

Electronic excitations in the condensed phase

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Differential solvation of the electronic states of a chromophore in a solvent, called solvatochromism, can be used as a measure of solute-solvent interactions. While multiple absorption and emission spectroscopic studies provide valuable information on the magnitude and dynamics of solute-solvent coupling, calculations in the condensed phase still remain a major challenge to the theoretical community. This is because the increased number of nuclear and electronic degrees of freedom makes accurate first-principles calculations on a condensed phase system unfeasible long before the system can approach the bulk. One general approach to this type of problem is to separate a system into two parts, such that one (active) part is treated by quantum mechanical (QM) techniques, and the other, usually larger, part is calculated by using classical (molecular) mechanics (MM). Recently, we have developed the QM/MM scheme which allows inclusion of solvent effects in calculations of the ground and excited electronic states of chromophores.

In this lecture we will discuss various ways in which the environment can affect electronic states, from modifying potential energy surfaces and coupling between the states to completely changing their character and creating new, so called charge transfer-to-solvent states. We will talk about origins of solvatochromic shifts in polar and apolar solvents as well as a competition between orbital relaxation of the solute in the electric field of the solvent and response of polarizable environment to the density of electronic states.