

# Excitation energy by Coupled-Cluster methods for large molecules: a fragmentation based approach

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While Coupled-Cluster methods have been proven to provide an accurate description of excited states, the scaling of the computational costs with the system size limits their applicability. In our recent research we design a fragment based approach which can be applied to non-covalently bound molecules with interacting chromophores localized on the fragments (so called *Frenkel pairs*), in particular those of  $\pi$  stacked nucleobases.

The interaction of the fragments needs to be considered at two distinct steps. First, the states localized on the fragments need to be described in the presence of the other fragment(s). Here, beside the often used electrostatic interaction, also the dispersion and the Pauli repulsion are indispensable parts of the interaction energy. Several approaches have been tested. The so called Huzinaga embedding,<sup>1,2</sup> describes the complete system by a DFT method, while the CCSD calculations are performed on the selected monomer in the presence of the electron density of the other fragment obtained in the dimer calculation. This way an accurate inclusion of the electrostatic and Pauli repulsion is possible, but the dispersion interaction – due to the underlying DFT calculation – is missing and needs to be added separately. Other QM/MM type calculations can also be suitable for this step, but in addition to the usual point charges, it is necessary to take into account Pauli repulsion and dispersion effects, as well.

In the second step, the interaction of the localized chromophores needs to be considered to properly describe the Frenkel pairs. Here the inclusion of purely electrostatic contributions appears to be sufficient: we have tested the Perturbed Matrix Method by Amadei and coworkers<sup>4</sup> which calculates the Frenkel coupling of the localized excited states using the transition dipole moments of the interacting fragments.

Several test calculations will be presented which guides us to select the most suitable combination of available methods.

<sup>1</sup> S. Huzinaga and A. A. Cantu, *The Journal of Chemical Physics* **55**, 5543 (1971).

<sup>2</sup> B. Hégyely, F. Bogár, G. G. Ferenczy, and M. Kállay, *Theoretical Chemistry Accounts* **134**, 132 (2015).

<sup>3</sup> R. Spezia, M. Aschi, A. Di Nola, and A. Amadei, *Chem. Phys. Lett.* **365**, 450 (2002).