MRSF-TDDFT: A Good Way of Introducing Strong Correlation

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A new quantum theory, MRSF-TDDFT (Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory) has been developed[*] for both ground and excited electronic states. With the help of a unique spinor-like transformation, a *hypothetical* single reference is constructed from the two M_S=+1 and -1 components of the RO-KS determinant, doubling its response space.

As a result, MRSF-TDDFT eliminates the problematic spin-contamination pitfalls of SF-TDDFT as well as the general topological problem of conical intersection by TDDFT. Unlike DFT, it allows to study open-shell ground singlet states such as diradicals. Furthermore, it produces the HOMO-to-LUMO *doubly* excited configuration, which is the main ingredient to properly account for the interplay of bright and dark excited states.

In short, MRSF formalism gives a balanced treatment of *dynamic and nondynamic* electron correlations, with the convenience of single determinant orbital optimization. Here, we highlight its advantages by presenting our recent results on Jahn-Teller distortions, excited state nonadiabatic dynamics, conical intersection, open shell singlet system, nonadiabatic coupling, spin-orbit coupling and X-ray absorption/ionization applications.

[*] (a) Lee, S., Filatov, M., Lee, S., & Choi, C. H. (**2018**). *J. Chem. Phys.*, 149(10), 104101. (b) Lee, S., Kim, E., Nakata, H., Lee, S. & Choi, C. H. (**2019**). *J Chem. Phys.*, 150(18), 184111. (c) Park, W., Shen, J., Lee, S., Piecuch, P., Filatov, M., Choi, C. H. (**2021**) *J. Phys. Chem. Lett.*, 12, 39, 9720–9729.