Pseudo-Gaussian Quantum Dynamics: Efficient Sampling of Potential Energy Surfaces for High-dimensional Quantum Molecular Dynamics

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Abstract

Quantum molecular dynamics requires an accurate representation of the molecular potential energy surface from a minimal number of electronic structure calculations, particularly for non-adiabatic dynamics where excited states are required. While trajectory-guided Gaussian basis sets have been very successful for studying high-dimensional quantum dynamics, in cases without an analytical potential energy surface the rate limiting step often becomes the electronic structure calculations. Therefore, we are interested in developing trajectory-based methods that minimize the number of potential energy evaluations while still accurately describing the quantum dynamics. We investigate a recently introduced method, pseudo-Gaussian dynamics, that achieves accurate quantum dynamics using efficient, real-space sampling of the time-dependent basis set. Unlike other Gaussian methods but similar to the pseudo-spectral method, the basis set is tested with N Dirac delta functions, where N is the number of basis functions, rather than using the basis function as test functions. The delta function reduces the evaluation of matrix elements to function evaluation. Pseudo-Gaussian dynamics only requires $\mathcal{O}(N)$ potential energy calculations, in contrast to $\mathcal{O}(N^2)$ evaluations in a variational calculation. We explore the accuracy of the pseudo-Gaussian method in single-surface calculations of up to six dimensions and in a two-dimensional non-adiabatic example. We find that the pseudo-Gaussian method is as accurate as the variational calculation despite requiring considerably less information of the potential energy surface. The implications of these results for future Gaussian-based work and the relationship of our method to existing literature will also be discussed.