Analytic gradient of spin-adapted time-dependent density functional theory (X-TD-DFT)

Zikuan Wang,[a] Zhendong Li,[b] and Wenjian Liu[c]

[a] Beijing National Laboratory for Molecular Sciences, Institute of Theoretical and Computational Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

[b] Key Laboratory of Theoretical and Computational Photochemistry of Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China

[c] Qingdao Institute for Theoretical and Computational Sciences, Shandong University, Qingdao, Shandong 266237, P. R. China

While TD-DFT has been very successful for excited states of closed-shell molecular systems, it is much less so for excited states of open-shell molecules due to severe spin contamination. This problem can be resolved by the spin-adapted version of TD-DFT (S-TD-DFT) [1-2], which is free of spin contamination. In particular, the simplified version of S-TD-DFT, X-TD-DFT [3], is very easy to implement: only a few Fortran lines are needed to add the one-electron corrections to a U-TD-DFT module taking ROKS orbitals as input. It has been shown [4,5] that X-TD-DFT for excited states of open-shell systems has a similar accuracy as TD-DFT for excited states of closed-shell systems, yet with no computational overhead. In this work, we derive and implement the analytic nuclear gradients of X-TD-DFT using a Lagrangian approach. Numerical results for the geometries and adiabatic excitation energies of excited states of prototypical open-shell systems will be presented to reveal the performance of X-TD-DFT.

References

[1] Z. Li and W. Liu, J. Chem. Phys. **133**, 064106 (2010).
[2] Z. Li, W. Liu, Y. Zhang and B. Suo, J. Chem. Phys. **134**, 134101 (2011).
[3] Z. Li and W. Liu, J. Chem. Phys. **135**, 194106 (2011).
[4] Z. Li and W. Liu, J. Chem. Theory Comput. **12**, 238 (2016).
[5] Z. Li and W. Liu, J. Chem. Theory Comput. **12**, 2517 (2016).