Internal consistency and quantum decoherence in surface hopping.

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Abstract

In this talk we address the problem of internal consistency in trajectory surface hopping methods, i.e. the requirement that the fraction of trajectories running on each electronic state equals the probabilities computed by the electronic time-dependent Schrödinger equation, after averaging over all trajectories. A formula for the hopping probability in Tully's "fewest switches" spirit, that would yield a rigorously consistent treatment, is derived. We show the relationship of Tully's widely used surface hopping algorithm with the "exact" prescription, that cannot be applied when running each trajectory independently. We also bring out the connection of the consistency problem with the coherent propagation of the electronic wavefunction, and the artefacts caused by coherent Rabi-like oscillations of the state probabilities in weak coupling regimes. A decoherence correction to the state probabilities determined by Tully's algorithm is proposed, and applied to some real and model systems.