LONG-RANGE CORRECTED TD-DFT ANALYSIS OF THE CHARGE TRANSFER AND EXCITON STATES OF STACKED DNA BASE OLIGOMERS

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Standard TD-DFT hybrid functionals fail to properly account for the 1/r dependence of charge transfer (CT) excitations[a]. To mitigate this error, we employ recently developed long-range corrected TD-DFT functionals for an improved assessment of CT states among low lying electronic excitations of stacked DNA base oligomers. We find that hybrid functionals grossly underestimate CT excitations compared to long-range corrected TD-DFT and wavefunction methods in both the gas phase and the solution phase. This evidence suggests that the the CT states of DNA oligomers are higher in energy than spectroscopically bright exciton states while in the Franck-Condon geometry. Furthermore, we explore base sequence, base pairing, and conformational effects on the excited states in effort to discover possible non-radiative channels into CT states from the bright exciton states.

[a] Andreas Dreuw and Martin Head-Gordon; *J. Am. Chem. Soc.* **126**, (12), 2004