Simulation of Nonadiabatic Chemical Reaction using TD-DFT

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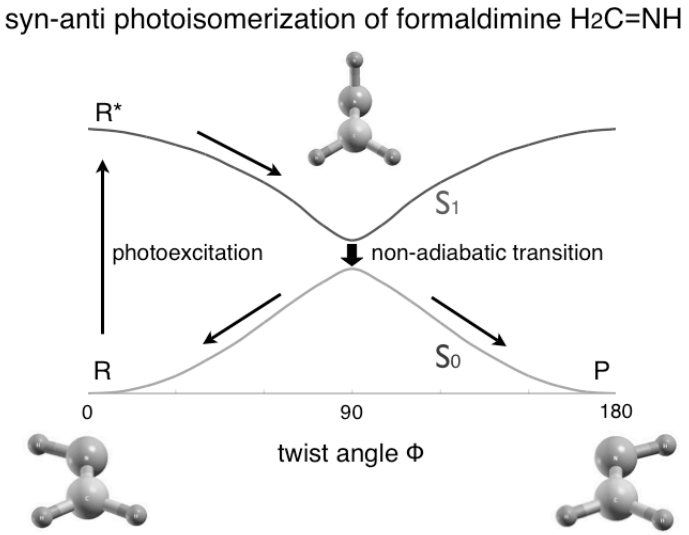
Density functional theory (DFT)[1] is one of the most widely used tools for studying the ground state properties of molecules and solids. And many properties of electronically excited systems can be determined using time-dependent density functional theory (TD-DFT)[2], such as excitation energies and the associated absorption spectra. Nowadays, also molecular dynamics of excited states have become possible using TD-DFT.

However, most of these calculations are based on a Born-Oppenheimer (BO) approximation to separate electronic and nuclear motions, i.e., the electrons follow the nuclei almost instantaneously. This approximation is not valid in a number of important cases, including radiationless decay of excited states, and electron-phonon couplings. Processes of photochemistry are inherently nonadiabatic.

In cases where the BO approximation is not applicable, the nonadiabatic couplings becomes the central quantity[3]. Because the nonadiabatic couplings are defined using many-electron wavefunction, the calculation of the couplings was generally thought to be difficult to realize in DFT or TD-DFT.

Recently we developed an efficient method to compute nonadiabatic couplings using TD-DFT[4]. So we can approach the problems of chemical reactions including nonadaibatic effects within framework of DFT and TD-DFT. In this poster, we present the syn-anti photoisomerization of folmaldimine, prototypical of photoisomerization about a double bond, as an example of DFT and TD-DFT application to the nonadiabatic chemical reaction.



[1] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford, New York, 1989)
[2] E. K. U. Gross, J. F. Dobson, and M. Petersilka, *Density Functional Theory* (Springer, Heidelberg, 1996)
[3] M. Bear, *Beyond Born-Oppenheimer* (Wiley, Hoboken, New Jersey, 2006)
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