REVIEW ARTICLE

Review of Feynman's Path Integral in Quantum Statistics: from the Molecular Schrödinger Equation to Kleinert's Variational Perturbation Theory

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Abstract. Feynman's path integral reformulates the quantum Schrödinger differential equation to be an integral equation. It has been being widely used to compute internuclear quantum-statistical effects on many-body molecular systems. In this Review, the molecular Schrödinger equation will first be introduced, together with the Born-Oppenheimer approximation that decouples electronic and internuclear motions. Some effective semiclassical potentials, e.g., centroid potential, which are all formulated in terms of Feynman's path integral, will be discussed and compared. These semiclassical potentials can be used to directly calculate the quantum canonical partition function without individual Schrödinger's energy eigenvalues. As a result, path integrations are conventionally performed with Monte Carlo and molecular dynamics sampling techniques. To complement these techniques, we will examine how Kleinert's variational perturbation (KP) theory can provide a complete theoretical foundation for developing non-sampling/non-stochastic methods to systematically calculate centroid potential. To enable the powerful KP theory to be practical for many-body molecular systems, we have proposed a new path-integral method: automated integration-free path-integral (AIF-PI) method. Due to the integration-free and computationally inexpensive characteristics of our AIF-PI method, we have used it to perform *ab initio* path-integral calculations of kinetic isotope effects on proton-transfer and RNA-related phosphoryl-transfer chemical reactions. The computational procedure of using our AIF-PI method, along with the features of our new centroid path-integral theory at the minimum of the absolute-zero energy (AMAZE), are also highlighted in this review.

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1 Introduction

1.1 Molecular Schrödinger equation

Ever since quantum mechanics was constructed in the 1920s [1–24], solving the non-relativistic time-independent Schrödinger equation for a system of nuclei and electrons has become an essential step to understand every single detail of atomic or molecular properties [1]. The non-relativistic time-independent Schrödinger equation for a molecular system (hereafter we shorten it as the molecular Schrödinger equation) is [25–27]:

$$\hat{H}_{mole}\Psi_n = E_n\Psi_n, \tag{1.1}$$

where $\hat{H}_{mole}$ is the complete (non-relativistic) molecular Hamiltonian, Ψ_n and E_n are an energy eigenfunction (or wave function) and an energy eigenvalue at an eigenstate n, respectively. In contrast to the (intra)nuclear or nucleon Hamiltonian [28], the complete molecular Hamiltonian [4, 5, 25–27, 29] for N_n nuclei and N_e electrons can fortunately be written in an analytic closed form (thanks to the inverse square-distance proportionality in Coulomb's electrostatic force law):

$$\hat{H}_{mole} = \sum_j^{N_n} -\frac{1}{2M_j}\nabla_j^2 + \sum_{j<j'}^{N_n}\frac{Z_{j'}Z_j}{x_{jj'}} - \frac{1}{2}\sum_i^{N_e}\nabla_i^2 - \sum_j^{N_n}\sum_i^{N_e}\frac{Z_j}{r_{ij}} + \sum_{i<i'}^{N_e}\frac{1}{r_{ii'}}. \tag{1.2}$$

In Eq. (1.2), the units are atomic units [30], M_j is the mass ratio of nucleus j to an electron, and Z_j is the atomic number of nucleus j. The Laplacian operators ∇_j^2 and ∇_i^2 denote the second order differentiation with respect to the coordinates of the jth nucleus and the ith electron. The first term in Eq. (1.2) represents the kinetic energy operator for nuclei; the