Assessing Time-Dependent DFT for Non-Covalent Interactions in Excited Complexes

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ABSTRACT

Linear-response time-dependent DFT (TD-DFT) in the adiabatic approximation has emerged as the method of choice for excited-state calculations. Within this approximation, the exchange-correlation kernel is known from ground-state DFT. As such, any ground-state Density Functional Approximation (DFA) may be applied to TD-DFT. A known limitation of most DFAs is their inability to accurately capture non-covalent interactions (NCIs), including dispersion forces, in the ground state. [1] However, the performance of TD-DFT methods for excited-state NCIs remains undertested. Exciplexes (excited complexes) are complexes which are more strongly bound in their electronically excited-state compared to the ground-state. As such, exciplex binding provide a useful case study for excited-state NCIs. We investigate the performance of various DFAs to describe exciplex binding. Additionally, we test whether ground-state dispersion corrections correctly recover dispersion forces in exciplexes.

References

[1] Kristyán, S.; Pulay, P. Can (semi)local density functional theory account for the London dispersion forces? *Chem. Phys. Lett.* **1994**, *229* (3), 175-180