Simulating Vibronic Spectra without Born-Oppenheimer Surfaces

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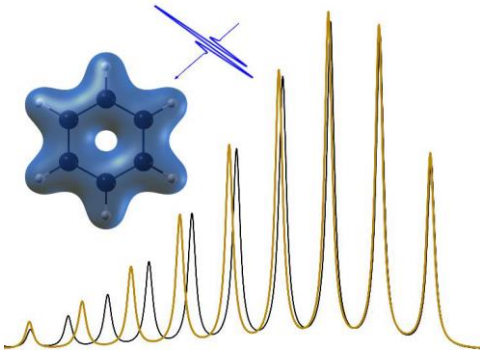

Being able to simulate coupled electron-nuclear processes for large molecular systems in a computationally tractable manner is a defining challenge of ab-initio condensed matter quantum dynamics. While the Born-Oppenheimer (BO) framework is a powerful framework, it's applicability is limited by the computational bottleneck of potential energy surface fitting and the calculation of non-adiabatic coupling terms. In this talk, we show how vibronic spectra in molecular systems can be simulated in an efficient and accurate way using first principles approaches without relying on the explicit use of multiple BO potential energy surfaces.

We demonstrate and analyze the performance of mean-field Multi Trajectory Ehrenfest (MTEF) and beyond mean-field Interacting Conditional Wavefunction (ICWF) dynamics techniques for the H_2 molecule in one dimension, in the both cases capturing the vibronic structure, including quantum Franck-Condon effects, with the ICWF results converging quite accurately to the exact results. In a practical application of this methodology we simulate the absorption spectrum of benzene in full dimensionality using Time-Dependent Density Functional Theory and MTEF, finding good qualitative agreement with experiment. These results show promise for future applications of this methodology in capturing phenomena associated