Simple wavepacket modeling of electron and nuclear dynamics

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Introduction

The current main-stream of theoretical/computational chemistry appears to be directed toward highly-accurate first-principles large-scale computational technologies. As an alternative, we are developing a simple and semi-quantitative method based on the Gaussian wavepacket (GWP). It has some similarity to the conventional thawed GWP [1], but has an advantage that the extended Hamiltonian formalism offers a pictorial view of effective quantum potential, an aspect shared with the expectation-value approaches such as the quantized Hamilton dynamics [2] and the quantized cummulant dynamics [3].

Semiquantal time-dependent Hartree approach

We will first briefly review the approach with applications to: a system-bath model deriving a semiquantal generalized Langevin equation [4], the geometric isotope effect of hydrogen-bond structure [5], the kinetic isotope effect in the adiabatic hydrogen transfer rate [6], and a realistic molecular dynamics simulation of liquid water [7].

Valence-bond electron wavepacket approach

The theory was extended to take account of the anti-symmetry of electronic wavefunctions by exploiting the valence-bond theory. To overcome the so-called $N!$-problem steming from the non-orthogonality of the wavepacket orbitals, various decoupling approximations to electron-pairs are examined [8]. Encouraging results have been obtained with use of a single floating and breathing wavepacket orbital per electron.

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