. I appreciate the constructive criticisms of the reviewers and have addressed each of their concerns as outlined below.
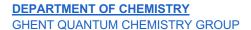
Reviewer 1

I found this work interesting and of overall good technical quality. However, due to its limited scope, I do not believe that it is suitable for a journal like JCTC with a broad readership. With relatively minor modifications, this work can be published in a more specialized journal.

> In this study, we provide much-needed reference data for those who aim to develop the next generation of density functionals. That is why we are submitting to JCTC: it has the broad readership that is required to turn that reference data into 'design principles'. Furthermore, our study is well within the scope of JCTC as it includes advances in theory and methodology with applications to compelling problems.

On page 11, the authors write: "To properly account for this discontinuous behavior, approximate methods should adequately restrict any unphysical flow of electrons, which is in sharp contrast to the general assumption that any increase in variability is beneficial as it generally leads to lower variational energies. Instead, in failing approximate methods the increased complexity should be directed towards restricting the unphysical flow of electron density, without, however, affecting the performance of that approximate method too adversely." While I very much agree with the general philosophy behind this statement, it is not

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clear to me what is the design principle that the authors advocate in this manuscript. In particular, the authors should clarify if and how the results provided in this work can practically be useful for the development of novel exchange correlation functionals.

> In this study we do not imply that we have uncovered 'design principles' for functional development. However, we do provide the computational data that supports the statement above and provide a novel benchmark for those who are developing density functionals. Our data points out that novel functional developments can be greatly aided by focusing on reproducing the energetics associated with constrained (spin)population redistributions.

As also acknowledged by the authors on page 7, there are several issues with the use of Mulliken populations for constraints at bonding distances. The authors should discuss how these issues could impact the results reported in the present work in more detail. It is true that Mulliken population becomes more reliable at long distances of separation, but at 4.5 a.u. the overlap between the basis functions on H and on the reservoir could still be significant. Ideally, the authors should include a comparison with the results obtained using different population schemes.

> We agree that a complete characterization of the impact of the deficiencies of Mulliken partitions on our results would require a comparison with the results obtained using different population schemes. However, not only does the associated complexity and computational cost rise dramatically when using other population schemes, imposing any additional approximations on those population schemes could lead to unexpected artifacts in this context. We have further substantiated this reasoning by including a critical analysis of the applicability of other population schemes in this context in our study (see pages 6 and 7). As the associated cost with performing the comparison proposed is extremely high at the full configuration interaction level and the requested additional population schemes are not (strictly) necessary in the current context, we propose to address such comparisons in another study.

The overall quality of the figures in this work should be improved. For example, I found Figure 5 very difficult to read. The authors should include the metadata used for generating the figures in the SI.

> We acknowledge that the graphs mentioned contained too few data points to provide an unambiguous interpretation. However, when we further characterized the relevant surface by sampling a denser grid of points, it emerged that the chosen hydrogen rings exhibited degenerate ground states for many imposed Lagrange multipliers due to their symmetric bond dissociation. As we have reported previously [2], this renders atomic charges (and the resulting energy vs charge surfaces) ill-defined. For this reason, we have chosen to limit ourselves in this study to the infinitely stretched hydrogen chains that were originally

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proposed by Zheng and co-workers [3]. These systems do not exhibit degeneracies and allow us to induce a wide range of asymmetrical distributions. We have added the energies which were sampled as a function of (spin)-resolved populations as reference data in the Supplementary Information. We have also provided interactive notebooks that illustrate how we have generated the data through our software package GQCP [4] on the website of our software package [5]. We are currently characterizing the influence of degenerate states on the computationally obtained flat plane conditions further and will report on our findings in follow-up studies.

Reviewer 2

On top of these specific queries, I also note that the manuscript is written in a very technical fashion. the authors _might_ want to look to ramp up some pedagogical descriptions, but this is certainly not a necessary change as most readers will be interested in the technical results.

> As Yang and coworkers have already written excellent pedagogical exposés (that are cited in our paper) on the flat plane conditions and their implications, we would opt not to explicitly include a similar discussion in this paper. As indicated by the reviewer, this would largely detract from the computational results we intend to highlight.

The authors have (to a first approximation) produced FCI data which use plateu potentials to control the density on a single 3D atom. This is, for want of a technical term, very cool and offers insights into how and why density functionals fail. It is, to my knowledge, the first time these sorts of techniques have been used in 3D. It would, however, be nice for the authors to reference prior work by Gould [10.1021/acs.jctc.9b00477 10.1063/1.5022832], Hodgson[10.1021/acs.jpclett.7b02615 10.1088/1361-648X/aaa4cd/meta and others] (and probably others) on very similar 1D chemistry problems.

> We thank the reviewer for pointing out these references and have included them in this paper. We would also like to point out that the additional literature review prompted by this comment uncovered additional work by Cioslowski, who applied a very similar methodology within a different context (electronegativity equalization). As such, we have also provided sufficient context for those papers of Cioslowski.

It would benefit the manuscript to briefly mention the (lack of) issues in Mulliken partitioning when it is first introduced. My first thought was "this seems like a bad idea" which was resolved when I found the discussion on the next page. This could be easily addressed by moving the relevant paragraph on p7 to the end of the first Mulliken paragraph on p6.

> We have implemented the proposed changes in the text.

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Figure 2 is wonderful. But I found it a little confusing to see the tent behaviour, until I realised that the charge is simply switching between identical atoms. Perhaps the x axis could highlight the charge on the other atom in some way (e.g. labels indicating all charge on left/right atom)

> To reduce confusion, we have explicitly added the above reasoning to the caption of this graph.

Finally, it would be really good if the authors could make the data available, at least for H2. I feel this would make the paper much stronger in its claims to provide benchmarks.

> We have added the energies which were sampled as a function of (spin)-resolved populations as reference data in the Supplementary Information. We have also provided interactive notebooks that illustrate how we have generated the data through our software package GQCP [4] on the website of our software package [5].

If you require any additional information regarding our manuscript, please do not hesitate to contact us directly via the resources above. Thank you for your time and consideration.

Sincerely,

Professor Dr. Patrick Bultinck

[1] Bultinck, P.; Van Alsenoy, C.; Ayers, P. W., Carbo-Dorca, R. Critical analysis and extension of the Hirshfeld atoms in molecules. J. Chem. Phys. 2007, 126, 14411

[2] Bultinck, P.; Cardenas, C.; Fuentealba, P.; Johnson, P. A.; Ayers, P. W. Atomic charges and the electrostatic potential are ill-defined in degenerate ground states. J. Chem. Theory Comput. 2013, 9, 11, 4779–4788

[3] Zheng, X.; Liu, M.; Johnson, E. R.; Contreras-Garcia, J.; Yang, W. Delocalization error of density-functional approximations: A distinct manifestation in hydrogen molecular chains. The J. Chem. Phys. 2012, 137, 214106

[4] Lemmens, L.; De Vriendt, X.; Tolstykh, D.; Huysentruyt, T.; Bultinck, P.; Acke, G. GQCP: The Ghent Quantum Chemistry Package, J. Chem. Phys. 2021, 155, 084802

[5] https://gqcg.github.io/GQCP/examples/Mulliken-constrained-CI.html

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