Density Functional Calculations of Challenging Electronic Excitations

GIANLUCA LEVI

[1]*Science Institute of the University of Iceland, VR-III, Reykjavík 107, Iceland*
giale@hi.is

Recent progress in time-*in*dependent density functional calculations of excited electronic states with variational orbital optimization will be presented. In this approach, the excited states are obtained as stationary points other than the ground state minimum on the electronic energy surface. The calculations can be performed efficiently and without the risk of collapse to lower energy states by directly optimizing the orbitals using algorithms for finding *n*-th order saddle points [1]. These methods hold the promise to greatly extend the applicability of orbital optimized calculations of excited states, as demonstrated by applications to challenging excitations in isolated molecules, molecules in solution and solid-state systems. The description of charge transfer and Rydberg states of molecules is significantly improved compared to linear-response time dependent density functional theory calculations, providing remarkably good results even at the generalized gradient approximation (GGA) level [2,3]. The method can also be used in combination with explicit solvation models to elucidate the photoinduced dynamics of solvated metal complexes [4]. Calculations of the long-debate electronic excitations in the charged nitrogen-vacancy center in diamond using meta-GGA functionals yield excitation energy values in close agreement with high-level many-body calculations [5].

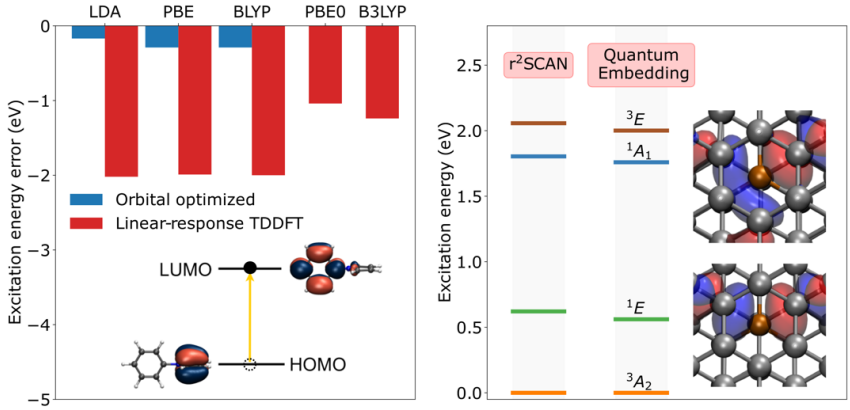

Figure 1: Orbital optimized density functional calculations of a charge transfer excited state in the *N*-Phenylpyrrole molecule (left) and excitations of the NV^- center in diamond (right).

References

[1] Schmerwitz, Y. L.; G. Levi, G.; Jónsson, H. *J. Chem. Theory Comput.* **2023**, 19, 3634.

[2] Selenius, E.; Sigurðarson, A. E.; Schmerwitz, Y. L.; Levi, G. arXiv:2311.01604, **2024**.

[3] Sigurðarson et al. *J. Chem. Phys.* **2023**, 159, 214109.

[4] Katayama, T. et al. *Chem. Sci.*, **2023**, 14, 2572.

[5] Ivanov, A. V.; Schmerwitz, Y. L.; Levi, G.; Jónsson, H. *SciPost Phys.*, **2023**, 15, 1–21.