

Different time slices for different degrees of freedom in Feynman path integration

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A general scheme is presented for using different numbers of ‘time slices’ for different degrees of freedom in a path integral evaluation of the Boltzmann operator for a large molecular system. This will be particularly useful, for example, in evaluating the ‘quantum instanton’ rate constant [cf. W.H. Miller, Y. Zhao, M. Ceotto, S. Yang. *J. Chem. Phys.*, **119**, 1329 (2003)] for H atom transfer reactions, or any applications involving atoms with largely differing masses.

1. Introduction

The Feynman path integral representation of the Boltzmann operator [1–3], $\exp(-\beta\hat{H})$, with Monte Carlo evaluation of the resulting (highly) multidimensional integrals that occur therein (*vide infra*) [4–6], provides one of the few methodologies available for performing accurate quantum calculations for systems with many degrees of freedom. This is useful, of course, only if the quantities of interest can be expressed in terms of the Boltzmann operator (where β is related to temperature in the usual way, $\beta = 1/(k_B T)$, and \hat{H} is the Hamiltonian of the molecular system), but this covers many topics: all types of equilibrium phenomena (e.g. radial distribution functions) are of course describable [7–13], but also short time properties of equilibrium time correlation functions [14–16]. The latter have been of interest in our research group recently with regard to applying the ‘quantum instanton’ model [17, 18] (and its extensions [19]) to determine chemical reaction rates.

If the system of interest (consisting of F degrees of freedom (DOFs)) is characterized by a Cartesian Hamiltonian,

$$\hat{H} = \sum_{i=1}^F \frac{\hat{p}_i^2}{2m_i} + V(\mathbf{x}), \quad (1)$$

with $\mathbf{x} = x^{[i]}$, $i = 1, 2, \dots, F$, then the standard (Trotter product) path integral expression for the equilibrium,

for example, is given by

$$\begin{aligned} & \langle \mathbf{x} | \exp(-\beta\hat{H}) | \mathbf{x} \rangle \\ &= \prod_{i=1}^F \left(\frac{m_i P}{2\pi \hbar^2 \beta} \right)^{P/2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_{P-1} \\ & \times \exp \left[- \sum_{i=1}^F \frac{m_i P}{2\hbar^2 \beta} \sum_{k=1}^P \left(x_k^{[i]} - x_{k-1}^{[i]} \right)^2 \right. \\ & \quad \left. - \frac{\beta}{P} \sum_{k=1}^P V(\mathbf{x}_k) \right], \quad (2) \end{aligned}$$

where P is the number of ‘time slices’ and $\mathbf{x}_k = \{x_k^{[i]}, i = 1, 2, \dots, F\}$ is the value of the (F -dimensional) coordinate at the k th imaginary time increment $\tau_k = k \hbar \beta / P$, $k = 1, 2, \dots, P$; i.e. $\mathbf{x}_k = \mathbf{x}(\tau_k)$, $k = 1, 2, \dots, P-1$ with $\mathbf{x}_0 = \mathbf{x}_P = \mathbf{x}$. The exact quantum result for the density is obtained in the limit $P \rightarrow \infty$, and note that $P = 1$ gives the classical mechanics result,

$$\begin{aligned} & \langle \mathbf{x} | \exp(-\beta\hat{H}) | \mathbf{x} \rangle_{P=1} \\ &= \prod_{i=1}^F \left(\frac{m_i}{2\pi \hbar^2 \beta} \right)^{1/2} \exp[-\beta V(\mathbf{x})]. \quad (3) \end{aligned}$$

The value of P (i.e. the number of time slices) needed to achieve effective convergence to the $P \rightarrow \infty$ limit is larger the smaller the mass of a given DOF, i.e. the more quantum-like the DOF. For example, for H atoms at room temperature, a value of $P \sim 50$ is typically large enough, while much smaller values of P are sufficient for heavier atoms such as C, N or O. When treating reaction rates in the ‘quantum instanton’ model [17]

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