Vibrational Self-Consistent Field Theory Based Wigner Distribution for Sampling Initial Conditions for Trajectory Surface Hopping Dynamics

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For trajectory surface hopping simulations, the choice of initial conditions can have a great impact on obtained photochemical observables [1, 2, 3]. One of the more popular methods for generating initial conditions is sampling from the harmonic Wigner distribution due to the fact that it is simple to use and has a low computational cost, while still taking into account the quantum nature of the nuclei. However, it doesn't take into account the anharmonicity and the coupling between normal modes [2]. This can greatly affect the obtained observables, as was recently demonstrated for methyl hydroperoxide (MHP) [3]. While sampling from a trajectory obtained using a quantum thermostat provides more reliable results for MHP [3], it is significantly more expensive compared to sampling from the harmonic Wigner distribution. The quantum thermostat can also introduce unknown errors, which is why it is advisable to validate the results with even more expensive path-integral molecular dynamics simulations [4].

In this work we will present a novel approach based on anharmonic Wigner distributions generated from the vibrational self-consistent field wavefunctions in the harmonic oscillator or the distributed Gaussian basis. The method takes anharmonicity and normal mode coupling into account in a mean-field manner, and when combined with an adaptive density-guided approach for automatic generation of the potential energy surfaces [5], provides a cheap and easy to use alternative to the above-mentioned methods. The performance of the method is illustrated on MHP and malonaldehyde.

References:

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