Modern density functional approximations are ill-designed to compute molecular properties

Eduard Matito[1,2]

[1]Donostia Int. Physics Center (DIPC), Donostia, Euskadi, Spain
[2]Ikerbasque Foundation for Science, Bilbao, Euskadi, Spain
ematito@dipc.org

ABSTRACT

We show that properties of molecules with low-frequency modes calculated with density functional approximations (DFAs) suffer from spurious oscillations along the nuclear displacement coordinate [1]. Occasionally, the problem can be alleviated using extensive integration grids that compromise the favorable cost-accuracy ratio of DFAs. Since spurious oscillations are difficult to predict or identify, DFAs are exposed to severe performance errors in IR and Raman intensities and frequencies and other molecular properties [2]. Using Fourier spectral analysis and digital signal processing techniques, we identify and quantify the error due to these oscillations for 45 widely used DFAs, and indicate whether the exchange or correlation functionals are responsible for it [3]. Finally, we show that spurious oscillations occur because the exchange-correlation energy functionals are ill-designed, exhibiting *local* spurious oscillations in the exchange-correlation energy density. We present a judicious modification of B97 and ωB97XD functionals, which drastically reduces spurious oscillations preserving the accuracy of the original functionals. The latter strategy can be applied to the design of modern DFAs that do not suffer from this problem.

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.

[2] Zalesny, R.; Medved, M.; Sitkiewicz, S.; Matito, E.; Luis, J.M.; Can Density Functional Theory Be Trusted for High-Order Electric Properties? The Case of Hydrogen-Bonded Complexes. *J. Chem. Theory Comput.* **2019**, *15*, 3570.

[3] Sitkiewicz, S.P.; Ferradás, R.R.; Ramos-Cordoba, E.; Zalesny R.; Matito, E.; Luis, J.M.; Spurious Oscillations Caused by Density Functional Approximations: Who is to Blame, Exchange or Correlation? *J. Chem. Theory Comput.* **accepted**.