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# Excitation energies through Becke's exciton model within a Cartesian-grid KS DFT

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**Abstract**

Photon-induced electronic excitations are ubiquitously observed in organic chromophore. In this context, we present a simple, alternative time-independent DFT procedure, for the computation of single-particle excitation energies, in particular, the lower bound excited singlet states, which are of primary interest in photochemistry. This takes inspiration from recently developed Becke's exciton model, where a key step constitutes the accurate evaluation of correlated singlet–triplet splitting energy. It introduces a non-empirical model, from both "adiabatic connection theorem" and "virial theorem" to analyze the role of $2e^-$ integral in such calculations. The latter quantity is efficiently mapped onto a real grid and computed accurately using a purely numerical strategy. Illustrative calculations are performed on 10 $\pi$-electron organic chromophores within a Cartesian grid implementation of pseudopotential Kohn–Sham (KS) DFT, developed in our laboratory, taking SBKJC-type basis functions within B3LYP approximation. The triplet and singlet excitation energies corresponding to first singly excited configuration are found to be in excellent agreement with TD-B3LYP calculations. Further, we perform the same for a set of larger molecular systems using the asymptotically corrected LC-BLYP, in addition to B3LYP. A systematic comparison with theoretical best estimates demonstrates the viability and suitability of current approach in determining optical gaps, combining predictive accuracy with moderate computational cost.