

Accurate studies of ultrafast photoexcited processes in polyatomic molecules: the MCTDH method.

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What occurs within the first few hundred femtoseconds after a molecule absorbs a photon is an interesting and challenging topic for computer simulations. Interesting, as often processes occur that dominate the subsequent photochemistry and photophysics of a molecule, as is observed in time-resolved laser spectroscopy experiments. Challenging, as an accurate simulation requires solution of the time-dependent Schrödinger equation (TDSE) to account for the coupling of nuclear and electronic motion (non-adiabatic effects) that lead to a breakdown of the Born-Oppenheimer Approximation.

The numerical solution of the TDSE has become an essential tool for the study of fundamental molecular processes, and the Multi-configuration time-dependent Hartree (MCTDH) method [1, 2] is a powerful quantum dynamics algorithm, able to include more degrees of freedom than other methods. This is particularly useful in photochemistry, where it is often difficult to isolate a few important degrees of freedom leading to the need to simulate a multi-dimensional problem [3]. A benchmark example was a study of the pyrazine molecule including explicitly all 24 vibrational modes [4]. In a more recent example that demonstrates the utility of the approach, simulations on benzene combined with experiments made by the Fielding group at UCL, have uncovered a channel with ultrafast inter-system crossing that plays a role in the classic channel 3 problem [5].

MCTDH is, however, a grid-based method. And like all grid-based quantum dynamics methods is restricted to small molecules. To extend it to more general systems, we are developing a direct dynamics version, in which the potential surfaces are calculated on-the-fly using quantum chemistry calculations only when required. The DD-vMCG method is fully quantum mechanical, and promises to have good convergence properties, essential for these expensive calculations [6].

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