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 Editor-in-Chief,

I am writing to submit 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. We imposed fractional charges and spins on atomic domains by extending the methodology of constraints and applying it to full configuration-interaction wavefunctions. Our (exact) results provide the much-needed numerical support for the findings of Cohen and co-workers [1] that the delocalization error and static correlation error can be characterized through the perspective of such fractional charges and fractional spins. Most importantly, our methodology computationally recovers the flat plane conditions as proposed by Perdew and co-workers [2].

This paper significantly expands on the prior research conducted and published by Zheng and co-workers [3], where charged hydrogen chains are infinitely stretched, and all electrons are symmetrically distributed. Using our methodology, we are no longer restricted to rational fractional populations and hydrogen molecular chains, but we can also induce the wide range of asymmetrical distributions that are characteristic during the bond formation process. Given that there is currently a high need for such reference data to know how far approximate methods are from the exact full configuration-interaction solution and given the generality of the framework proposed, we believe that the findings presented in our paper will appeal to the method developers that subscribe to JCTC.

We confirm that this manuscript has not been published elsewhere and is not under consideration by another journal. All authors have approved the manuscript and agree with its submission to the Journal of Chemical Theory and Computation.

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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] Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Insights into current limitations of density functional theory. Science 2008, 321, 792–794.

[2] Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. Density-functional theory for frac- tional particle number: Derivative discontinuities of the energy. Physical Review Letters 1982, 49, 1691–1694.

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

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