

Electronic Excitation Spectra of Very Large Diradicals: A Simplified Spin-Flip Time-Dependent Density Functional Theory Approach

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Experimentalists working with diradicals are often facing the question of what kind of species among singlet or triplet diradicals or closed-shell molecules are observed. To treat large diradicals with a high density of electronic states, we propose a simplified version of the SF-TD-DFT method[1] for a fast computation of their state energies and absorption spectra with a similar accuracy as the non-simplified scheme. An ultra-fast tight-binding variant called SF-sTD-DFT-xTB is also developed to treat even larger systems. For a benchmark set of nine diradicals, good agreement between simplified and conventional SF excitation energies for standard functionals is found. This shows that the proposed parametrization is robust for a wide range of Fock exchange mixing values. With the asymptotically correct response integrals used in SF-sTD-DFT and a correction factor of $\sqrt{2}$ for the transition moments, the SF-sTD-DFT/B5050LYP/cc-pVDZ method even outperforms the non-simplified scheme when comparing to the experimental absorption spectra for this set of diradicals while drastically reducing the computational effort. To showcase the actual performance of the method, absorption spectra of two μ -hydroxo-bridged dimers of corrole type Ga(III) complexes derivatives were computed and compared to experiment, providing good qualitative agreement.

As a first application, we characterized the absorption spectra of indeno[1,2b]fluorene and [2,1-c]diindeno[n]thiophene derivatives to determine if they are diradicals.[2] To interpret spectra, we implemented natural transition orbitals (NTOs) at this level of theory. They provide a simple interpretation for the low-lying excited states in terms of three different types of NTOs: “quinoid”, “aromatic”, and “ π -bonded”. When comparing with experiment, we found that only one molecule of this set is actually a high-spin triplet diradical. Others are almost closed-shell molecules with a very small contribution from a doubly-excited configuration that only the spin-flip method was able to capture. The small amount of static correlation recovered by the spin-flip active space provides a linear relation between the first visible theoretical and experimental excitation energies among this set.

[1] de Wergifosse, M., Bannwarth, C., Grimme, S. *J. Phys. Chem. A* **2019**, *123*, 5815-5825.

[2] de Wergifosse, M., Seibert, J., Champagne, B., Grimme, S. *J. Phys. Chem. A* **2019**, *123*, 9828-9839.