Quantum Dynamics Simulations of Photo-excited Molecules - From Grid-based to Direct Dynamics

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The direct numerical solution of the time-dependent Schrödinger equation has become an essential tool for the theoretical study of fundamental molecular processes. The Multi-configuration time-dependent Hartree (MCTDH) method [1, 2] provides a powerful quantum dynamics algorithm, which enables us to include more degrees of freedom than other methods. This is particularly useful in the study of photochemistry, where non-adiabatic effects can couple the motion of a number of degrees of freedom leading to the need to simulate a multi-dimensional problem [3]. A Recent examples showing how simulations can help interpret experiments include the uncovering of ultrafast inter-system crossing in the classic channel 3 problem in benzene [4], and the involvement of Rydberg states in the dynamics of pyrrole [5] and aniline [6].

MCTDH is, however, a grid-based method. And like all grid-based quantum dynamics methods is still restricted to small molecules. To extend the method to larger and 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 by the system. The DD-vMCG method is fully quantum mechanical, and promises to have good convergence properties, which are essential for these expensive calculations [7].

References

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