Non-empirical local range separation: Accurate excitation gaps from DFT

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ABSTRACT

Being able to reliably predict the spectroscopic properties of molecular systems with density functional theory (DFT) remains a major theoretical challenge and is highly relevant in view of technological applications. Range-separated hybrid (RSH) functionals are commonly used for that purpose. Optimally tuned RSHs have been particularly successful as they offer a way to adjust the parameter for range separation to the varying electronic properties of diverse systems. However, this system-specific procedure also has well-known drawbacks that can compromise the predictive power of optimally tuned RSHs.
This contribution demonstrates that RSHs become yet more powerful by going from global to local range separation, i. e., by turning the range-separation parameter into an explicit density functional [1]. The focus of our work is to construct a functional that allows to reliably predict excitation gaps from first principles [2]. We follow a non-empirical construction strategy: Our functional respects the important constraints of the homogeneous and slowly varying density limits and eliminates one-electron self-interaction. It does not contain adjustable parameters that need to be determined by fitting to reference data or any kind of system-specific tuning. We demonstrate the functional's accuracy for predicting the fundamental gap in generalized Kohn-Sham theory for a large number of relevant organic molecules, among them systems with a notoriously difficult electronic structure.

References

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