On the efficient path integral evaluation of thermal rate constants within the quantum instanton approximation

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We present an efficient path integral approach for evaluating thermal rate constants within the quantum instanton (QI) approximation that was recently introduced to overcome the quantitative deficiencies of the earlier semiclassical instanton approach [Miller, Zhao, Ceotto, and Yang, J. Chem. Phys. 119, 1329 (2003)]. Since the QI rate constant is determined solely by properties of the (quantum) Boltzmann operator (specifically, by the zero time properties of the flux—flux and delta—delta correlation functions), it can be evaluated by well-established techniques of imaginary time path integrals even for quite complex chemical reactions. Here we present a series of statistical estimators for relevant quantities which can be evaluated straightforwardly with any nonlinear reaction coordinates and general Hamiltonians in Cartesian space. To facilitate the search for the optimal dividing surfaces required by the QI approximation, we introduce a two-dimensional quantum free energy surface associated with the delta—delta correlation function and describe how an adaptive umbrella sampling can be used effectively to construct such a free energy surface. The overall computational procedure is illustrated by the application to a hydrogen exchange reaction in gas phase, which shows excellent agreement of the QI rates with those obtained from quantum scattering calculations. © 2004 American Institute of Physics. [DOI: 10.1063/1.1641005]

I. INTRODUCTION

A recent paper has presented a new theoretical approach for calculating thermal rate constants for chemical reactions, the quantum instanton (QI) approximation, so called because of its relation to the semiclassical (SC) “instanton” model. Though SC instanton methods have been widely used in chemistry and condensed matter physics, and have many qualitatively desirable attributes, they are sometimes not as quantitative as one would like. The new quantum instanton approximation is modeled after the SC instanton approach, but is expressed wholly in terms of the quantum Boltzmann operator, exp(−βH), rather than the SC approximation to it, and this largely corrects the quantitative deficiencies of the SC theory. Indeed, applications to several model problems showed the QI approximation to give thermal rate constants accurate to ±20% over the whole temperature range, from the “deep” tunneling regime at low temperature to the regime of over-barrier dynamics at high temperature.

This QI rate theory is in the category of a “quantum transition state theory,” of which there are a variety of others. The primary attractive feature of the QI result for the rate constant is that all information about a tunneling path, tunneling probability, partition function of the activated complex, etc., is expressed solely in terms of the (quantum) Boltzmann operator.

In the previous work the quantum Boltzmann operator involved in the QI rate expression was evaluated by quantum basis set methods, but the whole rationale for developing the QI approach is that the quantum Boltzmann operator can be evaluated for complex molecular systems (i.e., those with many degrees of freedom) by using Monte Carlo path integral (MCPI) methods. The purpose of this paper is therefore to describe the implementation of MCPI methods for evaluating the Boltzmann operator (and related quantities) relevant to the QI expression for thermal rate constants. Application is carried out for a simple, but nontrivial example [the D+H₂→DH+H reaction in full three-dimensional (3D) space] to illustrate the methodology.

Section II A first reviews and summarizes the quantum instanton (QI) theory for thermal rate constants. Sec. II B describes the computational strategy, and Secs. II C and II D the specifics of the path integral expansions and Monte Carlo evaluation. Section III A describes the special aspects of the theoretical expressions relevant to a bimolecular reaction, and application to the 3D D+H₂ reaction is presented in Sec. III B. Section IV concludes.

II. GENERAL METHODOLOGY

A. Quantum instanton approximation for thermal rate constants

First we summarize the basics of the quantum instanton approximation for a thermal rate constant that was presented in Ref. 1. The original derivation begins with the following formally exact expression of the quantum mechanical thermal rate constant:

\[ k(T)Q_r(T) = kQ_r = \frac{1}{2\pi \hbar} \int dE \ e^{-\beta EN(E)} \]  

(2.1)
where $Q_r(T)$ is the reactant partition function per unit volume at temperature $T$, $\beta$ is the inverse temperature $1/k_BT$, and $N(E)$ is the cumulative reaction probability at total energy $E$ which may be written as:

$$N(E) = \frac{(2\pi\hbar)^2}{2} \text{tr} \{ \hat{F}_a \delta(E - \hat{H}) \hat{F}_b \delta(E - \hat{H}) \} \quad (2.2)$$

with the flux operators $\hat{F}_a$ and $\hat{F}_b$ being defined by

$$\hat{F}_\gamma = \frac{i}{\hbar} \{ \hat{H}, h(\xi_\gamma(\mathbf{q})) \} \quad (\gamma = a, b), \quad (2.3)$$

where $h(\xi_\gamma)$ is the Heaviside function and $\hat{H}$ the Hamiltonian of the system. The above equations involve two dividing surfaces, defined by $\xi_a(\mathbf{q}) = 0$, $\gamma = a, b$; i.e., $\xi_a(\mathbf{q})$ and $\xi_b(\mathbf{q})$ are generalized reaction coordinates, functions of the coordinates $\mathbf{q}$ (typically Cartesian) that take on positive (negative) values on the product (reactant) sides of the dividing surfaces. One next expresses the microcanonical density operator $\delta(E - \hat{H})$ in Eq. (2.2) in terms of the Boltzmann operator through an inverse Laplace transform,

$$\delta(E - \hat{H}) = \frac{1}{4\pi i} \int_{c-i\infty}^{c+i\infty} d\beta \ e^{\beta(E - \hat{H})/2} \quad (2.4)$$

which $\hat{A}_a$ and $\hat{A}_b$ being a modified version of the Dirac delta function:

$$\hat{A}_\gamma = \delta(\xi_\gamma(\mathbf{q})) = \delta(\xi_\gamma(\mathbf{q}))[m^{-1/2} \nabla \xi_\gamma(\mathbf{q})] \quad (\gamma = a, b). \quad (2.8)$$

Here we note that $\Delta H$ above can also be expressed in terms of the “delta–delta” correlation function $C_{dd}(t)$,

$$C_{dd}(t) = \text{tr} [ e^{-\beta\hat{H}/2} \hat{A}_a e^{-\beta\hat{H}/2} \hat{A}_b e^{-\beta\hat{H}/2} \hat{H} ]$$

as

$$\Delta H = \frac{\hbar}{2} \left[ C_{dd}(0) \right]^{1/2}. \quad (2.10)$$

The location of the two dividing surfaces in Eqs. (2.5)–(2.7) [defined by $\xi_a(\mathbf{q}) = 0$ and $\xi_b(\mathbf{q}) = 0$] is determined within the QI model by requiring that $C_{dd}(0)$ be stationary with respect to their location. We thus choose them so that

$$\frac{\partial}{\partial c_k} C_{dd}(0; \{c_k\}) = 0 \quad \text{for all } k, \quad (2.11)$$

where $\{c_k\}$ are a set of parameters on which those reaction coordinates depend. This stationary (or variational) condition originates from semiclassical considerations of the periodic orbit in imaginary time with period $\hbar/\beta$ (i.e., the “instanton’’); the two dividing surfaces correspond qualitatively to the location of the turning point surfaces of this periodic orbit.

### B. Computational strategy

We now proceed to the numerical evaluation of the quantum instanton rate constant using imaginary time path integral techniques. To this end it is useful first to examine the similarity between the QI rate expression in Eq. (2.5) and the classical transition state theory (TST) rate constant, since the former can be viewed as a sort of quantum transition state theory, and it is therefore anticipated that numerical techniques for the latter may be employed for the present purpose. Thus consider the classical TST expression for the rate constant,

$$k_{CL}^{TST} = \frac{\int d\mathbf{p} d\mathbf{q} \ e^{-\beta H(\mathbf{p},\mathbf{q})} \delta(\mathbf{q} - \mathbf{\xi}) h(\mathbf{\xi})}{\int d\mathbf{p} d\mathbf{q} e^{-\beta H(\mathbf{p},\mathbf{q})} h(\mathbf{\xi} - \mathbf{\xi})} \quad (2.12)$$

which is obtained by taking the limit $t \to 0$ of the classically exact reactive flux correlation function.\(^{28-30}\) In the above equation $\mathbf{\xi}(\mathbf{q})$ is a reaction coordinate that becomes larger (smaller) than $\mathbf{\xi}$ in the product (reactant) region, and $H(\mathbf{p},\mathbf{q})$ is the classical Hamiltonian of the system. The simi-
larity between $k_{QI}$ in Eq. (2.5) and $k_{\text{TST}}^{\text{CL}}$ in Eq. (2.12) can roughly be understood by noting the following form of the flux operator equivalent to that in Eq. (2.3):

$$
\hat{F}_y = \frac{1}{2m} (\hat{p} \cdot \nabla \xi_y (\hat{q}) \delta (\xi_y (\hat{q})) + \delta (\xi_y (\hat{q})) \nabla \xi_y (\hat{q}) \cdot \hat{p} ;
$$

(13)

namely, both the expressions represent an average of the “velocity” factor $[\hat{p} / m$ in Eq. (2.5) and $\hat{\xi} (\hat{q})$ in Eq. (2.12)] over a constrained canonical distribution (or equivalently, thermal probability flux that passes through the dividing surface). To be more specific, we rewrite the classical TST rate as

$$
k_{\text{TST}}^{\text{CL}} = \frac{\int d\hat{p} d\hat{q} e^{-\beta H (\hat{p}, \hat{q})} \delta (\hat{\xi} (\hat{q}) - \hat{\xi})}{\int d\hat{p} d\hat{q} e^{-\beta H (\hat{p}, \hat{q})} \delta (\hat{\xi} (\hat{q}) - \hat{\xi})} \cdot \frac{\int d\hat{p} d\hat{q} e^{-\beta H (\hat{p}, \hat{q})} \delta (\hat{\xi} (\hat{q}) - \hat{\xi})}{\int d\hat{p} d\hat{q} e^{-\beta H (\hat{p}, \hat{q})} \delta (\hat{\xi} (\hat{q}) - \hat{\xi})}.
$$

(14)

Here the second factor is an average of the positive velocity of the reaction coordinate over the constrained canonical distribution, $e^{-\beta H (\hat{p}, \hat{q})} \delta (\hat{\xi} (\hat{q}) - \hat{\xi})$, which can be evaluated straightforwardly via, e.g., constrained molecular dynamics simulations.135 The first factor, on the other hand, represents the probability density to find the value of $\hat{\xi} (\hat{q})$ at $\hat{\xi}$ in the equilibrium canonical ensemble. Here it should be noted that the computation of the latter requires some tricks; in principle one can obtain the probability density at $\hat{\xi}$ from a histogram of the values of $\hat{\xi} (\hat{q})$ generated during an equilibrium simulation, but this direct approach fails in most cases because the system will almost never visit a region around the top of the barrier due to an exponentially small probability density, which results in very poor statistics at $\hat{\xi} (\hat{q}) = \hat{\xi}$. This is a well-known problem associated with statistical sampling of rare events, which is usually handled by a technique such as thermodynamic integration or umbrella sampling with respect to the reaction coordinate. A common feature of these techniques is that they artificially bias the sampling toward the top of the barrier, and evaluate an exponentially small value of the probability density in the barrier region from results of the biased (or constrained) simulations.

In light of the formal similarity between $k_{QI}$ and $k_{\text{TST}}^{\text{CL}}$ discussed above, it is natural to rewrite the QI rate constant in Eq. (2.5) as the product of two contributions, namely

$$
k_{QI} = C_{\text{ad}} (0) C_{\text{nd}} (0) / C_{\text{ad}}^{\text{CL}} (0) C_{\text{nd}}^{\text{CL}} (0).
$$

(15)

Here $C_{\text{ad}} (0) / C_{\text{ad}}^{\text{CL}} (0)$ and $\Delta H$ [as seen in Eq. (2.7)] that appear in the factor in curly brackets represent an average of some quantity over a constrained canonical distribution, because all of the relevant factors include the common product $\delta (\xi_y (\hat{q})) \delta (\hat{\xi} (\hat{q})) \exp (-\beta H)$ (if we disregard the order of operators). On the other hand, the first factor is not of this form, but rather represents some probability density that can be handled by the methods of rare events discussed above. In the following subsections we will substantiate the above discussion on the basis of discretized path integrals.

### C. Path integral representation of relevant quantities

We first focus on evaluating the two quantities in curly brackets in Eq. (2.15), namely

$$
C_{\text{ad}} (0) / C_{\text{ad}}^{\text{CL}} (0)
$$

(16a)

and

$$
\Delta H^2 = \frac{1}{2} C_{\text{ad}}^{\text{CL}} (0) / C_{\text{ad}} (0).
$$

(16b)

Since these quantities involve only the (quantum) Boltzmann operator, the most effective procedure for evaluating them for systems with many degrees of freedom is imaginary time path integral techniques implemented via Monte Carlo or molecular dynamics methods (except for a system with only a few degrees of freedom, for which basis set methods are more straightforward). In this section we will develop such path integral expressions which can readily be employed for a general (Cartesian) system with arbitrary nonlinear reaction coordinates. Here we suppose that the system is of $d$ degrees of freedom and the Hamiltonian takes the simple form $\hat{H} = \hat{p}^2 / 2m + V(\hat{q})$.

Consider first the “normalization factor” (i.e., the denominator) in Eq. (2.16), $C_{\text{ad}} (0)$,

$$
C_{\text{ad}} (0) = \text{tr} [e^{-\beta \hat{H}} e^{-\hat{\xi} (\hat{q})} e^{-\hat{\xi} (\hat{q})}].
$$

(17)

A discretized path integral of Eq. (2.17) is readily obtained by invoking the standard procedure, i.e., approximating the (half) Boltzmann operator as

$$
e^{-\beta \hat{H}} \approx e^{-\hat{\xi} (\hat{q})} e^{-\beta \hat{\xi} (\hat{q})} e^{-\hat{\xi} (\hat{q})} e^{-\beta \hat{\xi} (\hat{q})} .
$$

(18)

and expanding the potential operator in terms of the position eigenstates to give

$$
C_{\text{ad}} (0) = \frac{mP}{2 \pi \hbar^2 \beta} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_p \
\exp [ - \beta \Phi (\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_p )].
$$

(19)

Here $P$ is the number of imaginary time slices, $\mathbf{x}_k$ is the path integral variable for the $k$th time slice, and $\Phi (\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_p )$ is the discretized action given by

$$
\Phi (\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_p ) = \frac{mP}{2 \hbar^2 \beta} \sum_{k=1}^{p} V(\mathbf{x}_k) + \frac{1}{P} \sum_{k=1}^{p} V(\mathbf{x}_k) ,
$$

(20)

with $\mathbf{x}_0 = \mathbf{x}_p$. The path integral above is essentially the same with that for a partition function, $\text{tr} (e^{-\beta \hat{H}})$, the only difference being the presence of the delta functions that constrain $\mathbf{x}_0$ and $\mathbf{x}_{p/2}$ onto the two dividing surfaces.

The treatment of $C_{\text{nd}} (0)$ is also straightforward. Setting $t=0$ in Eq. (2.6) gives the following trace formula, which is rewritten in the coordinate representation as
\[ C_{df}(0) = \text{tr}[e^{-\beta \hat{H}/2} \hat{F}_a e^{-\beta \hat{H}/2} \hat{F}_b] \]
\[ = \int dx \int dy \int dx' \int dy' \langle x| \hat{F}_a(y) \rangle \langle y'| \hat{F}_b(x') \rangle \times \langle y| e^{-\beta \hat{H}/2} |y'\rangle \langle y'| e^{-\beta \hat{H}/2} |x\rangle. \]  

(2.21)

Substituting the following matrix element of the flux operator
\[ \langle x'| \hat{F}_b(x) |x\rangle = \frac{\hbar}{2mi} \left( -\delta(x' - y') \delta(x, x') \cdot \frac{\partial}{\partial x} \delta(x' - x') \right) \]
\[ \times \nabla \xi_a(x) \left( \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right) \nabla \xi_b(x') \left( \frac{\partial}{\partial y'} - \frac{\partial}{\partial x'} \right) \]
\[ \times \langle y| e^{-\beta \hat{H}/2} |y'\rangle \langle y'| e^{-\beta \hat{H}/2} |x\rangle. \]  

(2.22)

We then discretize the Boltzmann operator as in Eq. (2.18), take the derivative of the canonical density matrix with respect to the end points, and relabel the relevant variables in an appropriate manner. The result becomes
\[ C_{df}(0) = \left( \frac{mP}{2\pi \hbar^2 \beta} \right)^{dP/2} \int dx_1 \int dx_2 \cdots \int dx_P \times \Delta(\xi_a(x_0)) \Delta(\xi_b(x_{P/2})) \exp[ -\beta \Phi(x_1, x_2, \ldots, x_P) ] \times f_o(x_1, x_2, \ldots, x_P), \]  

(2.23)

which differs from the path integral of \( C_{dd}(0) \) in that the following “velocity” factor arises due to the action of the flux operator:
\[ f_o(x_1, x_2, \ldots, x_P) = \frac{mP}{\hbar \beta} \left\{ \sum_{l=1}^{P/2} \sum_{k=1}^{P-2l+1} \right\} \times \left\{ \sum_{k=1}^{P/2-1} \left( x_k - x_{k-1} \right)^2 \right\}. \]  

(2.24)

where \( n_a(x) = \nabla \xi_a(x)/\nabla \xi_a(x) \) with \( \gamma = a, b \). Note that the above expression for \( C_{df}(0) \) is quite similar to that of a velocity–velocity autocorrelation function in imaginary time,\(^{34,35}\) which is attributed to the presence of the “velocity” factor in Eq. (2.13). Another important point to note is that derivatives of the potential function do not appear in the above expression, since they cancel with each other due to the symmetric treatment of the flux operator with respect to the end points such as \( x \) and \( y \). A similar idea has been employed to obtain a path integral expression of the force–force correlation function that avoids higher-order potential derivatives.\(^{34}\)

We now turn attention to \( \tilde{C}_{dd}(0) \) in order to obtain \( \Delta H \) via Eq. (2.16b). [Direct use of Eq. (2.7) for \( \Delta H \) would require the Hamiltonian squared and thus derivative operators up to fourth order.] To this end it is useful to switch from real time \( t \) to imaginary time \( \pm \hbar \lambda \) and recast the problem as differentiation with respect to the intermediate inverse temperature \( \lambda \),
\[ C_{dd}(0) = \frac{d^2}{dt^2} C_{dd}(t) \bigg|_{t=0} = -\frac{1}{\hbar^2} \frac{d^2}{d\lambda^2} C_{dd}(\lambda) \bigg|_{\lambda=0}, \]  

(2.25)

where \( \tilde{C}_{dd}(\lambda) \) is the imaginary time correlation function defined by
\[ \tilde{C}_{dd}(\lambda) = C_{dd}(-i\hbar \lambda) \]
\[ = \text{tr}[e^{-(\beta/2-i\lambda)\hat{H}} \Delta(\xi_a(q)) e^{-(\beta/2+i\lambda)\hat{H}} \Delta(\xi_b(q))], \]  

(2.26)

in terms of which \( \Delta H \) is
\[ \Delta H^2 = \frac{1}{2} \tilde{C}_{dd}(0)/C_{dd}(0). \]  

(2.27)

The subsequent procedure is then straightforward: one first discretizes the shifted Boltzmann operators, \( \exp[-(\beta/2 \pm \lambda)\hat{H}] \), with a primitive approximation similar to Eq. (2.18), takes the second derivative of the resulting expression with respect to \( \lambda \), and considers the limit \( \lambda \to 0 \), which yields the following result:
\[ \tilde{C}_{dd}(0) = \left( \frac{mP}{2\pi \hbar^2 \beta} \right)^{dP/2} \int dx_1 \int dx_2 \cdots \int dx_P \times \Delta(\xi_a(x_0)) \Delta(\xi_b(x_{P/2})) \times \exp[ -\beta \Phi(x_1, x_2, \ldots, x_P) ] \times \left\{ F(x_1, x_2, \ldots, x_P) + G(x_1, x_2, \ldots, x_P) \right\}, \]  

(2.28)

with \( F(x_1, x_2, \ldots, x_P) \) and \( G(x_1, x_2, \ldots, x_P) \) being defined by
\[ F(x_1, x_2, \ldots, x_P) = -\frac{mP}{\hbar^2 \beta^2} \left\{ \sum_{k=1}^{P/2} \sum_{l=1}^{P-2k+1} \right\} \times \left( x_k - x_{k-1} \right)^2 + \frac{2}{P} \]
\[ \times \left\{ \sum_{k=1}^{P/2-1} \sum_{k=1}^{P-2k+1} \right\} V(x_k), \]  

(2.29a)

and
\[ G(x_1, x_2, \ldots, x_P) = \frac{2}{\beta^2} \frac{dP}{2} - \frac{4mP}{\hbar^2 \beta^2} \sum_{k=1}^{P} \left( x_k - x_{k-1} \right)^2, \]  

(2.29b)

respectively.

Having obtained the relevant path integral formulas, we now express the ratio \( C_{df}(0)/C_{dd}(0) \) and \( \Delta H \) in a Monte Carlo form as follows:
\[ C_{df}(0)/C_{dd}(0) = \left\langle f_o(x_1, x_2, \ldots, x_P) \right\rangle, \]  

(2.30a)

\[ \Delta H^2 = \frac{1}{2} \left\langle F(x_1, x_2, \ldots, x_P) + G(x_1, x_2, \ldots, x_P) \right\rangle, \]  

(2.30b)
where \( \langle \cdots \rangle \) denotes an ensemble average
\[
\langle \cdots \rangle = \frac{\int dx_1 \cdots dx_p \rho(x_1, x_2, \ldots, x_p) \langle \cdots \rangle}{\int dx_1 \cdots dx_p \rho(x_1, x_2, \ldots, x_p)}
\] (2.31)
over the weight function defined by
\[
\rho(x_1, x_2, \ldots, x_p) = \Delta(\xi_a(x_0)) \Delta(\xi_b(x_{P/2})) \times \exp[-\beta \Phi(x_1, x_2, \ldots, x_p)].
\] (2.32)
These ratios can be evaluated numerically—and simultaneously, since they have the same weight function—by performing a path integral Monte Carlo (PIMC)23–25 or molecular dynamics (PIMD)23 simulation. In particular, the PIMD methods may be more convenient in that it can handle the delta functions in Eq. (2.32) without difficulty (e.g., in combination with the SHAKE algorithm).36 On the other hand, if one employs the PIMC methods, one may need to replace the delta function by a Gaussian with sufficiently small width,
\[
\delta(\xi(q)) \to \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{1}{2} \left(\frac{\xi(q) - \xi_e}{\sigma}\right)^2\right),
\] (2.33)
because the treatment of a delta function (i.e., a “hard constraint”) is generally not straightforward in Monte Carlo methods. We thus present in Appendix A a series of alternative path integral expressions for the same quantities treated above, in which the strict delta function is replaced by an effective Gaussian with its width determined locally by the gradient of the reaction coordinate. The latter formulas will be employed in the numerical example in Sec. III B. Finally, we discuss in Sec. IV below a possible alternative way of obtaining \( C_{dd}(0) \) which may prove to be more advantageous computationally.

D. Adaptive umbrella sampling for \( C_{dd}(0)/Q_r \)

Although the calculation of \( C_{d}(0)/C_{dd}(0) \) and \( \Delta H \) is straightforward as described in Sec. II C, the computation of the first factor in Eq. (2.15), i.e., \( C_{dd}(0)/Q_r \), is more involved because \( C_{dd}(0) \) is a property associated with the top of the potential barrier while \( Q_r \) is that with the bottom of the reactant well. As mentioned in Sec. II B, this difficulty is usually handled via techniques such as thermodynamic integration or umbrella sampling.

To proceed, we suppose that the reaction coordinates, \( \xi_a(q) \) and \( \xi_b(q) \), take the following form:
\[
\xi_a(q) = \xi(q) - \xi_a, \quad \xi_b(q) = \xi(q) - \xi_b.
\] (2.34a, 2.34b)
where \( \xi(q) \) provides some “reference” reaction coordinate, while \( \xi_a \) and \( \xi_b \) are adjustable parameters that shift the location of the dividing surfaces. With this definition \( C_{dd}(0) \) becomes a function of \( (\xi_a, \xi_b) \), namely
\[
C_{dd}(0; \xi_a, \xi_b) = \text{tr}\left[e^{-\beta \frac{d}{2}} \Delta(\xi(q) - \xi_a) \times e^{-\beta \frac{d}{2}} \Delta(\xi(q) - \xi_b)\right].
\] (2.35)
Our goal then becomes (i) to seek a stationary point (a saddle point in particular) of \( C_{dd}(0; \xi_a, \xi_b) \),
\[
\frac{\partial C_{dd}(0; \xi_a, \xi_b)}{\partial \xi_a} = 0, \quad \frac{\partial C_{dd}(0; \xi_a, \xi_b)}{\partial \xi_b} = 0,
\] (2.36)
according to the condition (2.11), and (ii) to compute the ratio \( C_{dd}(0; \xi_a, \xi_b)/Q_r \) at that point.

To achieve this we first note the fact that the discretized path integral of \( C_{dd}(0; \xi_a, \xi_b)/Q_r \), may be expressed as
\[
\frac{C_{dd}(0; \xi_a, \xi_b)}{Q_r} = \kappa P(\xi_a, \xi_b),
\] (2.37)
where \( P(\xi_a, \xi_b) \) is a joint probability density function to find the value of \( (\xi(x_0), \xi(x_{P/2})) \) at \( (\xi_a, \xi_b) \),

The probability density function \( P(\xi_a, \xi_b) \) can be written as
\[
P(\xi_a, \xi_b) = \frac{\int \cdots \int \delta(\xi(q) - \xi_a) \delta(\xi(q) - \xi_b) \exp[-\beta \Phi'(x_1, x_2, \ldots, x_p)]}{\int \cdots \int \rho(x_1, x_2, \ldots, x_p) \exp[-\beta \Phi'(x_1, x_2, \ldots, x_p)]}
\] (2.38)
with
\[
\Phi'(x_1, x_2, \ldots, x_p) = \Phi(x_1, x_2, \ldots, x_p) - k_B T \log[m^{-1/2} \nabla \xi(x_0)]^2[m^{-1/2} \nabla \xi(x_{P/2})],
\] (2.39)
which satisfies the following normalization condition by definition:
\[
\int_{-\infty}^{\xi_e} d\xi_a \int_{-\infty}^{\xi_e} d\xi_b P(\xi_a, \xi_b) = 1,
\] (2.40)
and \( \kappa \) is the correction factor given by
\[
\kappa = \frac{\int \cdots \int \delta(\xi(q) - \xi_a) \delta(\xi(q) - \xi_b) \exp[-\beta \Phi'(x_1, x_2, \ldots, x_p)]}{\int \cdots \int \rho(x_1, x_2, \ldots, x_p) \exp[-\beta \Phi'(x_1, x_2, \ldots, x_p)]},
\] (2.41)
Here $\Phi(x_1, x_2, \ldots, x_P)$ is the discretized action in Eq. (2.20) and $\xi$ is a parameter introduced to roughly discriminate between the reactant and product regions. Using the above expressions, one can in principle obtain the value of $C_{ad}(0)/Q_r$ from a direct equilibrium simulation as follows: 

1. Perform a path integral Monte Carlo or molecular dynamics simulation to sample the path variables $(x_1, x_2, \ldots, x_P)$ according to the weight function,
   $$\rho(x_1, x_2, \ldots, x_P) = h(\xi - x_0)h(\xi - x_{P/2})$$
   $$\times \exp\left[ -\beta V^\prime(x_1, x_2, \ldots, x_P) \right].$$

2. Construct a two-dimensional histogram of the values of $(\xi(x_0), \xi(x_{P/2})).$

3. Normalize the histogram according to the condition (2.40), thereby estimating the absolute value of $P(\xi_a, \xi_b)$ at a particular value of $(\xi_a, \xi_b)$ of interest. The correction factor $\kappa$ can also be obtained from the same equilibrium simulation.

As discussed in Sec. II B, however, this direct approach fails to provide an accurate value of $P(\xi_a, \xi_b)$ if the dividing surfaces corresponding to the given $(\xi_a, \xi_b)$ are located near the top of the potential barrier. This is because the overwhelming majority of the statistical samples will be generated around the bottom of the reactant well, and it is thus impossible to obtain sufficient statistics near the top of the barrier. In the present paper we deal with this problem by use of adaptive umbrella sampling, which has been successfully employed for obtaining a classical free energy surface associated with, e.g., a conformational change of biomolecules. This method differs from conventional umbrella sampling in that (i) it uses a global umbrella potential to artificially bias the sampling toward the top of the barrier, and (ii) the umbrella potential is iteratively updated so that an approximately flat distribution of a target quantity (here the reaction coordinates) is achieved.

In the present work we employ a simplified version of this method to compute the probability density in Eq. (2.38), or equivalently a two-dimensional quantum free energy surface $F(\xi_a, \xi_b)$ defined by

$$F(\xi_a, \xi_b) = -k_B T \log P(\xi_a, \xi_b).$$

Specifically, we add a global biasing (or umbrella) potential $U_g(\xi(x_0), \xi(x_{P/2}))$ to the discretized action $\Phi(x_1, x_2, \ldots, x_P)$ and define a biased probability density $P_g(\xi_a, \xi_b)$ as follows:

$$P_g(\xi_a, \xi_b) = \int dx_1 \int dx_2 \cdots \int dx_P \delta(\xi(x_0) - \xi_a) \delta(\xi(x_{P/2}) - \xi_b) \exp\left[ -\beta \Phi'(x_1, x_2, \ldots, x_P) \right]$$

$$\times \exp\left[ -\beta U_g(\xi(x_0), \xi(x_{P/2})) \right].$$

Note that the asterisk is attached to all the biased quantities. Since $U_g$ is a function of only $\xi(x_0)$ and $\xi(x_{P/2})$, the biased density $P_g(\xi_a, \xi_b)$ can be related to the original, unbiased density $P(\xi_a, \xi_b)$ as

$$P_g(\xi_a, \xi_b) = C \exp\left[ -\beta U_g(\xi_a, \xi_b) \right] P(\xi_a, \xi_b),$$

where $C$ is a constant that does not depend on $(\xi_a, \xi_b)$. Now suppose that $(\xi_a^0, \xi_b^0)$ and $(\xi_a^1, \xi_b^1)$ correspond to the dividing surfaces which are located near the top of the potential barrier and the bottom of the reactant well, respectively. Equation (2.45) then suggests

$$P_g(\xi_a^0, \xi_b^0) = \frac{\exp\left[ -\beta U_g(\xi_a^1, \xi_b^1) \right]}{\exp\left[ -\beta U_g(\xi_a^0, \xi_b^0) \right]} P_g(\xi_a^1, \xi_b^1),$$

which allows an accurate evaluation of $P(\xi_a, \xi_b)$ if the values of $P_g(\xi_a^0, \xi_b^0)/P_g(\xi_a^1, \xi_b^1)$ and $P(\xi_a^0, \xi_b^0)$ are available. The value of $P(\xi_a^0, \xi_b^0)$ can be obtained directly from an equilibrium simulation of the type discussed above. The accurate evaluation of $P_g(\xi_a^1, \xi_b^1)/P_g(\xi_a^0, \xi_b^0)$, on the other hand, is possible only if the biasing potential $U_g(\xi_a, \xi_b)$ creates a sufficiently flat distribution of $P_g(\xi_a, \xi_b)$ over the domain of $(\xi_a, \xi_b)$ that includes both $(\xi_a^1, \xi_b^1)$ and $(\xi_a^0, \xi_b^0)$. Therefore, the optimal definition of $U_g(\xi_a, \xi_b)$ is such that
in the \(m\)th simulation. The above definition directs the statistical samples toward unexplored regions of 
\((\xi_a, \xi_b)\).\(^{40,41}\)

3. Repeat steps (1) and (2) until \(P^{(m)}(\xi_a, \xi_b)\) becomes sufficiently flat.

4. Perform a long simulation with a fixed \(U(\xi_a, \xi_b)\) to generate an accurate value of both \(P_a(\xi_a, \xi_b)\) and \(P_b(\xi_a, \xi_b)\).

The above iterative procedure is essentially the same with that employed in a multicanonical sampling\(^{31,42}\) and the only difference is that in the former we seek a uniform sampling of the reaction coordinates while in the latter a uniform sampling of the total energy is pursued.

### III. APPLICATION TO BIMOLECULAR REACTIONS IN GAS PHASE

#### A. Modifications to the methodology

We now consider how to apply the computational procedure described above to bimolecular reactions in gas phase, in which several modifications are needed due to the fact that reactant molecules can be infinitely far apart. Here we take a simple atom–diatom reaction as an example,

\[
\text{A} + \text{BC} \rightarrow \text{AB} + \text{C},
\]

but the discussion below can readily be extended to larger polyatomic reactions. We describe the system in terms of the Jacobi coordinates, i.e., the interatomic vector \(r\) that connects B and C, and the scattering vector \(R\) that connects A and the center-of-mass of BC (here the center-of-mass of the whole system has been removed). The Hamiltonian of the system may be written as\(^{43}\)

\[
H = \frac{\mathbf{p}_R^2}{2\mu_R} + \frac{\mathbf{p}_r^2}{2\mu_r} + V(\mathbf{R}, \mathbf{r}),
\]

where \(p_R\) and \(p_r\) are the momenta conjugate to \(R\) and \(r\), respectively, while the associated reduced masses are given by

\[
\mu_R = \frac{m_A(m_B + m_C)}{m_B + m_C}, \quad \mu_r = \frac{m_B m_C}{m_B + m_C}
\]

with \(m_X\) being the mass of atom X. For simplicity of notation we employ the following collective coordinates \(q\) rather than \((\mathbf{R}, \mathbf{r})\):

\[
q = \sqrt{\frac{\mu_R}{m}} \mathbf{R}, \sqrt{\frac{\mu_r}{m}} \mathbf{r},
\]

in terms of which the scaled Hamiltonian takes a simple form as used in Sec. II C.

A major difference arises when one treats a bimolecular reaction in gas phase, that is, the reactant partition function \(Q_r\) in Eq. (2.5) is not defined for a single, bound system but for a pair of noninteracting reactant molecules:\(^{43}\)

\[
Q_r = Q_{\text{trans}} \times Q_{\text{int}}.
\]

Here \(Q_{\text{trans}}\) is the partition function for relative translational motion per unit volume,

\[
Q_{\text{trans}} = \left(\frac{\mu_R}{2\pi\hbar^2 \beta}\right)^{3/2},
\]

while \(Q_{\text{int}}\) is the internal partition function for noninteracting reactant molecules, which in the case of the reaction (3.1) becomes the rovibrational partition function of diatomic BC,

\[
Q_{\text{int}} = \text{tr}_r [\exp(-\beta \hat{H}_r)] = \sum_b \sum_j (2j + 1) \exp(-\beta \epsilon_{ij})
\]

with \(\hat{H}_r\) being the Hamiltonian of the diatomic and \(\{\epsilon_{ij}\}\) its eigenenergies. An important consequence of this fact is that the correction factor \(\kappa\) in Eq. (2.37) cannot be expressed as a simple equilibrium average as in Eq. (2.41), and thus some alternate information becomes necessary to fix the absolute value of the rate constant. Here we proceed by noting that one can nevertheless compute the ratio \(C_{\text{dd}}(0; \xi_a, \xi_b)/C_{\text{dd}}(0; \xi_a^0, \xi_b^0)\) via straightforward use of the umbrella sampling in Sec. II B. We thus rewrite the factor \(C_{\text{dd}}(0; \xi_a, \xi_b)/Q_r\) as follows:

\[
\frac{C_{\text{dd}}(0; \xi_a, \xi_b)}{Q_r} = \frac{C_{\text{dd}}(0; \xi_a^0, \xi_b^0)}{Q_r} \frac{C_{\text{dd}}(0; \xi_a, \xi_b)}{C_{\text{dd}}(0; \xi_a^0, \xi_b^0)}
\]

then the problem will be solved if we find a way of computing the ratio \(C_{\text{dd}}(0; \xi_a, \xi_b)/Q_r\) or the absolute value of \(C_{\text{dd}}(0; \xi_a^0, \xi_b^0)\) for some “reference” point \((\xi_a^0, \xi_b^0)\).

In the present paper we choose such a reference value by moving the dividing surface deep into the reactant asymptotic valley and eliminating the interaction potential between the two reactant molecules. To achieve this we define the reaction coordinate by linearly interpolating between a pair of constituent reaction coordinates, \(s_0(q)\) and \(s_1(q)\), as follows:

\[
s(q; \xi) = s_1(q) + (1 - \xi)s_0(q)
\]

with \(\xi\) being a switching parameter. With this definition \(s(q; \xi)\) becomes \(s_1(q)\) as \(\xi \rightarrow 1\) while it reverts to \(s_0(q)\) as \(\xi \rightarrow 0\). \(s_1(q)\) and \(s_0(q)\) are designed to represent a reaction coordinate whose dividing surface is located in the interaction region and in the reactant asymptotic region, respectively. A typical definition of such \(s_1(q)\) and \(s_0(q)\) is

\[
s_1(q) = r(C - B) - r(B - A) - [r_1(C - B) - r_1(B - A)],
\]

\[
s_0(q) = R_s - |\mathbf{R}|,
\]

where \(r(X - Y)\) denotes the interatomic distance between atoms X and Y and \(r_1(X - Y)\) its value at the transition state. \(|\mathbf{R}|\) is the length of the scattering vector, while \(R_s\) is an adjustable parameter that will be chosen sufficiently large. In Fig. 1 we depict the dividing surfaces (or lines in this case) corresponding to \(s(q; \xi)\) for a collinear version of the reaction (3.1), from which it is seen that \(\xi\) behaves roughly as a rotational angle of the dividing surface. We now define a parametrized \(C_{\text{dd}}(0)\) in terms of \(s(q; \xi)\) as

\[
C_{\text{dd}}(0; \xi_a, \xi_b) = \text{tr}[e^{-\beta \hat{H}_r} \Delta(s(q; \xi_a))] \\
\times e^{-\beta \hat{H}_r} \Delta(s(q; \xi_b)),
\]

where

\[
\Delta(s(q; \xi_a)) = e^{-\beta \hat{H}_r} \delta(s(q; \xi_a) - s_1(q)), \quad \Delta(s(q; \xi_b)) = e^{-\beta \hat{H}_r} \delta(s(q; \xi_b) - s_0(q)).
\]
The remaining modification to the methodology is for the treatment of the delta function in the umbrella sampling of $C_{dd}(0; \xi_a, \xi_b)$. Since the parameter $\xi$ enter the reaction coordinate $s(q; \xi)$ in a different manner from Sec. II D, one needs to rewrite $\Delta(s(q; \xi))$ as

$$\Delta(s(q; \xi)) = \Delta[(s_0(q) - s_1(q))(\xi(q) - \xi)] = \Delta(\xi(q) - \xi),$$

(3.18)

where the effective reaction coordinate $\xi(q)$ is defined by

$$\xi(q) = \frac{s_0(q)}{s_0(q) - s_1(q)},$$

(3.19)

and the second equality in Eq. (3.18) can be shown by using the invariance property of the $\Delta$ function with respect to a scaling of the reaction coordinate. The umbrella sampling of $C_{dd}(0; \xi_a, \xi_b)$ then proceeds by constructing a two-dimensional histogram of $(\xi(x_0), \xi(x_{p/2}))$ as described in Sec. II D.

B. Numerical example

We now apply the above computational procedure to the following hydrogen exchange reaction in gas-phase:

$$D + H_a H_\beta \rightarrow [DH_a + H_\beta],$$

(3.20)

discuss some details of numerical calculations. The above reaction is described in terms of the Jacobi coordinates with the assignment of atoms being $A = D$, $B = H_a$, and $C = H_\beta$. In the present work we employ the distinguishable particle approximation to the hydrogen atoms, which can be justified for the temperatures studied in the present work. The gross rate coefficient $k(T)$ for the reaction (3.20) is defined via the rate equation,

$$\frac{d}{dt}([DH_a] + [DH_\beta]) = k(T)[D][H_a H_\beta],$$

(3.21)

where $[X]$ denotes the number of molecule $X$. To appropriately define the reaction coordinate $s_1(q)$ in Eq. (3.9), we first consider the following two reaction coordinates that are associated with the individual arrangement channels in Eq. (3.20):

$$s_{1a}(q) = r(H_\beta - H_a) - r(H_a - D) - [r^3(H_\beta - H_a) - r^3(H_a - D)],$$

(3.22a)

$$s_{1b}(q) = r(H_a - H_\beta) - r(H_\beta - D) - [r^3(H_a - H_\beta) - r^3(H_\beta - D)].$$

(3.22b)

We then define $s_1(q)$ as follows:

$$s_1(q) = \max\{s_{1a}(q), s_{1b}(q)\},$$

(3.23)

i.e., $s_1(q)$ becomes positive when either of the H atoms comes close to the D atom (see Fig. 6 of Ref. 45 for a schematic representation of the corresponding dividing surface). The above $s_1(q)$ is not differentiable when $s_{1a}(q)$ is precisely equal to $s_{1b}(q)$, but the latter situations do not arise in actual finite-precision calculations, and hence we evaluated the derivative of $s_1(q)$ simply as

FIG. 1. The dividing surface corresponding to the interpolative reaction coordinate $s(q; \xi)$ in Eq. (3.9) for a collinear version of the $A + BC$ reaction. $s(q; \xi)$ reverts to $s_1(q)$ and $s_2(q)$ in Eqs. (3.10a) and (3.10b) as $\xi = -1$ and 0, respectively.

and set the reference point as $(\xi^0_{a, b}) = (0, 0)$ to obtain

$$C_{dd}(0; \xi_a, \xi_b) = \text{tr}[e^{-\beta \hat{H}_R^2/2}(\hat{R}_q - |\hat{R}|)] \times e^{-\beta \hat{H}_R^2/2}(\hat{R}_q - |\hat{R}|)].$$

(3.12)

An important point here is that we can evaluate $C_{dd}(0; \xi_a, \xi_b)$ directly, i.e., in a way independent of other path integral calculations. This is because the full Hamiltonian $\hat{H}$ in Eq. (3.12) may be replaced by that for the non-interacting pair of reactant molecules, namely

$$\hat{H} = \hat{T}_R + \hat{h}_R,$$

(3.13)

with $\hat{T}_R = \hat{p}_R^2/2 \mu_R$ and $\hat{h}_R = \hat{p}_R^2/2 \mu_R + u_{BC}(r)$ as long as the parameter $\mu_R$ is chosen sufficiently large. $C_{dd}(0; \xi_a, \xi_b)$ can thus be factored into two contributions as

$$C_{dd}(0; \xi_a, \xi_b) = C_{dd}^{\text{trans}}(0; Q_{\text{int}},$$

(3.14)

where $C_{dd}^{\text{trans}}(0)$ is the contribution from relative translational motion

$$C_{dd}^{\text{trans}}(0) = \text{tr}[e^{-\beta \hat{T}_R^2/2}(\hat{R}_q - |\hat{R}|)] e^{-\beta \hat{T}_R^2/2}(\hat{R}_q - |\hat{R}|)].$$

(3.15)

while $Q_{\text{int}}$ is the internal partition function in Eq. (3.7). $C_{dd}^{\text{trans}}(0)$ above can readily be evaluated analytically to give

$$C_{dd}^{\text{trans}}(0) = \text{AR}^2 \frac{2}{\pi} \left(\frac{\mu_R}{h^2} \right)^2$$

(3.16)

with $A = |m^{-1/2} \nabla |\hat{R}||^2$, which becomes $1/\mu_R$ if one uses the Jacobi coordinates in Eq. (3.4). By combing Eqs. (3.5) and (3.14), we find that the factor $C_{dd}(0; \xi_a, \xi_b)/Q_{\text{r}}$ in Eq. (3.8) is simplified to

$$\frac{C_{dd}(0; \xi_a, \xi_b)}{Q_{\text{r}}} = \frac{C_{dd}^{\text{trans}}(0)}{Q_{\text{trans}}} = 4 \pi A R^2 \left(\frac{2 \mu_R}{\pi h^2} \right)^{1/2}.$$
\[ \nabla s_1(q) = \begin{cases} 
\nabla s\alpha(q) & s\alpha(q) > s\beta(q), \\
\nabla s\beta(q) & s\beta(q) > s\alpha(q), 
\end{cases} \]

which was found to cause no numerical problems in actual simulations.

The computational details of path integral calculations are as follows. The statistical sampling of discretized imaginary time paths was performed via Monte Carlo methods. In the adaptive umbrella sampling for computing the ratio \( C_{dd}(0; \xi, \xi')/C_{dd}(0; \xi_0, \xi') \), the path variables were sampled via combined use of the staging algorithm \(^{46-48}\) (i.e., segment move that samples the kinetic action) and the whole-chain move \(^{24}\) for each of the Jacobi vectors \( R \) and \( r \). In particular, the whole-chain move for \( R \) was quite effective in accelerating the statistical convergence; this is because the \( R \) vector can be moved with a rather large stepsize, which leads to a faster diffusion of the path variables between the interaction region and the reactant asymptotic valley. In the calculation of \( C_{dd}(0)/C_{dd}(0) \) and \( \Delta H \) we employed the alternative path integral expressions presented in Appendix A, where the following four time slices, namely \( x_{1}, x_{p/2}, x_{p/2+1} \), and \( x_{p} \), were sampled with the single-slice free-particle move \(^{24}\) while other slices with the staging algorithm. The exceptional treatment of the former is due to the fact that they are strongly bound to the dividing surfaces through the smeared delta function in Eq. (A8). All the path integral calculations were performed for three values of the Trotter number \( P \) and the resulting data were extrapolated to the limit \( P \to \infty \) by assuming \( P^{-2} \) scaling of discretization error. For example, \( P = \{8, 12, 16 \} \) and \( \{40, 60, 80 \} \) were used for \( P = 1000 \) and \( 200 \) K, respectively. The number of Monte Carlo cycles employed was \( 5 \times 10^{7} - 1 \times 10^{8} \), which was sufficient to converge the relevant quantities within \( 1-2 \% \) statistical error.

According to the prescription in Sec. III A, the quantum instanton rate in Eq. (2.5) is obtained as the product of three factors:

\[ k_{QI} = \frac{C_{dd}^{\text{trans}}(0)}{C_{dd}^{\text{trans}}(0; \xi_{a}, \xi_{b})} \left[ \frac{C_{d}(0)}{C_{d}(0; \xi_{a}, \xi_{b})} \right] \frac{\sqrt{\pi}}{2} \frac{\hbar}{\Delta H} \]

where \((\xi_{0}, \xi_{b}) = (0, 0)\), and \((\xi_{a}, \xi_{b})\) is a stationary point of \( C_{dd}(0; \xi_{a}, \xi_{b}) \) with which the factor in curly brackets is evaluated. To locate the latter point it is useful to examine the topography of the quantum free energy surface defined by

\[ F(\xi_{a}, \xi_{b}) = -k_{B}T \log C_{dd}(0; \xi_{a}, \xi_{b}) \]

the computation of which proceeds by setting up a two-dimensional histogram on a domain of \((\xi_{a}, \xi_{b})\) and performing an adaptive umbrella sampling as described in Sec. II D. In practice, we employ the following sum and difference variables rather than \((\xi_{a}, \xi_{b})\):

\[ \tilde{\xi} = (\xi_{a} + \xi_{b})/2, \quad \Delta \xi = \xi_{b} - \xi_{a} \]

since these variables can describe a relevant portion of the free energy surface in a more compact manner (see Appendix B for more details). We show in Fig. 2(a) the free energy surface obtained for \( T = 1000 \) K, from which it is seen that \( F(\tilde{\xi}, \Delta \xi) \) exhibits a barrierlike profile along the \( \tilde{\xi} \) axis, while it grows quadratically as \( |\Delta \xi| \) deviates from 0. This behavior of \( F(\tilde{\xi}, \Delta \xi) \) can be understood qualitatively by considering a simple one-dimensional system with the Hamiltonian \( H = p^{2}/2m + V(q) \). With the primitive approximation for the canonical density matrix, the free energy of the system may be written as

\[ F(\tilde{\xi}, \Delta \xi) = -\beta^{-1} \log \{(\xi_{a})e^{\beta[H]}|\xi_{b}\}^{2}/m \]

\[ = \frac{1}{2} \{V(\tilde{\xi} + \Delta \xi/2) + V(\tilde{\xi} - \Delta \xi/2)\} + \frac{2m}{\hbar^{2}} \Delta \xi^{2}/\text{const} \]

from which it is evident that the variation of \( F(\tilde{\xi}, \Delta \xi) \) along \( \tilde{\xi} \) is determined primarily by the underlying classical potential energy, while that along \( \Delta \xi \) is dominated by thermal fluctuation of the imaginary time path. [We note in passing that in three-dimensional systems the variation of \( F(\tilde{\xi}, \Delta \xi) \) along \( \tilde{\xi} \) is somewhat different from that of the classical potential even in the high-temperature limit; this is due to the volume effect associated with the scattering vector \( R \).] At low temperatures, the topography of the free energy surface changes because of the enhanced delocalization of the imaginary time path. Figure 2(b) shows the free energy at \( T = 200 \) K, from which it is seen that (i) the curvature of \( F(\tilde{\xi}, \Delta \xi) \) along \( \Delta \xi \) is significantly reduced, and (ii) the height of the free energy barrier is also lowered. In particular,
the free energy surface around the top of the barrier exhibits an interesting structure depending on a subtle balance between the delocalization of the path and the variation of the classical potential energy. This is illustrated in Fig. 3, where the local topography of $F(\xi, \Delta \xi)$ for $T = 200$, 250, and 300 K is plotted. We see from this figure that at $T = 300$ K there exists only a single saddle point at $(\xi, \Delta \xi) = (0.98, 0)$ [Fig. 3(a)], which with increase in the temperature moves toward

![FIG. 3. Local topography of the quantum free energy surface around the top of the barrier. (a) $T = 300$ K; (b) $T = 250$ K; (c) $T = 200$ K. The single saddle point observed at $T = 300$ K bifurcates into two distinct saddle points at $T = 200$ K.](image)

Table I. Various quantities obtained from Monte Carlo path integral calculations for the $D + H_2$ reaction in Eq. (3.20) with use of the LSTH potential energy surface (Ref. 50). $(\xi^*, \Delta \xi^*)$ is the stationary point of the quantum free energy surface defined by Eq. (3.26). The parameter $R_e$ in Eq. (3.10b) is chosen as 8.0 Å for all the temperatures considered. All the values in the table are given in atomic units, and figures in parentheses refer to powers of 10.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$(\xi^<em>, \Delta \xi^</em>)$</th>
<th>$C_{ad}(0)/C_r$</th>
<th>$C_{ff}(0)/C_{ad}(0)$</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>(1.0)$^a$</td>
<td>2.97(−3)</td>
<td>5.24(−3)</td>
<td>7.21(−3)</td>
</tr>
<tr>
<td>1000</td>
<td>(0.99,0)$^a$</td>
<td>5.59(−4)</td>
<td>3.73(−3)</td>
<td>5.02(−3)</td>
</tr>
<tr>
<td>500</td>
<td>(0.985,0)$^a$</td>
<td>8.82(−6)</td>
<td>2.39(−3)</td>
<td>3.02(−3)</td>
</tr>
<tr>
<td>300</td>
<td>(0.98,0)$^a$</td>
<td>6.60(−8)</td>
<td>2.39(−3)</td>
<td>2.58(−3)</td>
</tr>
<tr>
<td>200</td>
<td>(0.975,0)$^a$</td>
<td>3.00(−10)</td>
<td>3.73(−3)</td>
<td>2.89(−3)</td>
</tr>
<tr>
<td></td>
<td>(0.98,0.3)$^a$</td>
<td>4.03(−10)</td>
<td>1.74(−3)</td>
<td>2.09(−3)</td>
</tr>
</tbody>
</table>

$^a$Saddle points of the free energy surface.

$^b$Top of the free energy curve along the $\xi$ axis.

$(\xi, \Delta \xi) = (1,0)$ (i.e., to the top of the classical barrier). As the temperature is lowered to $T = 200$ K, on the other hand, the single saddle point bifurcates into a distinct pair at $(\xi, \Delta \xi) = (0.98, \pm 0.3)$ [Fig. 3(c)].

Having identified the stationary points of $C_{ad}(0; \xi, \Delta \xi)$, we now compute the necessary quantities such as $C_{ff}(0)/C_{ad}(0)$ at those points and combine all the information to generate the quantum instanton rate via Eq. (3.25). The results are summarized in Tables I and II, in which the following modified version of $k_{QI}$,

$$
\kappa_{QI}^{\text{mod}} = \frac{1}{Q_r} C_{ff}(0) \sqrt{\frac{\pi}{2}} \frac{\hbar}{\Delta H + (\sqrt{\pi} - \sqrt{2})/\beta},
$$

and the “simplest” QI rate

$$
K_{\text{SQI}} = \frac{1}{Q_r} \sqrt{\pi \hbar} C_{ad}(0),
$$

are also included. (Here $K_{QI}^{\text{mod}}$ is obtained in a rather ad hoc manner by requiring that $K_{QI}^{\text{mod}}$ become exact for a free particle, or equivalently, in the high-temperature limit for a general system.\(^{1}\) We see from Table II that $K_{QI}$ and $K_{QI}^{\text{mod}}$ are in excellent agreement with the accurate quantum mechanical rates\(^{48}\) with 20–30% and ~10% deviations for all the temperatures considered, respectively, while the accuracy of $K_{\text{SQI}}$ is moderate at high temperatures (~80% deviation) and improves at lower temperatures (~20% deviation), which is very similar to the results obtained for several one- and two-dimensional model systems.\(^{1}\) Of particular interest is the fact that at the lowest temperature ($T = 200$ K) where the saddle point bifurcates into two distinct points, the full QI rate evaluated at the saddle point is considerably better than that obtained at the top of the free energy curve along the $\xi$ axis (the deviation is reduced from 19% to 3%), which numerically supports the choice of saddle points in the QI approximation. Although the improvement gained by shifting the dividing surfaces toward the saddle point was not so dramatic in the present example, it is expected to become rather large for chemical reactions with strongly asymmetric poten-
tial profiles. In any case, the accuracy of the QI rates thus observed is very encouraging, particularly considering the fact that the rate varies by seven orders of magnitude over the temperature range examined.

IV. CONCLUDING REMARKS

We have presented a rather straightforward way of evaluating thermal rate constants within the quantum instanton approximation, here implemented by use of imaginary time path integrals. The necessary computational techniques are well-established ones of statistical mechanics, namely, (i) path integral Monte Carlo (PIMC) or molecular dynamics (PMID) techniques for sampling discretized paths in imaginary time, and (ii) methods for computing a two-dimensional free energy surface such as adaptive umbrella sampling. The application of the present QI methodology to more complex chemical reactions in gas and condensed phase is a future subject.52

There are two remaining issues that are worth mentioning. The first is a possible alternative way of computing $\Delta H$ in Eq. (2.7). Since the statistical estimator of that quantity, i.e., Eq. (2.29), is analogous to the thermodynamic estimator of internal energy $^{53}$ or the heat capacity estimator, $^{54}$ it may exhibit a rather large statistical variance when the number of imaginary time slices or the size of the system becomes large. In that case one may directly compute a fragment of the imaginary time correlation function $C_{dd}(\lambda)$ in Eq. (2.26) on a small interval of $\lambda$, fit some analytic function to the fragment, and compute the second derivative of the fitted function at $\lambda = 0$. The second issue is an alternative for obtaining the first factor in Eq. (2.15), namely $C_{dd}(0)/Q_r$. In Sec. II D the latter quantity was obtained by constructing a two-dimensional free energy surface associated with $C_{dd}(0)$, but this approach becomes rather awkward when one wishes to use two reaction coordinates that are characterized by more than two parameters (e.g., by incorporating the rotation or deformation of the dividing surfaces). In that case it may be more convenient to perform a thermodynamic integration of $C_{dd}(0)$ with respect to the reaction coordinates, i.e., one integrates the log derivative of $C_{dd}(0)$ from the bottom of the reactant well to the saddle point of $C_{dd}(0)$ (probably in conjunction with some numerical techniques for searching the saddle point). One can also perform a thermodynamic integration of $C_{dd}(0)$ with respect to temperature, which will obviate the need for determining the absolute value of $C_{dd}(0)/Q_r$ for each temperature of interest. $^{55}$ Investigating the utility of these approaches is of course outside the scope of this paper and may be addressed in future work.

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APPENDIX A: ALTERNATIVE PATH INTEGRAL EXPRESSIONS

Here we derive a series of alternative path integral estimators for $C_{dd}(0)$, $C_{dd}(0)$, and $C_{dd}(0)$ which are free from the strict Dirac delta function and may thus be employed straightforwardly in a Monte Carlo calculation. To obtain such expressions we employ a potential-referenced primitive approximation to the high temperature Boltzmann operator, 

$$e^{-\epsilon_i} \approx \int d\mathbf{x} e^{-\epsilon_i \mathbf{x}/2} |\mathbf{x}\rangle e^{-\epsilon V(\mathbf{x})} \langle \mathbf{x}| e^{-\epsilon_i \mathbf{x}/2},$$

(A1)

with which $C_{dd}(0)$ in Eq. (2.17) is discretized as follows:
with $\Delta \beta = \beta / P$. The matrix elements of the delta function above are now approximated by Fourier transforming the delta function as

$$\langle x''| e^{-\Delta \beta \hat{T}/2} \Delta(\xi(y)) e^{-\Delta \beta \hat{T}/2} | x' \rangle$$

$$= \int \frac{dk}{2\pi} \int d\mathbf{x}' \langle x''| e^{-\Delta \beta \hat{T}/2} y(\mathbf{y}) e^{-\Delta \beta \hat{T}/2} | x' \rangle$$

$$\times e^{i\mathbf{k} \cdot \mathbf{x}'/m^{1/2} \nabla \xi(y)}, \quad (A3)$$

and Taylor expanding the reaction coordinate locally up to the first order about $\mathbf{x} = (\mathbf{x''} + \mathbf{x}')/2$:

$$\xi(y) = \xi(\mathbf{x}) + \nabla \xi(\mathbf{x})(\mathbf{x''} - \mathbf{x}). \quad (A4)$$

This approximation is expected to be accurate for sufficiently small $\Delta \beta$ because (i) $\mathbf{x''}$ and $\mathbf{x}'$ are kept close due to the factor $e^{-\Delta \beta \hat{T}/2}$, and (ii) the reaction coordinate is generally a slowly varying function of the system coordinates. The integrations over $\mathbf{y}$ and $k$ in Eq. (A3) can then be performed analytically, which gives

$$\langle x''| e^{-\Delta \beta \hat{T}/2} \Delta(\xi(y)) e^{-\Delta \beta \hat{T}/2} | x' \rangle$$

$$= \Delta(\xi(\mathbf{x}))/\langle x''| e^{-\Delta \beta \hat{T}/2} | x' \rangle \quad (A5)$$

with

$$\Delta(\xi(\mathbf{x})) = \delta(\xi(\mathbf{x})) m^{-1/2} \nabla \xi(\mathbf{x}) \quad (A6)$$

and $\delta(f(x))$ being a “smear” delta function defined by

$$\delta(f(x)) = \left( \frac{2m}{\pi \hbar^2 \Delta \beta} \right)^{1/2} \frac{1}{|f(x)|}$$

$$\times \exp \left[ - \frac{2m}{\hbar^2 \Delta \beta} \left( \frac{f(x)}{|f(x)|} \right)^2 \right]. \quad (A7)$$

Note that $\delta(f(x))$ can be regarded as a Gaussian of $f(x)$ with its standard deviation being $\sqrt{\hbar^2 \Delta \beta / 4m |f(x)|}$. Introducing the above approximation into Eq. (A2) gives

$$C_{dd}(0) = \int dx_1 \int dx_2 \cdots \int dx_P \Delta(\xi(\mathbf{x}))$$

$$\times \Delta(\xi(\mathbf{x}_{P+1})) \left( \frac{m P}{2 \pi \hbar^2 \Delta \beta} \right)^{d P/2}$$

$$\times \exp \left[ - \beta \Phi(x_1,x_2,\ldots,x_P) \right], \quad (A8)$$

where $\mathbf{x}_0 = x_P$, $\mathbf{x}_k = (x_k + x_{k-1})/2$, and $\Phi(x_1,x_2,\ldots,x_P)$ is the discretized action in Eq. (2.20). The above expression is essentially the same with Eq. (2.19) except that the strict delta function is now replaced by its smeared counterpart.

A path integral expression for $C_{dd}(0)$ is also derived along the same lines. With the flux operator in Eq. (2.13) one can readily show the following identity relation:

$$\langle x''| e^{-\Delta \beta \hat{T}/2} \Phi e^{-\Delta \beta \hat{T}/2} | x' \rangle$$

$$= \frac{i}{\hbar \Delta \beta} \int dy \delta(\xi_y(y)) \nabla \xi_y(y) \cdot (x'' - x')$$

$$\times \langle x''| e^{-\Delta \beta \hat{T}/2} y(\mathbf{y}) e^{-\Delta \beta \hat{T}/2} | x' \rangle, \quad (A9)$$

to which we will apply the approximation (A4). To be consistent with the linear expansion of $\xi_y(y)$, we replace $\nabla \xi_y(y)$ above by $\nabla \xi(\mathbf{x})$ with $\mathbf{x} = (\mathbf{x''} + \mathbf{x}')/2$, which gives

$$\langle x''| e^{-\Delta \beta \hat{T}/2} \Phi e^{-\Delta \beta \hat{T}/2} | x' \rangle$$

$$= \frac{i}{\hbar \Delta \beta} \nabla \xi(\mathbf{x}) \cdot (x'' - x')$$

$$\times \langle x''| e^{-\Delta \beta \hat{T}/2} | x' \rangle, \quad (A10)$$

i.e., the matrix element of the flux operator is explicitly factored into a “velocity” factor and the matrix element of the delta function. Now invoking the approximate factorization (A5) yields

$$C_{dd}(0) = \int dx_1 \int dx_2 \cdots \int dx_P \Delta(\xi(\mathbf{x}))$$

$$\times \Delta(\xi(\mathbf{x}_{P+1})) \left( \frac{m P}{2 \pi \hbar^2 \Delta \beta} \right)^{d P/2}$$

$$\times \exp \left[ - \beta \Phi(x_1,x_2,\ldots,x_P) \right]$$

$$\times \tilde{f}_v(x_1,x_2,\ldots,x_P), \quad (A11)$$

where the velocity factor is defined by

$$\tilde{f}_v(x_1,x_2,\ldots,x_P) = m \frac{i}{\hbar \Delta \beta} \left\{ \frac{1}{\tilde{n}_v(x)} (x_1 - x_P) \right\}$$

$$\times \{ \tilde{n}_v(x_{P+1}) (x_{P+1} - x_P) \}, \quad (A12)$$

with $\tilde{n}_v(x) = \nabla \xi_y(y)/|\nabla \xi_y(y)|$.

The derivation of $C_{dd}(0)$ requires some care. The basic strategy is the same as in Sec. II C, namely to take the second derivative of $C_{dd}(\lambda) = C_{dd}(-i \hbar \lambda)$ with respect to $\lambda$, but in order to make the final formula as simple as possible we split the Boltzmann operator as follows:
\[ C_{dd}(\lambda) = \text{tr} \left[ e^{-\Delta \bar{H}} (e^{-(\Delta \beta + \Delta \lambda) \bar{H}})^{p/2-2} e^{-\Delta \bar{H}} (e^{-(\Delta \beta + \Delta \lambda) \bar{H}})\right] \]

with \( \Delta \lambda = \lambda / (P/2 - 2) \), which allows direct use of the approximation (A5). Now introducing the potential-referenced primitive approximation (A1) and performing the first-order expansion of \( \xi_\lambda(q) \) gives

\[
\tilde{C}_{dd}(\lambda) = \int dx_1 \int dx_2 \cdots \int dx_P \Delta(\xi_a(x_1))\Delta(\xi_b(x_{P/2+1})) \left( \prod_{k=1}^{P} \langle x_k | e^{-(\Delta \beta + a_k \Delta \lambda) \bar{T}} | x_{k-1} \rangle \right)
\]

\[
\times \exp \left[ - \sum_{k=1}^{P} (\Delta \beta + b_k \Delta \lambda) V(x_k) \right],
\]

where the indices \( \{ a_k \} \) and \( \{ b_k \} \) are defined by

\[
a_k = \begin{cases} 
0, & k = 1, \\
1/2, & k = 2, 3, \ldots, P/2, \\
1, & 3 \leq k \leq P/2 - 1
\end{cases}
\]

and

\[
b_k = \begin{cases} 
0, & k = 1, P/2, \\
1, & 2 \leq k \leq P/2 - 1
\end{cases}
\]

with \( a_k = -a_{k-P/2} \) and \( b_k = -b_{k-P/2} \) for \( P/2 + 1 \leq k \leq P \). Taking the second derivative of Eq. (A14) with respect to \( \lambda \) and considering the limit \( \lambda \rightarrow 0 \) leads to the following:

\[
\tilde{C}_{dd}(0) = \int dx_1 \int dx_2 \cdots \int dx_P \Delta(\xi_a(x_1))\Delta(\xi_b(x_{P/2+1})) \left( \frac{mP}{2 \pi \hbar^2 \beta} \right)^{dp/2}
\]

\[
\times \exp[\beta \Phi(x_1, x_2, \ldots, x_P)] \frac{1}{(P/2 - 2)^2} \{ F(x_1, x_2, \ldots, x_P)^2 + \tilde{G}(x_1, x_2, \ldots, x_P) \}
\]

with

\[
F(x_1, x_2, \ldots, x_P) = -\frac{m}{2 \hbar^2 \Delta \beta^2} \sum_{k=1}^{P} a_k(x_k - x_{k-1})^2
\]

\[
+ \sum_{k=1}^{P} b_k V(x_k)
\]

and

\[
\tilde{G}(x_1, x_2, \ldots, x_P) = \frac{d}{2 \Delta \beta^2} \sum_{k=1}^{P} a_k^2 + \frac{m}{\hbar^2 \Delta \beta^2}
\]

\[
\times \sum_{k=1}^{P} a_k^2 (x_k - x_{k-1})^2.
\]

**APPENDIX B: USE OF (\tilde{\xi}, \Delta \tilde{\xi}) VARIABLES IN FREE ENERGY CALCULATIONS**

As mentioned in the main text, it is computationally more advantageous to employ the (\( \tilde{\xi}, \Delta \tilde{\xi} \)) variables in the quantum free energy calculations. This is mainly because a rectangular domain defined in terms of the original \((\xi_a, \xi_b)\) variables includes a region with significantly high free energy (or extremely low probability density), which degrades the rate of statistical convergence. In the present work we circumvented this problem by using the following two-step procedure to obtain the ratio \( C_{dd}(0; \tilde{\xi}, \Delta \tilde{\xi}) / C_{dd}(0; \tilde{\xi}, \Delta \xi) \). In the first step we set up a narrow rectangular domain such as \(-0.1 < \tilde{\xi} < 1.1 \) and \(-0.1 < \Delta \tilde{\xi} < 0.1 \). A histogram analysis on that narrow domain provides a one-dimensional free energy curve along the \( \tilde{\xi} \) axis, and as a result the ratio of \( C_{dd}(0; \tilde{\xi}, \Delta \tilde{\xi}) \) between \((\tilde{\xi}, \Delta \tilde{\xi}) = (1, 0)\) and \((0, 0)\). Here it is worth noting that the width of the domain in the \( \Delta \tilde{\xi} \) direction should not be too small because it would suppress the diffusion of the path variables along the \( \tilde{\xi} \) axis, thus deteriorating the statistical convergence. In the second step we set up a local rectangular domain around the top of the barrier (for example, \( 0.9 < \tilde{\xi} < 1.1 \) and \(-0.5 < \Delta \tilde{\xi} < 0.5 \)), identify the saddle point \((\tilde{\xi}, \Delta \tilde{\xi})\), and compute the ratio of \( C_{dd}(0; \tilde{\xi}, \Delta \tilde{\xi}) \) between \((\tilde{\xi}, \Delta \tilde{\xi}) = (\tilde{\xi}, \Delta \xi)\) and \((1, 0)\). We note in addition that the delta functions in Eq. (2.19) needs to be rewritten as

\[
\delta(\xi(x_0) - \xi_a) \delta(\xi(x_{P/2}) - \xi_b)
\]

\[
= \delta(\tilde{\xi}(x_0, x_{P/2}) - \tilde{\xi}) \delta(\Delta \xi(x_0, x_{P/2}) - \Delta \xi)
\]

with

\[
\tilde{\xi}(x_0, x_{P/2}) = (\xi(x_0) + \xi(x_{P/2}))/2
\]

\[
\Delta \xi(x_0, x_{P/2}) = \xi(x_{P/2}) - \xi(x_0)
\]

which can be shown by Fourier transforming the delta function and changing the relevant wave vectors into sum and difference variables.
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27. The factor \( |m|^{1/2} \psi_{\xi}(\mathbf{q}) | \) is included so that the \( \hat{\Delta} \) operator [and hence the quantum instanton rate] become invariant to (i) a scaling of the reaction coordinate such as \( \xi_{\lambda}(\mathbf{q}) \sim \lambda \xi_{\lambda}(\mathbf{q}) \) and (ii) an orthogonal transformation among mass-weighted coordinate systems (e.g., that between Cartesian and Jacobi coordinates).
33. M. E. Tuckerman and A. Hughes, Chap. 14 in Ref. 29.
37. In Sec. II we suppose an isomerization reaction so that the integral of \( C_{\alpha \beta}(0; \xi_{\alpha}, \xi_{\beta}) \) over \( \xi_{\alpha}, \xi_{\beta} \) becomes finite; see Sec. III for the treatment of scattering systems.
41. Adaptive umbrella sampling is an example of the so-called extended-ensemble Monte Carlo methods. For an extensive review of the latter, see Y. Iba, Int. J. Mod. Phys. C 12, 623 (2001).
52. See, for example, Y. Zhao, T. Yamamoto, and W. H. Miller, J. Chem. Phys. 120, 3100 (2004).