

Construction of Diabatic Electronic States of Configuration Interaction type by Localization of Molecular Orbitals with Floating Occupations

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Diabatic states can be qualitatively defined as electronic states with a vanishing or weak dependence on the internal nuclear coordinates [1, 2]. In particular, they preserve a well defined character (i.e. charge distributions, bonding and nodal properties) throughout the nuclear coordinate space of interest and represent a convenient tool to characterize the nature of the usual adiabatic electronic states, i.e. the eigenstates of the electronic Hamiltonian.

In this poster communication, we present a method to construct diabatic electronic states for a system that can be clearly separated into groups of atoms (the “monomers”). The method is based on two steps: (i) first, the relevant molecular orbitals (MO) are rotated to produce MOs localized on the monomers (LMO); (ii) next, diabatic reference states are built on the LMO basis and a set of adiabatic states of the system is transformed so as to achieve maximum overlap with the references [3].

In the first place the method was implemented in the framework of semiempirical Configuration Interaction based on Floating Occupation Molecular Orbitals (FOMO-CI) [4]. However, it can be applied without changes to ab initio wavefunctions, obtained for instance by state-average CASSCF or ab initio FOMO-CI [5].

We show how to employ the procedure to compute the low-lying diabatic states and electronic couplings involved in singlet fission [6] and exciton coupling for systems consisting of well separated chromophores. Moreover, we present a successful application of the method on the cis-trans isomerization in hexatriene, where the subsystems are covalently bound. Finally, we present the application of the algorithm to analyze adiabatic or time-dependent electronic wavefunctions obtained in excited state dynamics simulations.

References

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