Minimal Auxiliary Basis set for TDDFT

Fabio Della Sala[1,2]

[1]Institute for Microelectronics and Microsystems (CNR-IMM)
[2]Center for Biomolecular Nanotechnologies @UNILE (CBN-IIT),
Lecce (Italy), e-mail:fabio.dellasala@unisalento.it

ABSTRACT

For the calculation of optical properties of finite systems, such as molecules and nanoparticles, the Time-Dependent Density Functional Theory (TD-DFT) with hybrid functionals is often the method of choice, due to its high accuracy-to-cost ratio. Nevertheless, routine hybrid TDDFT calculations are yet limited to systems with a few hundreds of atoms. Here, we show that the computational cost of hybrid TD-DFT can be reduced by a factor between one and two orders of magnitude, employing a minimal auxiliary basis set which includes only one (optimized) s-type function per atom (TDDFT-ris[1]), and with an averaged error of only 60 meV (see Fig. 1b). Comparison with the related TDDFT tight-binding approximations is also discussed[1]. Including an additional (optimized) p-type orbital per atom (TDDFT-risp[1, 2]) the whole absorption spectra is then almost indistinguishable from the reference TDDFT spectrum, see Fig. 1a.

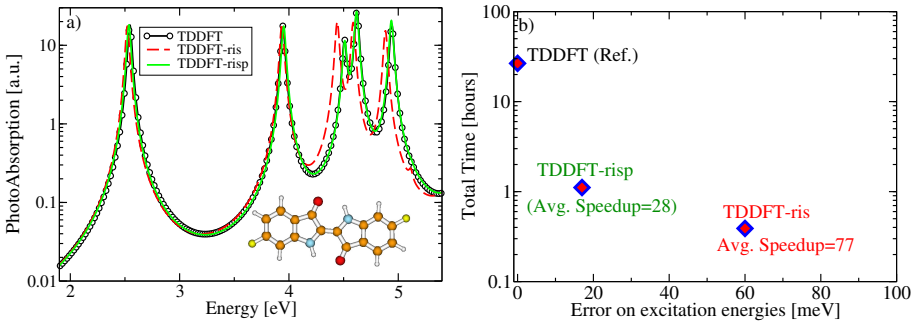

Figure 1: a) TDDFT absorption spectrum of the indigo molecule; b) Compulational cost vs accuracy on a benchmark of 54 small-to-medium size organic molecules[2]. Calculations with the PBE0 functional. TDDFT-ris/risp is available in TURBOMOLE[3].

References

[1] Zhou, Z.; Della Sala, F; Parker, S.M., "Minimal Auxiliary Basis Set Approach for the Electronic Excitation Spectra of Organic Molecules", *J. Phys. Chem. Lett* **2023**, *14*, 1968–1976

[2] Della Sala, F., in preparation.

[3] Franzke, Y. J. et al., "TURBOMOLE: Today and Tomorrow", *J. Chem. Theory Comput.*, **2023**, *19*, 6859–6890.