Improved Design of Semi-Empirical Density Functional Approximations

Andrei Paulau[1], Josep Maria Luis[3], Pedro Salvador[3], Eloy Ramos-Cordoba[1], Eduard Matito[1,2]

[1]Donostia International Physics Center (DIPC), Donostia, Spain

[2]Ikerbasque, Basque Foundation for Science, Bilbao, Spain

[3]Institut de Química Computacional i Catàlisi (IQCC), Girona, Spain
andrei.paulau@dipc.org

ABSTRACT

While density functional theory is the most widely used method to calculate molecular properties of medium and large sized molecules, vast majority of modern density functional approximations (DFAs) are unreliable for the calculation of vibrational properties. [1] This can lead to errors in frequencies, intensities and nuclear relaxation contributions to electric response properties of up to thousands of percent in systems with low-frequency modes. We have since found that the problem of the same origin appears in the calculation of purely electronic properties. We show that the fundamental origin of this problem lies in the unphysical oscillations of the real-space exchange-correlation energy density derivatives with respect to external perturbations. By directly connecting the magnitude of these oscillations to specific behaviors of the DFAs at different reduced density gradients, we developed a strategy to design functionals that are robust for calculating molecular properties. Using this strategy, we designed DFAs which are loosely based on the mathematical structure of the ωB97 family of functionals, yet are robust for calculating molecular properties while achieving similar accuracy as the base functionals. Finally, by adding purely density and density-gradient based range-separation of the correlation energy, we construct a DFA that is not only robust for the calculation of molecular properties, but also has a competitive edge in the general performance compared to state of the art density functional approximations.

References

[1] Sitkiewicz, S.P.; Zalesny, R., Ramos-Cordoba, E., Luis, J.M., Matito, E.; How reliable are density functional approximations to compute vibrational spectroscopies? *J. Phys. Chem. Lett.* **2022**, *13*, 5963.