Many-electron band structures based on Non-Orthogonal Configuration Interaction to study exciton dispersion and charge transport

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A many-electron tight-binding (METB) approach is presented to use the results of non-orthogonal configuration interaction with fragments (NOCI-F) calculations on small ensembles for the study of much larger (or even periodic) systems [1]. NOCI-F is designed such to include full orbital relaxation, account for static and dynamic electron correlation, but at the time remain as close as possible to the intuitive interpretation of the results typical of (semi-)empirical model Hamiltonians. NOCI-F is implemented in the GPU-accelerated and massively parallel computer code GronOR [2], allowing for calculations on systems with up to 150 atoms [3].

The METB approach is validated against NOCI-F for a stack of 15 ethene molecules, small enough to be handled in full by the NOCI-F approach and large enough to extract relevant information from the METB treatment. Thereafter, METB is used to show how the singlet fission coupling depends on the degree of delocalisation of the singlet excitonic state. Finally, METB is applied to extract the dispersion of some many-electron states in the tetracene crystal. The insight gained from these METB calculations based on NOCI-F parametrisation can be used to further study the fundaments of singlet fission and the subsequent fate of the biexciton.

References

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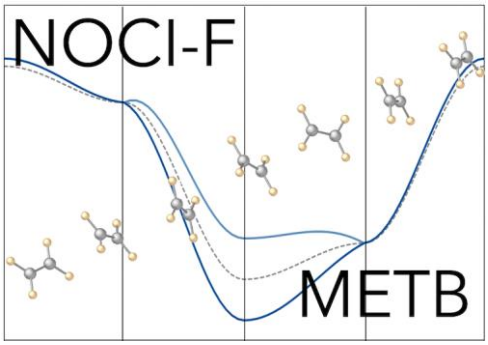

Figure 1: Many-electron bandstructure of the singlet excitonic state in tetracene constructed from NOCI-F calculations on dimers and trimers