Quantum simulation of vibration states and Franck-Condon overlap in non-separable potentials

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Summary. Taking into consideration nuclear motion in non-separable potentials, we have probed the solution of the Schrödinger equation by random walk sampling in imaginary time on a two-dimensional example. Evaluation of the many-dimensional Franck-Condon overlap and the chemical species conversion rate is outlined.

Key words: Quantum simulation — Non-separable vibrations — Franck-Condon overlap

1. Introduction

Our aim in this paper is to prepare for further numerical exploration of local chemical processes in condensed systems or at interfaces [1, 2]. As a starting point of the following, we note that in the chemical species conversion probability expression

\[
\langle P_{a \rightarrow b} \rangle = \frac{2\pi}{\hbar} A_v |T_{ba}|^2 \delta(\Delta E_{\text{vib}} + \Delta E),
\]

(1)

the vibrational, or Franck-Condon overlap \( \langle \phi_b | \phi_a \rangle \) contained in the transition matrix elements \( T_{ba} \), is not restricted to separable vibration states; \( \phi_a, \phi_b \) are the vibration state functions of the initial and final state in diabatic or quasi-adiabatic potentials. In Eq. (1), \( \Delta E_{\text{vib}} \) is the change of vibration energy in the conversion process, \( \Delta E \) the difference of total energy zero points of states \( (a) \) and \( (b) \), \( A_v \) indicates thermal weighting. Taking into consideration general potential surface characteristics, the question of including non-separable anharmonic vibrations in the transition matrix treatment arises.
Calculation of vibration states in non-separable systems has received much attention over the last decade [3–6]. Semiclassical quantization, as well as variational approximations using expansions in terms of products of harmonic functions reveal, in general, stable (or regular) vibrations in lower quantum states.

Pursuing the question raised above, we have applied a numerical random walk sampling technique for the \textit{ab initio} solution of the Schrödinger equation. This method was devised recently for the calculation of many-electron total energies including electron correlation [7, 8], but it is also suited to vibration problems [9]. The method works as follows: in imaginary time $t = t_{\text{real}} \cdot i/\hbar$, the Schrödinger equation assumes the form of a diffusion equation

$$\frac{\partial \phi}{\partial t} = D \nabla^2 \phi - V \phi, \quad D = \hbar^2/2\mu.$$  

Using a known trial wave function $\phi_T$, one gets a diffusion equation with a reaction and a drift term for the product function $f(t) = \phi(t) \cdot \phi_T$:

$$\frac{\partial f}{\partial t} = D \nabla^2 f - (E_L - E_{\text{ref}})f - D \nabla f F,$$

where $E_L = H\phi_T/\phi_T$ is a local energy, $E_{\text{ref}}$ a reference energy, and $F = \nabla \ln|\phi_T|^2$ a quantum drift velocity. The propagator for Eq. (3) is the Green's function [8, 10]

$$G(R, R', \Delta t) = (4\pi D \Delta t)^{-N/2} \exp \left\{ - \frac{[R' - R - D \Delta t \cdot F(R)]^2}{4D \Delta t} \right\} \times \exp \left\{ -\left[ (E_L(R) + E_L(R'))/2 - E_{\text{ref}} \right] \Delta t \right\},$$

from which

$$f(R', t + \Delta t) = \int dR G(R, R', \Delta t) f(R, t)$$

is sampled. The total energy is obtained from $\langle E_L \rangle$. $N$ in (4) is the dimension of the vector space $R$. Propagation using Eqs. (4, 5) yields the stationary ground state; excited states are accessible, from, e.g., orthogonalization or fixed node constraints [7–9].

2. An example of vibration in anharmonic 2D potential surfaces

As well as the total energy, we are particularly interested in the wave function $\phi = f/\phi_T$ which can be sampled together with energy. We begin with considering the vibration ground state in a two-dimensional (2D) potential surface in cartesian coordinates.

As a trial function $\phi_T$ in Eqs. (3, 4) one may use the known solution of the Schrödinger equation with the separable hamiltonian:

$$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2; \quad V = V_1(x) + V_2(y).$$

As an example we consider a superposition of a Morse and a harmonic potential component:

$$V_1(x) = D_1[1 - \exp(-ax)]^2; \quad V_2(y) = (k_2/2)y^2.$$