Simulating Non-adiabatic Photochemistry using Grids and Gaussians

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In this talk, methods to solve the TDSE will be presented showing how the dynamical behaviour of photo-excited molecules can be described. Quantum effects are often key due to strong coupling between nuclear and electronic motion when potential surfaces are close in energy, or cross at conical intersections and a both electrons and nuclei should be treated quantum mechanically for good results. A basic problem, still an area of active research, is solving the huge computational resources needed by accurate quantum dynamics simulations. This scaling manifests itself in two ways. Firstly in the computer resources required for the propagation of the nuclear wavepacket. Secondly in the space to be covered when calculating the potential energy surfaces.
The multi-configurational time-dependent Hartree (MCTDH) algorithm has gone a long way in solving the first problem [1]. In particular the multi-layer form (ML-MCTDH) is able to propagate multi-dimensional wavepackets with 100s of degrees of freedom. These grid based methods, however, in general require global potential surfaces which can restrict it to using model Hamiltonians rather than general, flexible molecular potentials. While this approach has been very useful in describing the initial stages of, e.g. non-adiabatic dynamics after photo-excitation [2] it is not able to describe the longer time photochemistry.
An approach to break both the exponential scaling and provide general potentials is the variational multi-configurational Gaussian (vMCG) method [3]. This uses a set of Gaussian wavepackets (GWP) as a time-dependent basis, but unlike conventional GWP methods, the GWPs follow variational rather than classical trajectories and retains the full quantum description of the system. It is also suited for direct dynamics simulations, calculating the potential on-the-fly using quantum chemistry programs and so opens up the use of flexible potentials [4]. The present state-of-the art of this method will be presented, showing its promise and highlighting the problems still to be solved.

References

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