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Let the trajectories tell a quantum story: Post-entangling the SHARC scheme

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Synopsis A new method is proposed to perform Quantum Wave Packet Nuclear Dynamics on large systems, by making use of information obtained by Semi-Classical Quantum Dynamics. The key of the method resides in expressing the nuclear wave function of the system in a basis set determined by the positions of multiple trajectories at each time.

Many approaches exist that take into account the nuclear motion in Quantum Dynamics simulations, from grid-based quantum dynamics techniques, discrete variable representation (DVR)[1] or multi-configurational time dependent Hartree (MCTDH)[2] methods, to mixed quantum classical dynamics (MQCD)[0, 0]. In particular, assuming the MQCD approach, we have recently developed the SHARC (Surface Hopping in the Adiabatic Representation including Random Couplings) scheme[0].

In the latter approach, the nuclear motion is determined classically from the electronic force field of a single representative reference electronic state, which is propagated by quantum dynamics. Electronic coherences and quantum interence effects (due to non-adiabatic couplins or laser-induced transitions) are therefore incorporated at the electronic level. Stochastic jumps from the chosen reference state (surface hopping) are accounted by Tully fewest schitches method. In order to statistically characterize the system dynamics, many trajectories must be propagated independently, but a clever choice of the quantum representation of the electronic basis allows to reduce the number of trajectories needed.

Although the MQCD approach (and the SHARC scheme in particular) was shown to reproduce many experimental results, any quantum effect at the nuclear level (such as quantum tunneling, zeroth point effects, symmetry and interference due to nodal patterns, etc.) are out of its reach. In order to deal with these problems, we have developed a method to recycle the information obtained by performing trajectory-based calculations to hugely reduce the complexity of full-dimensional quantum treatment of the nuclear motion.

In our method, the nuclear wave function is expressed as a linear combination of *trajectory based* basis functions. Each basis function consists on a product of monodimensional Gaussians, each of them centered at the correspondent position for a trajectory at each time. For each classical step a new set of orthonormal basis is obtained and the coefficients rotated accordingly. In this way, our basis set moves following the trajectories, allowing them to populate only the relevant regions of the potential energy surface (PES).

One great advantage of the method is the simplicity of the Hamiltonian expression and the economy of the calculation. Since MQCD methods require the calculation of the molecule's energy and its gradient at each step, the same information is used to obtain the potential energy operator, so that an analytical description of the PES is not required.

To show the performance of the method, we will present results for simple models for which it is affordable to compare them with full quantum dynamical simulations.

References

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