

Quantum Dynamics Methods for Molecular Excited States: MCTDH and beyond.

G. A. Worth

Dept. of Chemistry, University College London,
London, WC1H 0AJ, U.K.

Solving the time-dependent Schrödinger Equation has a natural exponential scaling with system size. This makes it hard to achieve complete quantum mechanical results for molecules with more than a few atoms without resorting to approximations. The exponential scaling manifests itself in 2 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. These problems are exacerbated for systems involving excited states where couplings between potential surfaces are required and high accuracy is sometimes necessary for even qualitatively correct results.

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, thus is able to study extended systems and condensed phases. It does, 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

- [1] M. Beck, A. Jäckle, G. Worth and H.-D. Meyer, *Phys. Rep.* **324**, 1 (2000).
- [2] G. A. Worth, H.-D. Meyer, H. Köppel, L. S. Cederbaum and I. Burghardt, *Int. Rev. Phys. Chem.* **27**, 569 (2008).
- [3] G. W. Richings, I. Polyak, K. E. Spinlove, G. A. Worth, I. Burghardt and B. Lasorne, *Int. Rev. Phys. Chem.* **34**, 269 (2015).
- [4] G. W. Richings and G. A. Worth, *Chem. Phys. Lett.* **683**, 606 (2017).