Modeling Localised Excitations and Electron Transfer with a Non-orthogonal Product Wave Function Approach

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The description of intermolecular transfer of electrons and electronic excitations is an important part of the theoretical investigation of molecular electronics. It requires models that allow accurate predictions and facilitate understanding of the underlying processes. For this purpose we employ a non-orthogonal product wave function approach, along with a Löwdin orthogonalization procedure[1], to obtain electronic coupling coefficients of multi-state systems.

The use of non-orthogonal wave functions has found renewed interest in, e.g. non-orthogonal configuration interaction (see for example [2]), and it has been applied in the calculation of electronic coupling coefficients at different levels of theory (e.g. [3], [4]). Here, we present our computational approach based on antisymmetrised products of individually selected determinants of the building blocks of the actual, extended system. We compare its performance to other approaches and apply it to singlet fission and the intermolecular transfer of electronic excitations.

References
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