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Increasing the efficiency and accuracy of time-resolved electronic spectra calculations with on-the-fly ab initio quantum dynamics methods[1]

JIRI VANICEK, Ecole Polytech Fed de Lausanne — Rigorous quantum-mechanical calculations of coherent ultrafast electronic spectra remain difficult. I will present several approaches developed in our group that increase the efficiency and accuracy of such calculations: First, we justified the feasibility of evaluating time-resolved spectra of large systems by proving that the number of trajectories needed for convergence of the semiclassical dephasing representation/phase averaging is independent of dimensionality. Recently, we further accelerated this approximation with a cellular scheme employing inverse Weierstrass transform and optimal scaling of the cell size. The accuracy of potential energy surfaces was increased by combining the dephasing representation with accurate on-the-fly ab initio electronic structure calculations, including nonadiabatic and spin-orbit couplings. Finally, the inherent semiclassical approximation was removed in the exact quantum Gaussian dephasing representation, in which semiclassical trajectories are replaced by communicating frozen Gaussian basis functions evolving classically with an average Hamiltonian. Among other examples I will present an on-the-fly ab initio semiclassical dynamics calculation of the dispersed time-resolved stimulated emission spectrum of the 54-dimensional azulene.

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