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An automated integration-free path-integral method based on Kleinert's variational perturbation theory

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Abstract

Based on Kleinert's variational perturbation (KP) theory [Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets, 3rd ed. (World Scientific, Singapore, 2004)], we present an analytic path-integral approach for computing the effective centroid potential. The approach enables the KP theory to be applied to any realistic systems beyond the first-order perturbation (i.e., the original Feynman-Kleinert [Phys. Rev. A **34**, 5080 (1986)] variational method). Accurate values are obtained for several systems in which exact quantum results are known. Furthermore, the computed kinetic isotope effects for a series of proton transfer reactions, in which the potential energy surfaces are evaluated by density-functional theory, are in good accordance with experiments. We hope that our method could be used by non-path-integral experts or experimentalists as a "black box" for any given system.

I. INTRODUCTION

The path-integral (PI) representation of the quantum canonical partition function Q_{QM} can be written in terms of the effective centroid potential W as a classical configuration integral,^{1,2}

$$Q_{\text{QM}} = \sqrt{\frac{Mk_B T}{2\pi\hbar^2}} \int_{-\infty}^{\infty} e^{-\beta W(x_0)} dx_0, \quad (1)$$

where M is mass, k_B is Boltzmann's constant, T is temperature, $\hbar$ is Planck's constant divided by 2π , $\beta = 1/k_B T$, and x_0 is a point in space. Given the W , thermodynamic and quantum dynamic quantities can be accurately estimated,^{1,2} including molecular spectroscopy of quantum fluids³ and the rate constant of chemical and enzymatic reactions.⁴⁻⁷ The mass-dependent property of W is also of particular interest because isotope effects can be determined, and it has been applied to chemical reactions^{6,7} and carbon nanotubes.⁸ Consequently, it is an important task to accurately determine the centroid potential as a practical approach to use Feynman path integrals in chemical and biological systems.

In the 1980s, three different research groups, which are Feynman and Kleinert⁹ (FK), Giachetti and Tognetti,¹⁰ and Voth *et al.*,⁵ have independently described a similar variational approach which yields an upper bound of W . The method is highly accurate and has been applied to a variety of systems.^{2,3,11-13} It was recently used to model quantum dynamic processes in condensed phases such as water and helium.^{3,13} Several attempts have

also been made to further improve the variational approach^{2,12,14,15} including the Cao-Voth “diagrammatic theory.”¹⁴ Among them, Kleinert’s variational perturbation (KP) theory² is one of the most complete and systematic theories. In the KP theory, the FK approach just corresponds to the first-order approximation. Kleinert showed in several model systems that his variational perturbation is exponentially and uniformly convergent.^{2,16} For example, the electronic ground state energy of a hydrogen atom can be determined by computing the W at the zero-temperature limit,^{2,17} and the accuracies of the first three orders of the KP expansion are 85%, 95%, and 98%,¹⁷ respectively. This example of a Coulomb potential not only illustrates that the original variational approach can still be significantly and systematically improved, but also shows that the accuracy of the KP theory is still impressive even for computing the electronic centroid potential at the zero-temperature limit. Discretized PI Monte Carlo (PIMC) or centroid molecular dynamics (CMD) simulations¹⁸ can be difficult to converge at the zero-temperature limit. Nevertheless, beyond the first-order approximation (i.e., the FK approach), the KP theory has only been applied to a few model systems.²

In this Communication, we present an automated analytic procedure based on the KP theory to compute the first- and second-order approximations to the W . The accuracy of the method is demonstrated by several systems in which the exact quantum results are known and by computation of the kinetic isotope effects for a series of proton transfer reactions.

II. KLEINERT’S VARIATIONAL PERTURBATION THEORY

Details of the derivation for the KP theory can be found in our Supplementary Material¹⁹ and in Kleinert’s textbook.² Here, we directly present the n th order KP approximation $W_n^\Omega(x_0)$ to the centroid potential $W(x_0)$ as

$$W_n^\Omega(x_0) = -k_B T \ln \left[\frac{\beta \hbar \Omega / 2}{\sinh(\beta \hbar \Omega / 2)} \right] + \frac{k_B T}{\hbar} \left\langle V_{\text{int}}^{x_0}(x(\tau_1)) \right\rangle_{\Omega}^{x_0} - \frac{k_B T}{2! \hbar^2} \left\langle V_{\text{int}}^{x_0}(x(\tau_1)) V_{\text{int}}^{x_0}(x(\tau_2)) \right\rangle_{\Omega, c}^{x_0} + \cdots + k_B T \frac{(-1)^{n+1}}{n! \hbar^n} \left\langle \prod_{k=1}^n V_{\text{int}}^{x_0}(x(\tau_k)) \right\rangle_{\Omega, c}^{x_0}, \quad (2)$$

where the angular frequency Ω is a variational parameter, τ is imaginary time, $V_{\text{int}}^{x_0}(x) = V(x) - (1/2) M \Omega^2 (x - x_0)^2$, $V(x)$ is the original potential of the system, $x(\tau)$ describes a path in space time, and the expectation value $\langle \cdots \rangle_{\Omega, c}^{x_0}$ is called the cumulant. The cumulants can be expressed in terms of the original expectation value $\langle \cdots \rangle_{\Omega}^{x_0}$ by the cumulant expansion.^{2,19} $\langle \cdots \rangle_{\Omega}^{x_0}$ can be calculated in terms of Gaussian smearing convolution integrals,¹⁷

$$\left\langle \prod_{k=1}^n F_k(x(\tau_k)) \right\rangle_{\Omega}^{x_0} = \left\{ \prod_{j=1}^n \int_0^{\beta \hbar} d\tau_j \right\} \left\{ \prod_{k=1}^n dx_k F_k(x_k) \right\} \times \frac{1}{\sqrt{(2\pi)^n \text{Det}[a_{\tau_k \tau_{k'}}^2(\Omega)]}} \times \left\{ \exp - \frac{1}{2} \sum_{k=1}^n \sum_{k'=1}^n (x_k - x_0) a_{\tau_k \tau_{k'}}^2(\Omega) (x_{k'} - x_0) \right\}, \quad (3)$$

where $\text{Det} \left[a_{\tau_k \tau_{k'}}^2(\Omega) \right]$ is the determinant of the $n \times n$ matrix consisting of the Gaussian width $a_{\tau_k \tau_{k'}}^2(\Omega)$, $a_{\tau_k \tau_{k'}}^{-2}(\Omega)$ is an element of the inverse matrix of $a_{\tau_k \tau_{k'}}^2(\Omega)$, and the Gaussian width is

$$a_{\tau \tau'}^2(\Omega) = \frac{1}{\beta M \Omega^2} \left\{ \frac{\beta \hbar \Omega}{2} \frac{\cosh \left[(|\tau - \tau'| - \beta \hbar / 2) \Omega \right]}{\sinh(\beta \hbar \Omega / 2)} - 1 \right\}. \quad (4)$$

As n tends to infinity, $W_n^\Omega(x_0)$ is independent of the . At a given order n , the optimal frequency for is given by the least dependence of $W_n^\Omega(x_0)$ on , i.e., zeroing the lowest order derivative of $W_n^\Omega(x_0)$ with respect to . Hence is a variational parameter.

An especially attractive feature of Eq. (2) is that if the real system potential V is expressed as a series of polynomials or Gaussians, analytic expressions of Eq. (2) can be obtained, making the computation extremely efficient because the time-demanding Monte Carlo samplings for the integrations in Eq. (2) could be avoided (hereafter, the level of calculations up to the m th order KP expansion for an m th-order-polynomial potential is denoted as KP n /P m). For other potentials, KP n theory still involves elaborate n -dimensional space-time ($2n$ degrees of freedom) smearing integrals in Eq. (3). The intricacy of the smearing integrals increases tremendously for multidimensional potentials, where becomes a $3N \times 3N$ matrix $_{ij}$ for N nuclei.^{2,17} This complexity is a major factor in limiting applications of the KP theory beyond KP1, the original FK approach.

III. AN AUTOMATED COMPUTATIONAL PROCEDURE

To render the KP theory feasible for many-body systems with N particles, we make the approximation of independent instantaneous normal mode (INM) coordinates²⁰ $\{q^{x_0}\}^{3N}$ for a given configuration $\{x_0\}^{3N}$. Hence, the multidimensional V effectively reduces to $3N$ one-dimensional potentials along each normal mode coordinate. Note that INMs are naturally decoupled through the second-order Taylor expansion. The INM approximation has also been used elsewhere.²⁰ This approximation is particularly suited for the KP theory because of the exponential decaying property of the Gaussian convolution integrals in Eq. (3). The total effective centroid potential for N nuclei can be simplified as

$$W_n^\Omega(\{x_0\}^{3N}) \approx V(\{x_0\}^{3N}) + \sum_{i=1}^{3N} w_{i,n}^\Omega(q_i^{x_0}), \quad (5)$$

where $w_{i,n}^\Omega(q_i^{x_0})$ is the centroid potential for normal mode i . Although the INM approximation sacrifices some accuracy, in return, it allows analyses of quantum mechanical vibration and tunneling, and their separate contributions to the W . Positive and negative values of w_i in Eq. (5) raise (vibration) and lower (tunneling) the original potential V , respectively.

To obtain analytical expressions for the expectation values in Eq. (2), we use an m th-order polynomial (P m) to approximate the V along q_i . Note that analytical results for P4 (Ref. 21) have been used by Kleinert for a quadraticquartic anharmonic potential and a double-well potential;^{2,21} however, higher order polynomials are needed to achieve the desired accuracy in real internuclear systems. We have thus derived the analytical closed forms of Eq. (2) up to P20 (all are available in the Supplementary Material¹⁹). Consequently, the W as a function of an arbitrary can be promptly obtained. This provides a convenient way to

determine the least dependent ϵ value without computing the complicated smearing integrals [Eq. (3)] iteratively for different trial values of ϵ by Monte Carlo simulations. In fact, after the interpolating potential along each instantaneous normal mode is determined, there is little computational cost for obtaining the W . Thereby, high level *ab initio* or density-functional (DFT) methods can be used to evaluate the internuclear potential energy function for path-integral calculations (e.g., Sec. IV C).

The computational procedure for obtaining the first- and second-order KP approximations to the centroid potential is summarized below:

1. For each $\{x_0\}^{3N}$, the mass-scaled Hessian matrix is diagonalized to obtain $\{q^{x_0}\}^{3N}$.
2. The original potential V is scanned from the configuration $\{x_0\}^{3N}$ along each $q_i^{x_0}$ for ten points, both in the forward and backward directions. We found that a step size of 0.1 Å is usually a reasonable choice to yield W within a few percent of the exact.
3. Each $w_{i,n}^\Omega(q_i^{x_0})$ as a function of $q_i^{x_0}$ is readily obtained using the analytical expressions of KP1/P20 or KP2/P20.¹⁹ Note that the path integrals for these polynomials have been analytically integrated.
4. The optimal values of $w_{i,n}^\Omega(q_i^{x_0})$ are determined by numerically locating the least dependence of $w_{i,n}^\Omega(q_i^{x_0})$ on $q_i^{x_0}$, i.e., zeroing the lowest order derivative of $w_{i,n}^\Omega(q_i^{x_0})$ with respect to $q_i^{x_0}$ (first derivative for KP1 and usually second derivative for KP2).

The procedure presented above is integration-free and essentially automated. We hope that it could be used by non-path-integral experts or experimentalists as a “black box” for any given system.

IV. RESULTS AND DISCUSSION

A. Vibrational partition function

The vibrational partition functions for two systems have been computed and compared with the exact results. The first is a Morse potential with parameters representing hydrogen fluoride.²² The Morse potential is chosen because the exact eigenenergy spectrum is available in a closed form. Table I shows that the KP theory yields extremely accurate results for the quantum partition function, particularly at the KP2 level. At a low temperature of 50 K, the accuracy of the KP2 value is 96.4% of the exact result, whereas the KP1 value deteriorates somewhat to 75.1% in accuracy, suggesting that higher order perturbations are essential for systems in which quantum mechanical effects dominate. Next, we estimate the quantum partition function for a water molecule, represented by the Hoy-Mills-Strey (HMS) potential energy surface.²³ The HMS potential is used because the Hessian matrix can be calculated analytically. At $T=200$ K, the lowest temperature in which the exact Q_{QM} is available, $Q_{QM}=2.9\times 10^{-15}$,²³ the KP2/P20 result is 2.4×10^{-15} or 83% of the exact value, similar to the accuracy of the second-order Rayleigh-Schrödinger perturbation theory without resonance corrections (86%).²³ For comparison, the accuracy of the displaced-point path-integral method in which the INM approximation was also used is 73% of the exact results.¹⁵ One source of error in the present KP2 result is due to the INM approximation. However, this type of errors may be partly cancelled out in actual applications because many thermodynamic properties of interest are associated with the ratios of partition functions rather than the absolute values (see below).

B. Collinear H+H₂ reaction

Both tunneling and vibrational quantum effects are important in the collinear H+H₂ reaction. The accuracy of the present KP2 approach is presented as a quantum correction factor κ , defined as the ratio of the exact quantum rate constant to the rate constant of classical transition state theory with quantum vibrational partition functions but neglecting tunneling effects. We estimated the values of κ by applying the path-integral quantum transition state theory with no correction for the transition state recrossing.⁴⁻⁶ Exact values of κ_{QM} for a temperature range from $T=200$ to 1000 K have been reported on the Porter-Karplus potential.²⁴ The exact κ_{QM} , and the present κ_{P1} and κ_{P2} values are listed in Table II. Both KP1 and KP2 results are in reasonable accordance with the exact results at high temperatures, whereas KP2 is still good at a lower temperature of 200 K, at which κ_{P1} has much greater deviations.

C. Kinetic isotope effects (KIEs) in proton transfer reactions

KIEs, which measure the ratio of the rates between light and heavy isotopic reactions, provide the most direct experimental probe into the transition state and mechanism of chemical reactions.⁷ To demonstrate the applicability of our approach, the KP2 method is used to estimate the KIE (protium/deuterium) for the addition of a proton to a series of aryl-substituted (R)-methoxystyrenes from chloroacetic acid in water.²⁵ In this case, we quantized about 90 degrees of freedom in our computation (Fig. 1). The minimum-energy reaction path was optimized using DFT at the B3LYP/6-31+G(*d,p*) level and the aqueous environment was modeled by the polarizable continuum model. We point out that since the present centroid path-integral method based on the KP theory is integration-free, this allows us to use high-level electronic structure methods such as DFT to construct the internuclear potential energy surface, which would be prohibitively expensive for such a large system using PIMC or CMD simulations.¹⁸ Figure 1 shows the computed KIEs using solely harmonic frequencies and the KP2 values with tunneling and anharmonic vibration corrections. Although the harmonic values correctly reproduce the experimental trend with different substituents, the absolute values are significantly smaller than the corresponding experimental data. Including anharmonicity and tunneling corrections is critical to obtain quantitative results for KIEs, and the present KP2 results are in good agreement with experiments.

V. CONCLUSION AND OUTLOOK

Our major achievement is using a polynomial interpolation of the potential on each INM coordinate for many-body systems to derive analytic expressions for the path integrals. This makes the KP theory beyond the first-order approximation to be applicable to realistic systems. The implementation is sufficiently general for any systems described by smooth internuclear potential energy functions. This paper shows that our method is accurate for fundamental systems and quantitatively reproduces a series of experimental KIEs in the INM approximation. Although the INM approximation neglects correlations between normal modes, it provides further insights into quantum contributions from vibration and tunneling. To go beyond the INM approximation, we are developing a formalism to systematically couple the INM.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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FIG. 1.
(Color online) Kinetic isotope effects on proton transfers (protium/deuterium) from chloroacetic acid to aryl-substituted (R) -methoxystyrenes in water.

TABLE I

Vibrational partition functions of the Morse potential at various temperatures with parameters representing hydrogen fluoride.

T (K)	Vibrational partition function			
	Exact classical	Exact quantum	KP1 Accuracy (%)	KP2 Accuracy (%)
500	$8.61E-02$	$3.12E-03$	99.0%	100.0%
300	$5.16E-02$	$6.67E-05$	97.0%	99.9%
100	$1.72E-02$	$2.97E-13$	87.9%	98.7%
50	$8.58E-03$	$8.84E-26$	75.1%	96.4%

TABLE IICorrection factor for collinear H+H₂ reaction.

T (K)	Exact	KP1	KP2
1000	1.5	1.2	1.2
600	2.5	1.7	1.7
300	8.7	5.3	6.6
200	46	15	55