Non-orthogonal configuration interaction to study singlet fission

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We have developed a variation of the non-orthogonal configuration interaction (NOCI) approach [1-2] to study the interaction between excited states on neighbouring molecules in a cluster. In our implementation, the NOCI wavefunction is written as a linear expansion of many electron basis functions (MEBFs), which are spin-adapted, antisymmetrized products of multi-determinantal molecular wavefunctions. Each molecular electronic state is expressed in its own set of optimized orbitals. NOCI can account for electron correlation and orbital relaxation in an efficient way, gives short wavefunction expansions, and allows for a clear chemical interpretation in terms of the localized molecular states.

We have drastically reduced the computational bottlenecks that arise due to the use of non-orthogonal orbitals for large molecular systems. We decreased the number of integrals by around 100 fold by expressing the integrals in a reduced common molecular orbital basis for the different electronic states [3]. The calculation was simplified further by including only the relevant determinant pairs. Hybrid OpenMP/MPI parallelization and GPU acceleration was used to speed up the calculations.

We present here our results of using NOCI to study energy transfer in singlet fission (SF), a molecular process that has been found to be a promising way to enhance the efficiency of organic photovoltaics [4]. Using NOCI we calculate the effective coupling between the initially photo-excited state and the state describing the two triplet excitations that are coupled into a singlet. Our results on using NOCI to study SF are very promising [5] and show that the method can also be used to study charge transfer processes.

References

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