Analysis of electronic states across ensembles of nuclear configurations

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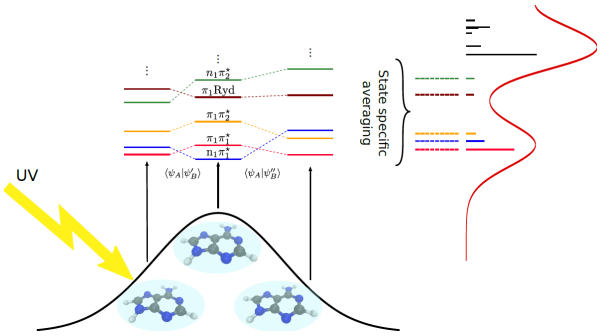
The nuclear ensemble approach is the method of choice for simulating spectroscopic observables based on mixed quantum-classical simulations. The method provides good estimates for many spectral features while naturally including all nuclear degrees of freedom and contributions from any number of electronic states which then sum to give the full spectrum [1]. However, analyzing the individual contributions of different states is not particularly useful when working in the adiabatic basis since the character of adiabatic states changes significantly with the change in nuclear geometry.

In this contribution, we propose a procedure based on the computation of electronic wave function overlaps for automatically determining the character of electronic transitions and apply it to the study of UV spectra of different molecules in the gas phase and in the aqueous environment [3]. Spectra are generated using the nuclear ensemble method in the gas phase and in solution and the electronic states at all nuclear geometries are assigned based on overlaps with a set of reference states defined at the ground state minimum geometry. This allows for an accurate black-box decomposition of the spectra in terms of diabatic contributions and a state specific analysis of solvation and other effects for any number of excited states of any type.



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