DFT Approach for Asserting Multi-Reference Character in Molecular Systems

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ABSTRACT

Electronic structure methods are fundamentally categorized based on their ability to account for dynamic and nondynamic electron correlation effects. For this reason, the accurate depiction of molecular systems is contingent upon the judicious selection of an electronic structure method. Specifically, multireference (MR) systems may be grossly misrepresented if analyzed using single-reference methods, making the discernment of the predominant type of electron correlation in a molecule an invaluable asset. In an era dominated by the generation of extensive molecular datasets requiring computational treatment, the need for cost-effective MR diagnostic methods is more pronounced than ever. Such economical diagnostics are essential for high-throughput computational studies, allowing for the rapid and accurate identification of MR features within extensive molecular datasets.

Recently, we have conducted a thorough analysis of MR diagnostics using extensive datasets [1], identifying a single well-behaved representative metric of electron correlation that could be employed in single-reference wavefunctions. In this work, we present the extension of the multireference diagnostic to be applied in density functional theory. Using machine learning, we have used a 4000-molecule training set to establish a map between Kohn-Sham orbital energies and the MR character of the molecule, achieving an excellent agreement with the predictions furnished by MP2 and CCSD calculations.

This work thus offers an economical approach requiring a single DFT calculation to assert the MR character of a molecular system, showcasing its potential as a cost-effective, high-accuracy solution for the detection of strong correlation.

References

[1] X. Xu, L. Soriano-Agueda, X. López, E. Ramos-Córdoba, E. Matito, *J. Chem. Theory Comput.* **2024**, *20(2)*, 721