

Semiclassical implementation of the Møller operators in reactive scattering; simplified calculation of the stability matrix

Sophya Garashchuk

Dept of Chemistry & Biochemistry,

University of South Carolina, Columbia, SC 29208

Abstract

Reaction probabilities can be efficiently obtained from the time-dependent correlation functions of wavepackets. Møller operators allow us to define the wavepackets in the interaction region rather than in the asymptotic region of the potential surface. We combine Møller operators with the semiclassical propagator of Herman and Kluk. This does not involve further approximations and can be used with any initial value representation semiclassical propagator. Time propagation in asymptotic regions of the potential due to Møller operators reduces the oscillations of the propagator integrand and improves convergence of the results with respect to the number of trajectories. The effectiveness of Møller operators for semiclassical reaction probability calculation is demonstrated for the collinear hydrogen exchange reaction. Full convergence is achieved and the number of classical trajectories is reduced by a factor of 10 compared to the calculation without Møller operators.

We also present a simple method of calculation of the stability (monodromy) matrix, which is a part of many semiclassical propagators. The method is based on the unitarity of classical propagation and does not involve approximations. The number of auxiliary differential equations per trajectory scales linearly rather than quadratically with the system size, and the second derivatives of the PES are not required.