Obtaining Potentials for Molecular Excited States Using On-The-Fly Simulation: The DD-vMCG Method

Graham Worth, UCL, U.K.

The non-equilibrium time evolution of a molecular system can be described by solving the time-dependent Schrödinger equation (TDSE). Efficient algorithms exist for the general solution of this equation, but a significant bottleneck in these studies is that potential energy functions are required that are non-trivial to obtain. After photo-excitation, a molecular wavepacket evolves in a manifold of electronic states and a set of coupled potential energy surfaces are required. These surfaces and couplings, however, are difficult to obtain for molecules beyond three atoms due to the size of the space to be covered. In addition, the *non-adiabatic* coupling between the surfaces is singular at nuclear configurations where the potential surfaces are degenerate, points known as conical intersections.

In traditional solutions to the TDSE using grid-like basis sets, a set of global potential functions is required a priori, which is impossible to obtain for polyatomic systems. Rather than prefitting potential surfaces, one approach is to calculate the potential functions on-the-fly using quantum chemistry programs in what are called *direct dyanmics* methods. These, however, require basis functions that are local in coordinate space and usually are only approximate solutions to the TDSE. In the *direct dynamics variational multi-configurational Gaussian* (DD-vMCG) method [1] a variational Gaussian function basis set is used to describe the evolving wavepacket in what is potentially an exact solution.

The DD-vMCG method is, however, numerically unstable due to the non-orthogonal basis functions and the form of the equations of motion. It also requires an on-the-fly diabatisation procedure that is not rigourously defined [2]. Despite this, the method shows promise as a general and flexible solution to the TDSE for polyatomic photo-excited molecules, but requires further testing.

References

[1] G. W. Richings, I. Polyak, K. E. Spinlove, G. A. Worth, I. Burghardt, and B. Lasorne, *Quantum Dynamics Simulations using Gaussian Wavepackets: The vMCG Method*, Int. Rev. Phys. Chem. **34** (2015), 269–308.

[2] G. W. Richings and G. A. Worth, *Multi-State Non-Adiabatic Direct-Dynamics on Propagated Diabatic Potential Energy Surfaces*, Chem. Phys. Lett., (2017) **683**, 606–612.