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Static correlation effects in flavin mediated hydride transfer

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Abstract: Many enzymatic reactions use flavin nucleotide cofactors (FAD) as electron acceptors. In cellular respiration, flavoenzymes mediate coupled proton-electron transfer reactions between FAD and succinate/fumarate [1]. Here, we modeled hydride transfer reactions mediated by flavins (Figure) isolated in the gas phase to understand the intrinsic energetics and mechanisms involved and ultimately choose a reliable method to study flavoenzymes reactions.

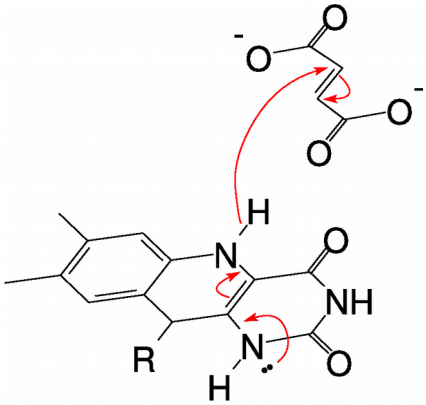

Figure. Flavin hydride transfer reaction

Reaction profiles were determined by density functional theory (DFT) with B3LYP functional and 6-31+G* basis set using the Gaussian 09 program. Relative energies were recalculated with functionals including dispersion corrections, with second-order Møller-Plesset perturbation theory (MP2) using the 6-311+G** basis set and with complete active space self-consistent field method (CASSCF), followed by a perturbative treatment with n-electron valence state perturbation theory (NEVPT2) all using the Def2-TZVP basis set in ORCA 3.0.1 package.

Our results show that the distribution of π electrons along flavin's isoalloxazine ring highly contributes to the complexation and orientation of the reactant complex. During flavin reduction, π electrons are rearranged and the isoalloxazine ring bends, losing planarity. As the system approaches the transition state, different electronic states become degenerate and the reaction barriers of hydride transfers are highly affected by static electronic correlation. Although MP2 can recover dynamical correlation and describe well flavin π stacking and dispersion interactions, the reaction barriers of hydride transfer are miscalculated, so multiconfigurational energy profiles have to be used to describe the reactions.

Key-words: multiconfigurational methods, electronic structure, reactivity
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References: [1] T.M. Iverson, Biochim. Biophys. Acta, 1827, 648-57 (2012)