

# Using Direct Quantum Dynamics to Study Non-adiabatic Photochemistry

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The accurate study of molecular dynamics after photo-excitation requires a full quantum dynamical treatment of the nuclei to correctly describe the flow of energy between vibrational and electronic states. This is particularly true when curve crossing processes, such as internal conversion (IC) through a conical intersection, or inter-system crossing (ISC) are involved. In these cases the coherence of the electronic wavepacket in the different states is key to the time-evolution of the system.

Quantum dynamics simulations are computationally hard problems. Traditional methods use a full direct-product grid basis set and the resources required scale exponentially with the number of degrees of freedom (DOF). The multi-configurational time-dependent Hartree (MCTDH) algorithm is the most efficient grid-based solution to the time-dependent Schrödinger equation (TDSE) [1], and is now able to treat wavepackets with 10s of DOF. Now, however, the bottleneck is obtaining realistic potential energy surfaces (PES) for polyatomic systems as the effort involved in calculating global surfaces also scales exponentially with system size.

To mitigate for the problem in calculating the potentials, an obvious approach is to use direct dynamics. Here, the potentials are calculated on-the-fly only when required using quantum chemistry calculations [2]. As only information about the PES local to a point in configuration space is obtained from these calculations, most direct dynamics methods rely on classical trajectories to describe the nuclear wavepacket.

We have developed the direct dynamics variational multiconfigurational Gaussian (DD-vMCG) method. Based on the MCTDH algorithm, but using a basis set of time-dependent Gaussian basis functions (GBFs) it is related to the class of methods based on Gaussian Wavepackets (GWPs), such as the multiple spawning of Martinez or coherent states of Shalashilin. Unlike GWP methods, however the vMCG basis functions follow coupled variational trajectories rather than classical trajectories. This makes them better at describing quantum processes as well as providing faster convergence, important in direct dynamics [3]. Combined with an on-the-fly diabatisation procedure [4], this provides an almost black-box approach to quantum dynamics.

## References

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