Single-Hessian thawed Gaussian approximation: The missing rung on the ladder

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To alleviate the computational cost associated with on-the-fly ab initio semiclassical calculations of molecular spectra, we propose the single-Hessian thawed Gaussian approximation [1], in which the Hessian of the potential energy at all points along an anharmonic classical trajectory is approximated by a constant matrix. The spectra obtained with this approximation are compared with the exact quantum spectra of a one-dimensional Morse potential and with the experimental spectra of ammonia and quinquethiophene. In all cases, the single-Hessian version performs almost as well as the much more expensive on-the-fly ab initio thawed Gaussian approximation [2, 3, 4] and significantly better than the global harmonic schemes. Remarkably, unlike the thawed Gaussian approximation, the proposed method conserves energy exactly, despite the time dependence of the corresponding effective Hamiltonian, and, in addition, can be mapped to a higher-dimensional time-independent classical Hamiltonian system. We also provide a detailed comparison with several related approximations [5, 6] used for accelerating prefactor calculations in semiclassical simulations.

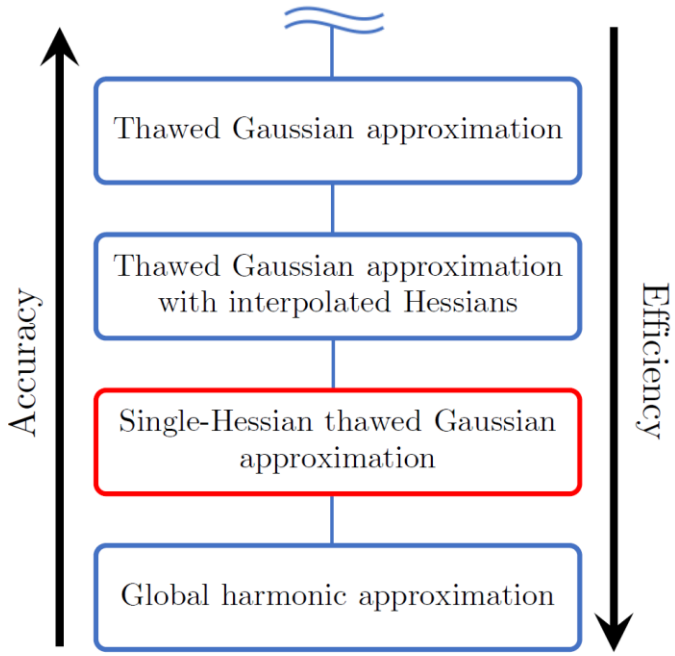

Figure 1: Hierarchy of several semiclassical wavepacket methods for simulating vibrationally resolved electronic spectra.

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