

Ab initio quantal treatment of nonadiabatic molecular photodynamics

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The paradigmatic role of conical intersections of potential energy surfaces¹ for nonadiabatic excited-states dynamics is reviewed briefly. In the literature the theoretical treatment of the dynamics is often based on classical trajectory calculations. To correctly capture quantal effects, which are especially important when surface hops occur, we instead rely on wavepacket propagation techniques such as the Multiconfiguration Time-dependent Hartree (MCTDH) method². In combination with the linear vibronic coupling approach¹ this provides a versatile tool to partly overcome the challenges resulting from the exponential scaling and related problems.

In the talk, the general considerations are illustrated by suitable examples to highlight the most relevant phenomena. These are taken from our work on the UV excitation spectra of small polyenes^{3,4} and photoelectron spectra of benzene⁵, featuring more than two strongly coupled electronic states.

References

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