Path-integral virial estimator for reaction rate calculation based on the quantum instanton approximation

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Abstract

The quantum instanton approximation is a type of quantum transition state theory that calculates the chemical reaction rate using the reactive flux correlation function and its low order derivatives at time zero. Here we present several path-integral estimators for the latter quantities, which characterize the initial decay profile of the flux correlation function. As with the internal energy or heat capacity calculation, different estimators yield different variances (and therefore different convergence properties) in a Monte Carlo calculation. Here we obtain a virial(-type) estimator by using a coordinate scaling procedure rather than integration by parts, which allows more computational benefits. We also consider two different methods for treating the flux operator, i.e., local-path and global-path approaches, in which the latter achieves a smaller variance at the cost of using second-order potential derivatives. Numerical tests are performed for a one-dimensional Eckart barrier and a model proton transfer reaction in a polar solvent, which illustrates the reduced variance of the virial estimator over the corresponding thermodynamic estimator.

I. INTRODUCTION

Developing an accurate and practical method for computing chemical reaction rates is one of the fundamental subjects of theoretical chemistry. In this regard the most successful approach is probably classical transition state theory (TST),[1–3] which has been applied widely to numerous reactions including biological systems such as enzyme catalysis.[4] The robustness of TST comes from its simplicity, i.e., the rate is determined solely from the free energy difference between the reactant and the activated complex. TST relies on the assumption of no "recrossing" trajectories through the dividing surface, which is usually valid at not too high temperature and for large dimensional systems. While successful in many cases, TST has the inherent deficiency that it accounts for no quantum effects, which needs to be addressed in order to treat low-temperature or light-atom transfer reactions. A conventional remedy to this problem is to add quantum corrections in a posteriori manner, e.g., by multiplying a tunneling factor that is computed along a prescribed tunneling path.[5] Another strategy is to try to develop a quantum TST (QTST) by starting from the rigorous quantum rate expression and make some approximations for neglecting recrossing effects. Several such theories exist,[6–15] though there is in principle no unique formulation (in contrast to the classical case).

The quantum instanton (QI) approximation[16–24] is a recently developed theory for chemical reaction rates that is among the category of QTST. While the original derivation was based on the semiclassical "instanton" (periodic orbit in imaginary time) model,[16] the working rate expression can be understood roughly as the second-order cumulant (or Gaussian) approximation to the flux-flux correlation function,

$$C_{\rm ff}(t) = C_{\rm ff}(0) + \frac{1}{2}\ddot{C}_{\rm ff}(0)t^2 + \cdots \simeq C_{\rm ff}(0)\exp\left[\frac{1}{2}\frac{\ddot{C}_{\rm ff}(0)}{C_{\rm ff}(0)}t^2\right], \tag{1}$$

for which the rate constant is given by

$$k(T) = \frac{1}{Q_r}\int_0^\infty dt C_{\rm ff}(t) \simeq \frac{C_{\rm ff}(0)}{Q_r}\sqrt{\frac{\pi}{2}}\frac{1}{\sqrt{-\ddot{C}_{\rm ff}(0)/C_{\rm ff}(0)}} \tag{2}$$

(see Sec. II for details). This approximation can be viewed as a quantum analog of the (classical) TST assumption in the sense that all possible oscillations in $C_{\rm ff}(t)$ at later times (quantum re-crossing flux) are neglected. Test calculations show that this QI approximation gives a rate accurate to within ∼10 % of the exact rate when the reaction is "direct", and

also to within a factor of 2 even for cases in which significant recrossing is expected (e.g., the collinear Cl+HCl reaction).[19] The computational merit of Eq. (2) is that it is expressed wholly in terms of the Boltzmann operator, and thus it can be evaluated rigorously even for complex molecular systems using imaginary-time path integrals. A previous paper has presented such a scheme,[17] in which the factor $C_{\rm ff}(0)/Q_r$ in Eq. (2) is evaluated as the barrier height of a particular free energy surface, while the remaining factor is calculated as the statistical average of some estimating function over the transition-state path ensemble. This computational scheme has been applied successfully to several benchmark systems including gas-phase reactions such as $CH_4 + H \rightarrow CH_3 + H_2$,[18] a model proton transfer reaction in a polar solvent,[22] and an isomerization reaction of pentadiene.[24]

The purpose of this paper is to present an improved path-integral estimator for computing the QI rate. In particular, we focus on the factor $\ddot{C}_{\rm ff}(0)/C_{\rm ff}(0)$ in Eq. (2) which characterizes the initial decay profile of $C_{\rm ff}(t)$. This quantity involves several different estimators because of the presence of the second time derivative. The estimator used in previous work was of "thermodynamic" type,[17] and its variance thus grows rapidly as a function of the number of path variables employed in the path integration. As with the internal energy or heat-capacity calculation,[25–33] it should be possible to transform the thermodynamic estimator into a virial form in order to reduce the statistical error. In this paper we present such a scheme based on a coordinate scaling procedure, rather than integration by parts, which is based on the recent study by Predescu *et al.*[32,34] and possesses the following computational benefits: (i) the transformation to a virial estimator is quite straightforward in contrast to integration by parts; (ii) one can use a finite-difference technique in order to avoid explicit calculation of potential derivatives in the virial estimator; and (iii) higher-order time derivatives of $C_{\rm ff}(t)$ such as $C_{\rm ff}^{(4)}(0)$, $C_{\rm ff}^{(6)}(0)$, ..., can also be generated with little modifications to the code, which can be used as input for more flexible approximations[21] to the true $C_{\rm ff}(t)$ than Eq. (1).

The remainder of this paper is as follows: In Sec. II we summarize the working expression of the QI theory. In Sec. III we first consider an "off-diagonal" average energy and derive its thermodynamic and virial estimators to describe the basic idea of coordinate scaling. In Secs. IV and V we apply the scaling procedure to quantum time correlation functions in order to obtain a virial estimator for the reaction rate. In Sec. VI we calculate the variance of the virial estimator for a one-dimensional Eckart barrier and a model proton transfer reaction in a polar solvent. Sec. VII concludes.

II. THE QUANTUM INSTANTON APPROXIMATION FOR CHEMICAL REACTION RATES

The QI theory approximates the reaction rate as follows (see Ref. 16 for the derivation motivated by semiclassical considerations):

$$k(T) \simeq \frac{C_{\rm ff}(0)}{Q_r}\frac{\sqrt{\pi}}{2}\frac{\hbar}{\Delta H}, \tag{3}$$

where $C_{\rm ff}(0)$ is the zero time value of the flux-flux correlation function,[35]

$$C_{\rm ff}(t) = {\rm tr}\left[e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}e^{i\hat{H}t/\hbar}\hat{F}e^{-i\hat{H}t/\hbar}\right] \tag{4}$$

with $\hat{F}$ being the flux operator,

$$\hat{F} = \frac{i}{\hbar}[\hat{H}, h(\hat{x}-x^\ddagger)] = \frac{1}{2m}[\hat{p}\delta(\hat{x}-x^\ddagger)+\delta(\hat{x}-x^\ddagger)\hat{p}], \tag{5}$$

and ΔH represents a specific type of energy variance (i.e., $\Delta H^2 = \langle\hat{H}^2\rangle - \langle\hat{H}\rangle^2$),

$$\Delta H^2 = \frac{\langle x^\ddagger|\hat{H}^2 e^{-\beta\hat{H}/2}|x^\ddagger\rangle}{\langle x^\ddagger|e^{-\beta\hat{H}/2}|x^\ddagger\rangle} - \left[\frac{\langle x^\ddagger|\hat{H}e^{-\beta\hat{H}/2}|x^\ddagger\rangle}{\langle x^\ddagger|e^{-\beta\hat{H}/2}|x^\ddagger\rangle}\right]^2. \tag{6}$$

In this paper we consider a one-dimensional system with the Hamiltonian $H = p^2/2m+V(x)$ for notational simplicity. In Eq. (5), $x^\ddagger$ is the location of the dividing surface that separates the reactant and product regions. ΔH in Eq. (6) can be written more compactly as

$$\Delta H^2 = -\frac{\hbar^2}{2}\frac{\ddot{C}_{\rm dd}(0)}{C_{\rm dd}(0)}, \tag{7}$$

where $C_{\rm dd}(t)$ is a "delta-delta" correlation function defined by

$$C_{\rm dd}(t) = {\rm tr}\left[e^{-\beta\hat{H}/2}\delta(\hat{x}-x^\ddagger)e^{-\beta\hat{H}/2}e^{i\hat{H}t/\hbar}\delta(\hat{x}-x^\ddagger)e^{-i\hat{H}t/\hbar}\right]. \tag{8}$$

Substituting Eq. (7) into Eq. (3) gives

$$k(T) \simeq \frac{C_{\rm ff}(0)}{Q_r}\sqrt{\frac{\pi}{2}}\frac{1}{\sqrt{-\ddot{C}_{\rm dd}(0)/C_{\rm dd}(0)}}, \tag{9}$$

which has a formal resemblance to the Gaussian approximation to $C_{\rm ff}(t)$ in Eq. (1). An extended version of the QI theory has also been proposed, which makes a log-augmented cumulant expansion of $C_{\rm ff}(t)$ as follows,[21]

$$C_{\rm ff}(t) \simeq C_{\rm ff}(0)\exp\left\{b_0\ln\left[1+\left(\frac{2t}{\hbar\beta}\right)^2\right] + b_1t^2 + \cdots b_Nt^{2N}\right\}, \tag{10}$$

where coefficients $\{b_k\}$ are determined by a matching procedure with the direct Taylor series expansion of $C_{\rm ff}(t)$. We note that the above approximation still falls among QTST because $C_{\rm ff}(t)$ in Eq. (10) is always positive and thus does not describe any recrossing effects (see Ref. 21 for how this extension improves upon the QI rate).

III. PATH-INTEGRAL ESTIMATORS FOR OFF-DIAGONAL AVERAGE ENERGY

Before proceeding, it is useful first to present the coordinate scaling idea in its simplest form by considering an "off-diagonal" average energy defined by

$$E_{ba}(\beta) = \frac{\langle x_b|\hat{H}e^{-\beta\hat{H}}|x_a\rangle}{\langle x_b|e^{-\beta\hat{H}}|x_a\rangle} = -\frac{\partial}{\partial\beta}\ln\rho_{ba}(\beta), \tag{11}$$

where $\rho_{ba}(\beta) = \langle x_b|e^{-\beta\hat{H}}|x_a\rangle$, since this quantity serves as the basis for treating a time correlation function. Using the primitive approximation to the Boltzmann operator,

$$e^{-\beta\hat{H}} \simeq \left(e^{-\epsilon\hat{V}/2}e^{-\epsilon\hat{T}}e^{-\epsilon\hat{V}/2}\right)^N \tag{12}$$

with $\epsilon = \beta/N$, a discretized path integral for ρ_{ba} is obtained as

$$\rho_{ba}(\beta) = \int dx_1 \cdots \int dx_{N-1} W_{ba}(x_1, \ldots, x_{N-1}; \beta), \tag{13}$$

where

$$W_{ba}(x_1, \ldots, x_{N-1}; \beta) = \left(\frac{mN}{2\pi\hbar^2\beta}\right)^{N/2} \exp\left[-\frac{mN}{2\hbar^2\beta}\sum_{k=1}^{N}(x_k - x_{k-1})^2 - \frac{\beta}{N}\sum_{k=0}^{N} w_k V(x_k)\right] \tag{14}$$

with $x_0 = x_a$, $x_N = x_b$, and $w_k = 1/2$ for $k = 0, N$ and $w_k = 1$ otherwise. Differentiating Eq. (13) with respect to β gives a thermodynamic estimator for the energy,

$$E_{ba}(\beta) = \langle \epsilon_T \rangle_{ba} \tag{15}$$

with

$$\epsilon_T = \frac{N}{2\beta} - \frac{mN}{2\hbar^2\beta^2}\sum_{k=1}^{N}(x_k - x_{k-1})^2 + \frac{1}{N}\sum_{k=0}^{N} w_k V(x_k), \tag{16}$$

where $\langle \cdots \rangle_{ba}$ denotes an ensemble average over the weight function $W_{ba}(x_1, \ldots, x_{N-1}; \beta)$. This estimator has the well-known drawback that the statistical error grows with N due

to cancellation of the first two terms in the right-hand side of Eq. (16). As in the case of the internal energy or heat capacity, one can transform the above estimator into a virial form through integration by parts. Here instead we employ a coordinate scaling procedure that we find more useful.[32–34] To this end we first write the density matrix at a different temperature β',

$$\rho_{ba}(\beta') = \int dx'_1 \cdots \int dx'_{N-1} W_{ba}(x'_1, \ldots, x'_{N-1}; \beta'), \tag{17}$$

and then transform the integration variables $\{x'_k\}$ into a set of new variables $\{x_k\}$ according to

$$x'_k = x^*_k + \sqrt{\frac{\beta'}{\beta}}(x_k - x^*_k), \tag{18}$$

where x^*_k is the reference point given by

$$x^*_k = x_a + (x_b - x_a)\frac{k}{N}. \tag{19}$$

Using the following identity (or with the method described in Appendix),

$$\frac{1}{\beta'}\sum_{k=1}^{N}(x'_k - x'_{k-1})^2 = \frac{1}{\beta}\sum_{k=1}^{N}(x_k - x_{k-1})^2 + \left(\frac{1}{\beta'} - \frac{1}{\beta}\right)\frac{(x_b - x_a)^2}{N}, \tag{20}$$

one can rewrite Eq. (17) as

$$\rho_{ba}(\beta') = \int dx_1 \cdots \int dx_{N-1} W_{ba}(x_1, \ldots, x_{N-1}; \beta) R_{ba}(\beta'), \tag{21}$$

where

$$R_{ba}(\beta') = \frac{\langle x_b | e^{-\beta'\hat{T}} | x_a \rangle}{\langle x_b | e^{-\beta\hat{T}} | x_a \rangle} \exp\left\{-\frac{1}{N}\sum_{k=0}^{N} w_k \left[V(x'_k) - V(x_k)\right]\right\}. \tag{22}$$

Note that all the β' dependence is now embedded in the R_{ba} factor. Differentiating Eq. (21) with respect to β' and taking the limit $\beta' \to \beta$ gives a virial estimator

$$E_{ba}(\beta) = \langle \epsilon_V \rangle_{ba} = \left\langle \left.\frac{\partial R_{ba}(\beta')}{\partial \beta'}\right|_{\beta'=\beta} \right\rangle_{ba} \tag{23}$$

with

$$\epsilon_V = \frac{1}{2\beta} - \frac{m}{2\hbar^2\beta^2}(x_b - x_a)^2 + \frac{1}{N}\sum_{k=0}^{N} w_k \left[\frac{1}{2}(x_k - x^*_k)V'(x_k) + V(x_k)\right]. \tag{24}$$

Alternatively, one may evaluate the virial estimator via finite difference as[32]

$$\epsilon_V \simeq \frac{R_{ba}(\beta + \delta\beta) - R_{ba}(\beta - \delta\beta)}{2\delta\beta}, \tag{25}$$

in order to avoid explicit calculation of the potential derivatives.

IV. VIRIAL ESTIMATOR FOR THE TIME DERIVATIVE OF CORRELATION FUNCTIONS

With the scaling procedure above it is now straightforward to derive a virial estimator for the time derivative of correlation functions such as $\ddot{C}_{\rm ff}(0)$ and $\ddot{C}_{\rm dd}(0)$. We start with the following correlation function,

$$C(t) = \mathrm{tr}\left[e^{-\beta\hat{H}/2}A(\hat{x})e^{-\beta\hat{H}/2}e^{i\hat{H}t/\hbar}B(\hat{x})e^{-i\hat{H}t/\hbar}\right], \tag{26}$$

where $\hat{A}$ and $\hat{B}$ are arbitrary position-dependent operators [note that $C(t)$ becomes the delta-delta correlation function in Eq. (8) if we set $A(x) = B(x) = \delta(x - x^{\ddagger})$]. For simplicity we work with the imaginary-time counterpart,

$$\bar{C}(\lambda) \equiv C(-i\hbar\lambda) = \mathrm{tr}\left[e^{-(\beta/2+\lambda)\hat{H}}A(\hat{x})e^{-(\beta/2-\lambda)\hat{H}}B(\hat{x})\right], \tag{27}$$

with which the time derivative is given by $(d/dt)^n C(0) = (i/\hbar)^n (d/d\lambda)^n \bar{C}(0)$. Discretizing the Boltzmann operators $\exp[-(\beta/2 \pm \lambda)\hat{H}]$ with $P/2$ time slices gives

$$\bar{C}(\lambda) = \int dx_1 \cdots \int dx_P A(x_0)B(x_{P/2})W(x_1, \ldots, x_P; \lambda), \tag{28}$$

where

$$W(x_1, \ldots, x_P; \lambda) = \left[\frac{mP}{2\pi\hbar^2(\beta + 2\lambda)}\right]^{P/4}\left[\frac{mP}{2\pi\hbar^2(\beta - 2\lambda)}\right]^{P/4}\exp(-S) \tag{29}$$

and

$$\begin{aligned} S \;=\; & \frac{mP}{2\hbar^2(\beta+2\lambda)}\sum_{k=1}^{P/2}(x_k - x_{k-1})^2 + \frac{1}{P}\sum_{k=0}^{P/2}\tilde{w}_k(\beta+2\lambda)V(x_k) \\ & + \frac{mP}{2\hbar^2(\beta-2\lambda)}\sum_{k=P/2+1}^{P}(x_k - x_{k-1})^2 + \frac{1}{P}\sum_{k=P/2}^{P}\tilde{w}_k(\beta-2\lambda)V(x_k) \end{aligned} \tag{30}$$

with $x_0 = x_P$ and $\tilde{w}_k = 1/2$ for $k = 0, P/2, P$ and $\tilde{w}_k = 1$ otherwise. Differentiating $\bar{C}(\lambda)$ in Eq. (28) with respect to λ and taking the $\lambda \to 0$ limit gives a thermodynamic estimator for $\ddot{C}(0)$ (note that the first derivative vanishes by symmetry):

$$\frac{\ddot{C}(0)}{C(0)} = -\frac{1}{\hbar^2}\left\langle F_T^2 + G_T\right\rangle, \tag{31}$$

where

$$F_T = \frac{mP}{\hbar^2\beta^2}\left(\sum_{k=1}^{P/2} - \sum_{k=P/2+1}^{P}\right)(x_k - x_{k-1})^2 - \frac{2}{P}\left(\sum_{k=1}^{P/2-1} - \sum_{k=P/2+1}^{P-1}\right)V(x_k) \tag{32}$$

and

$$G_T = \frac{2P}{\beta^2} - \frac{4mP}{\hbar^2\beta^3}\sum_{k=1}^{P}(x_k - x_{k-1})^2 \tag{33}$$

with $\langle\cdots\rangle$ denoting an ensemble average over the weight function $A(x_0)B(x_{P/2})W(x_1,\ldots,x_P;0)$. This is the estimator that has been employed in previous work.[17,18,22,23] To transform it into virial form, we write $\bar{C}(\lambda)$ in terms of temporary variables $\{x'_k\}$,

$$\bar{C}(\lambda) = \int dx'_1 \cdots \int dx'_P A(x'_0)B(x'_{P/2})W(x'_1,\ldots,x'_P;\lambda), \tag{34}$$

and introduce a set of new variables $\{x_k\}$ as follows:

$$x'_k = \begin{cases} x^*_k + \sqrt{\frac{\beta+2\lambda}{\beta}}(x_k - x^*_k) & (0 < k < P/2) \\ x^*_k + \sqrt{\frac{\beta-2\lambda}{\beta}}(x_k - x^*_k) & (P/2 < k < P) \\ x_k & (k = 0, P/2, P) \end{cases} \tag{35}$$

with

$$x^*_k = x^*_{P-k} = x_0 + (x_{P/2} - x_0)\frac{k}{P/2} \quad (0 \le k \le P/2). \tag{36}$$

The expression for $\bar{C}(\lambda)$ then becomes

$$\bar{C}(\lambda) = \int dx_1 \cdots \int dx_P A(x_0)B(x_{P/2})W(x_1,\ldots,x_P;0)R(\lambda), \tag{37}$$

where $R(\lambda) = R_{\rm kin}R_{\rm pot}$ with

$$R_{\rm kin} = \frac{\langle x_P|e^{-(\beta/2-\lambda)\hat{T}}|x_{P/2}\rangle\langle x_{P/2}|e^{-(\beta/2+\lambda)\hat{T}}|x_0\rangle}{\langle x_P|e^{-\beta\hat{T}/2}|x_{P/2}\rangle\langle x_{P/2}|e^{-\beta\hat{T}/2}|x_0\rangle} \tag{38}$$

and

$$R_{\rm pot} = \exp\left\{-\frac{1}{P}\sum_{k=0}^{P/2}\tilde{w}_k\left[(\beta+2\lambda)V(x'_k) - \beta V(x_k)\right]\right. \tag{39}$$

$$\left. -\frac{1}{P}\sum_{k=P/2}^{P}\tilde{w}_k\left[(\beta-2\lambda)V(x'_k) - \beta V(x_k)\right]\right\}. \tag{40}$$

Differentiating this expression for $\bar{C}(\lambda)$ with respect to λ gives the desired virial estimator,

$$\frac{\ddot{C}(0)}{C(0)} = -\frac{1}{\hbar^2}\left\langle F_V^2 + G_V\right\rangle \tag{41}$$

with

$$F_V = -\frac{2}{P}\left(\sum_{k=1}^{P/2-1} - \sum_{k=P/2+1}^{P-1}\right)\left[\frac{1}{2}(x_k - x_k^*)V'(x_k) + V(x_k)\right] \tag{42}$$

and

$$G_V = \frac{4}{\beta^2} - \frac{16m}{\hbar^2\beta^3}(x_0 - x_{P/2})^2 - \frac{1}{\beta P}\sum_{k=1}^{P}\left[3(x_k - x_k^*)V'(x_k) + (x_k - x_k^*)^2 V''(x_k)\right]. \tag{43}$$

In practice we can avoid the calculation of first- and second-order potential derivatives by numerically differentiating $R(\lambda)$ as

$$\frac{\ddot{C}(0)}{C(0)} \simeq -\frac{1}{\hbar^2}\left\langle \frac{R(\delta\lambda) + R(-\delta\lambda) - 2R(0)}{(\delta\lambda)^2}\right\rangle. \tag{44}$$

V. TREATMENT OF THE FLUX OPERATOR

A. Local-path approach

Applying the above scheme to the flux-flux correlation function is somewhat tricky because of the nonlocal character of the flux operator (i.e., a derivative operator). Different estimators arise depending on the route of the derivation, which in general exhibit different magnitudes of the variance. In previous work[17,18,22,23] we have employed a "local-path" estimator, in which the flux operator was evaluated in terms of a few path variables near the dividing surface. This local estimator can be combined with the coordinate scaling procedure as follows. First we construct a discretized path integral for $\bar{C}_{\rm ff}(\lambda) = C_{\rm ff}(-i\hbar\lambda)$ as in Sec. IV, in which the following matrix element appears:

$$K_{\rm fi} = \langle x_1'|e^{-(\beta+2\lambda)\hat{H}/P}\hat{F}e^{-(\beta-2\lambda)\hat{H}/P}|x_{-1}'\rangle, \tag{45}$$

where $\{x_k'\}$ are temporary variables to be scaled later. Making the primitive approximation to $e^{-(\beta\pm 2\lambda)\hat{H}/P}$ and evaluating the flux operator analytically via Eq. (5) gives

$$K_{\rm fi} \simeq \int dx_0'\delta(x_0' - x^\ddagger)v_0(\lambda)\langle x_1'|e^{-(\beta+2\lambda)\hat{H}/P}|x_0'\rangle\langle x_0'|e^{-(\beta-2\lambda)\hat{H}/P}|x_{-1}'\rangle, \tag{46}$$

where the velocity factor $v_0(\lambda)$ is defined by

$$v_k(\lambda) = \frac{iP}{2\hbar}\left(\frac{x_{k+1}' - x_k'}{\beta + 2\lambda} + \frac{x_k' - x_{k-1}'}{\beta - 2\lambda}\right) - \frac{i\hbar\lambda}{mP}V'(x_k') \tag{47}$$

with $k = 0$. The effect of the flux operator is thus expressed in terms of only three path variables. Treating another flux operator in $\bar{C}_{\rm ff}(\lambda)$ with the same method and performing the coordinate scaling precisely as in the preceding section gives

$$\bar{C}_{\rm ff}(\lambda) = \int dx_1 \cdots \int dx_P W(x_1, \ldots, x_P; 0)\delta(x_0 - x^\ddagger)\delta(x_{P/2} - x^\ddagger)\tilde{R}(\lambda) \tag{48}$$

with

$$\tilde{R}(\lambda) = v_0(\lambda)v_{P/2}(-\lambda)R(\lambda), \tag{49}$$

where $W(x_1, \ldots, x_P; 0)$ and $R(\lambda)$ has the same definition as in Sec. IV. Thus, the time derivative of $C_{\rm ff}(t)$ can be obtained as

$$\frac{\ddot{C}_{\rm ff}(0)}{C_{\rm dd}(0)} \simeq -\frac{1}{\hbar^2}\left\langle \frac{\tilde{R}(\delta\lambda) + \tilde{R}(-\delta\lambda) - 2\tilde{R}(0)}{(\delta\lambda)^2} \right\rangle. \tag{50}$$

Similarly, virial estimators for higher time derivatives, $d^n C_{\rm ff}(0)/dt^n (n = 4, 6, \ldots)$, can be generated using an appropriate finite-difference formula of higher order.[34]

B. Global-path approach

One can also devise an alternate "global-path" estimator by first performing the coordinate scaling and then applying the flux operator (i.e., in an opposite order to the preceding section). To be specific, we insert the coordinate representation of the flux operator,

$$\hat{F} = \frac{\hbar}{2mi}\int dx \left[-|x\acute{\rangle}\langle x| + |x\rangle\grave{\langle} x|\right] \tag{51}$$

with $|x\acute{\rangle} = \partial|x\rangle/\partial x$ into the imaginary-time flux correlation function as

$$\begin{aligned}\bar{C}_{\rm ff}(\lambda) \;=\; & \left(\frac{\hbar}{2m}\right)^2 \int dx_a \int dx_b \delta(x_a - x^\ddagger)\delta(x_b - x^\ddagger) \\ & \times \Big\{ \grave{\langle} x_a|e^{-(\beta/2-\lambda)\hat{H}}|x_b\acute{\rangle}\langle x_b|e^{-(\beta/2+\lambda)\hat{H}}|x_a\rangle \\ & + \langle x_a|e^{-(\beta/2-\lambda)\hat{H}}|x_b\rangle\grave{\langle} x_b|e^{-(\beta/2+\lambda)\hat{H}}|x_a\acute{\rangle} \\ & - \grave{\langle} x_a|e^{-(\beta/2-\lambda)\hat{H}}|x_b\rangle\grave{\langle} x_b|e^{-(\beta/2+\lambda)\hat{H}}|x_a\rangle \\ & - \langle x_a|e^{-(\beta/2-\lambda)\hat{H}}|x_b\acute{\rangle}\langle x_b|e^{-(\beta/2+\lambda)\hat{H}}|x_a\acute{\rangle} \Big\},\end{aligned} \tag{52}$$

which can be written more compactly as

$$\begin{aligned}\bar{C}_{\rm ff}(\lambda) \;=\; & \int dx_a \int dx_b \delta(x_a - x^\ddagger)\delta(x_b - x^\ddagger) \\ & \times \mathcal{F}^2 \langle x_a^-|e^{-(\beta/2-\lambda)\hat{H}}|x_b^-\rangle\langle x_b^+|e^{-(\beta/2+\lambda)\hat{H}}|x_a^+\rangle,\end{aligned} \tag{53}$$

where an operator representing the "square" of the flux operator is given by

$$\mathcal{F}^2 = \left(\frac{\hbar}{2m}\right)^2 \lim_{x_a^\pm \to x_a} \lim_{x_b^\pm \to x_b} \left\{ \frac{\partial^2}{\partial x_a^+ \partial x_b^+} + \frac{\partial^2}{\partial x_a^- \partial x_b^-} - \frac{\partial^2}{\partial x_a^+ \partial x_b^-} - \frac{\partial^2}{\partial x_a^- \partial x_b^+} \right\}. \tag{54}$$

Next we use a generalized scaling relation of the form (see Appendix):

$$\langle x_b' | e^{-\beta' \hat{H}} | x_a' \rangle = \int dx_1 \cdots \int dx_{N-1} W_{ba}(x_1, \ldots, x_{N-1}; \beta) R_{ba}^{\#}(\beta'), \tag{55}$$

where

$$R_{ba}^{\#}(\beta') = \frac{\langle x_b' | e^{-\beta' \hat{T}} | x_a' \rangle}{\langle x_b | e^{-\beta \hat{T}} | x_a \rangle} \exp\left\{ -\frac{1}{N} \sum_{k=0}^{N} w_k \left[\beta' V(x_k') - \beta V(x_k) \right] \right\}, \tag{56}$$

and

$$x_k' = \bar{x}_k' + \sqrt{\frac{\beta'}{\beta}} (x_k - x_k^*), \tag{57}$$

$$\bar{x}_k' = x_a' + (x_b' - x_a') \frac{k}{N}. \tag{58}$$

Other quantities such as W_{ba} and x_k^* are defined the same as in Sec. III. We note that the end-points (x_a', x_b') are included in the coordinate transformation in addition to β'. Applying the above relation to the density matrix elements in Eq. (53) with $N = P/2$ and appropriate choice of end-points gives

$$\bar{C}_{\rm ff}(\lambda) = \int dx_1 \cdots \int dx_P \delta(x_0 - x^\ddagger) \delta(x_{P/2} - x^\ddagger) W(x_1, \ldots, x_P; 0) \mathcal{F}^2 R^{\#}(x_a^\pm, x_b^\pm, \lambda), \tag{59}$$

where $R^{\#}(x_a^\pm, x_b^\pm, \lambda) = R_{\rm kin}^{\#} R_{\rm pot}^{\#}$ with

$$R_{\rm kin}^{\#} = \frac{\langle x_a^- | e^{-(\beta/2-\lambda)\hat{T}} | x_b^- \rangle \langle x_b^+ | e^{-(\beta/2+\lambda)\hat{T}} | x_a^+ \rangle}{\langle x_P | e^{-\beta \hat{T}/2} | x_{P/2} \rangle \langle x_{P/2} | e^{-\beta \hat{T}/2} | x_0 \rangle}, \tag{60}$$

$$\begin{aligned} R_{\rm pot}^{\#} = \exp\Bigg\{ & -\frac{1}{P} \sum_{k=0}^{P/2} \tilde{w}_k \left[(\beta + 2\lambda) V(x_k^{+'}) - \beta V(x_k) \right] \\ & -\frac{1}{P} \sum_{k=P/2}^{P} \tilde{w}_k \left[(\beta - 2\lambda) V(x_k^{-'}) - \beta V(x_k) \right] \Bigg\}, \end{aligned} \tag{61}$$

and

$$x_k^{\pm'} = \bar{x}_k^\pm + \sqrt{\frac{\beta \pm 2\lambda}{\beta}} (x_k - x_k^*), \tag{62a}$$

$$\bar{x}_k^+ = x_a^+ + (x_b^+ - x_a^+) \frac{k}{P/2}, \tag{62b}$$

$$\bar{x}_k^- = x_b^- + (x_a^- - x_b^-) \frac{k - P/2}{P/2}. \tag{62c}$$

The kth coordinate in Eq. (62) with plus and minus signs are defined for $0 \leq k \leq P/2$ and $P/2 \leq k \leq P$, respectively. The time derivative of $C_{\rm ff}(t)$ can be obtained by differentiating the factor $\mathcal{F}^2 R^{\#}(x_a^{\pm}, x_b^{\pm}, \lambda)$ with respect to λ, where the $\mathcal{F}^2$ operator is applied analytically using up to second-order potential derivatives.[34] The latter operation is costly but often not too demanding because $\mathcal{F}^2$ involves only the coordinates that define the (generalized) reaction coordinate, e.g., only a few Cartesian coordinates that describe the reacting atoms.

VI. NUMERICAL TESTS

We now apply the above estimators to a one-dimensional system with the Eckart potential barrier,

$$V(x) = V_0 \mathrm{sech}^2(x/a), \tag{63}$$

where $V_0 = 0.425$ eV, $a = 0.734$ au, and the mass is 1060 au, which corresponds roughly to the H+H_2 reaction. Table 1 lists the statistical error of $C_{\rm dd}^{(2)}/C_{\rm dd}$ and $C_{\rm ff}^{(n)}/C_{\rm dd}$ ($n = 2, 4, 6$) obtained with 1 million path samples (note that the time arguments are always $t = 0$ and are omitted hereafter). Three estimators are compared: the thermodynamic estimator, the local-path virial estimator in Sec. V A, and the global-path virial estimator in Sec. V B. The latter two differ only in the treatment of the flux operator. The number of path variables used was $P = 8$ for T =1000 K and P =40 for T =200 K, which have a discretization error of ∼2 % of the exact ($P \to \infty$) value. The dividing surface was always set at the top of the barrier with $x^{\ddagger} = 0$ in Eq. (5). The reader is referred to Refs. 21 and 34 on how these time derivatives can be used to improve the approximate rates.

We see from Table 1 that the virial estimators always exhibit a smaller statistical error than the thermodynamic estimator, as expected. Between the two virial estimators, the global-path version has a smaller variance than the local one by using more information on the entire path. The exceedingly small errors of the global-path estimator (< 0.1 %) at $T = 1000$ K are somewhat fortuitous, because at this temperature the system is close to the free-particle limit and the global-path estimator becomes exact for a free particle irrespective of the number of path variables.[36] This situation does not occur for the local-path virial estimator, where the velocity factor in Eq. (47) must be averaged even for a free particle to give the correct result. Another important fact is that the variance of the virial estimators is nearly independent of the order of time derivatives in contrast to the

thermodynamic estimator, which agrees qualitatively with the previous study by Predescu for the same system using a Fourier-like path integral.[34]

Figure 1 plots the statistical error of $C_{\rm ff}^{(2)}/C_{\rm dd}$ and $C_{\rm ff}^{(6)}/C_{\rm dd}$ at $T = 200$ K as a function of the number of path variables P. The variance of the thermodynamic estimator grows rapidly with P, and the growth rate is especially large for $C_{\rm ff}^{(6)}$. The local-path virial estimator also exhibits an increasing variance, which is caused by the appearance of P in the numerator of the velocity factor in Eq. (47). The global-path virial estimator, on the other hand, has a nearly constant variance regardless of the value of P, thus facilitating the systematic convergence to the $P \to \infty$ limit.

Next we apply the present method to a model proton transfer reaction[37] in a polar solvent, $\mathrm{A}H + B \to A^- + HB^+$, where A, H, and B represent a hydrogen-bonding complex dissolved in liquid methyl chloride at $T = 250$ K. The details of the model is given in Ref. 37. Here we quantize only the proton degree of freedom with $P = 40$ and use the path integral Monte Carlo (MC) scheme described in Ref. 22. Figure 2 shows the convergence of $\ddot{C}_{\rm dd}/C_{\rm dd}$, $C_{\rm ff}^{(n)}/C_{\rm dd}$ ($n = 2,4$) as a function of MC cycles. In all cases the virial estimators outperform the thermodynamic estimators in convergence rate. In particular, the convergence of $\ddot{C}_{\rm dd}$ is very rapid when using the virial estimator, which is beneficial in calculating the QI rate in Eq. (9). On the other hand, the statistical error becomes larger for $C_{\rm ff}^{(n)}/C_{\rm dd}$, and it was difficult to converge with 2 million path samples for $n \geq 6$. This is in contrast to the one-dimensional Eckart barrier studied above, where the variance of the virial estimator was nearly independent of the order of time derivatives. Apart from differences in the dimensionality of the system, the variance may be increased by stiff potential walls in the solute potential (defined with Morse-like functions),[37] because the virial estimator for $C_{\rm ff}^{(n)}$ depends implicitly on the higher-order potential derivatives. For example, the local-path and global-path virial estimators for $C_{\rm ff}^{(6)}$ depend on 7th- and 8th-order potential derivatives, although the numerical calculation by finite difference needs only the 1st- and 2nd-order derivatives of the potential. It is not clear at present to what extent this behavior is common for other potentials (including polynomial potentials). Nevertheless, the fast convergence of 2nd time derivatives even for the present stiff potential is very encouraging when considering future applications of the QI theory to more complex chemical reactions in condensed phases.

VII. CONCLUDING REMARKS

Our main purpose in this paper has been to show how a virial estimator for the time derivative of correlation functions can be obtained straightforwardly via a coordinate scaling procedure, and that the resulting estimator has an expected smaller variance than the thermodynamic estimator. We have also presented two methods for treating the flux operator, i.e., local-path and global-path approaches, in which the latter has a smaller variance. The second time derivative of $C_{\rm dd}(t)$ and $C_{\rm ff}(t)$ are clearly the most important quantities for the QI rate in Eq. (9) or in Eq. (2). An open problem is how to best utilize the higher-order derivatives in order to improve the accuracy of approximate rates. While some progress has been made in this direction,[21,34] more studies would be useful if we consider the availability of $C_{\rm ff}^{(n)}(0)$ at least for systems with well-behaved potentials.

Acknowledgments

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APPENDIX: USING THE FEYNMAN-KAC FORMULA

The scaled expression (21) can also be obtained as follows. Utilizing the integration variables $\{y_k\}$ defined by

$$x'_k = x^*_k + \sqrt{\frac{\hbar^2\beta'}{m}}y_k, \tag{A.1}$$

one can transform Eq. (17) as follows,

$$\rho_{ba}(\beta') = \langle x_b|e^{-\beta'\hat{T}}|x_a\rangle \mathbb{E}\exp\left\{-\frac{\beta'}{N}\sum_{k=0}^{N} w_k V(x'_k)\right\} \tag{A.2}$$

with

$$\mathbb{E}(\cdots) = \frac{\int dy_1 \cdots \int dy_{N-1} \exp\left\{-\frac{N}{2}\sum_{k=1}^{N}(y_k - y_{k-1})^2\right\}(\cdots)}{\int dy_1 \cdots \int dy_{N-1} \exp\left\{-\frac{N}{2}\sum_{k=1}^{N}(y_k - y_{k-1})^2\right\}}, \tag{A.3}$$

which becomes the Feynman-Kac formula in the $N \to \infty$ limit with $\{y_k\}$ representing the standard Brownian bridge. Rewriting the above equation as

$$\rho_{ba}(\beta') = \langle x_b|e^{-\beta\hat{T}}|x_a\rangle \mathbb{E} \exp\left\{-\frac{\beta}{N}\sum_{k=0}^{N} w_k V(x_k)\right\} R_{ba}(\beta'), \tag{A.4}$$

where $R_{ba}(\beta')$ is defined by Eq. (22) and

$$x_k = x_k^* + \sqrt{\frac{\hbar^2\beta}{m}} y_k, \tag{A.5}$$

and changing integration variables from $\{y_k\}$ to $\{x_k\}$ results in Eq. (21). Combining Eqs. (A.1) and (A.5) gives the coordinate transformation in Eq. (18). Similar procedures can be used to obtain a generalized expression in Eq. (55).

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FIG. 1: Relative statistical error (%) of the thermodynamic, local-path virial, and global-path virial estimators for (a) $C_{\mathrm{ff}}^{(2)}/C_{\mathrm{dd}}$ and (b) $C_{\mathrm{ff}}^{(6)}/C_{\mathrm{dd}}$ computed for the one-dimensional Eckart barrier at $T = 200$ K. P is the number of path variables.

FIG. 2: Statistical convergence of the thermodynamic, local-path virial, and global-path virial estimators for (a) $C_{\mathrm{dd}}^{(2)}/C_{\mathrm{dd}}$, (b) $C_{\mathrm{ff}}^{(2)}/C_{\mathrm{dd}}$, and (c) $C_{\mathrm{ff}}^{(4)}/C_{\mathrm{dd}}$ computed for a model proton transfer reaction in a polar solvent.

Fig. 1 (a)

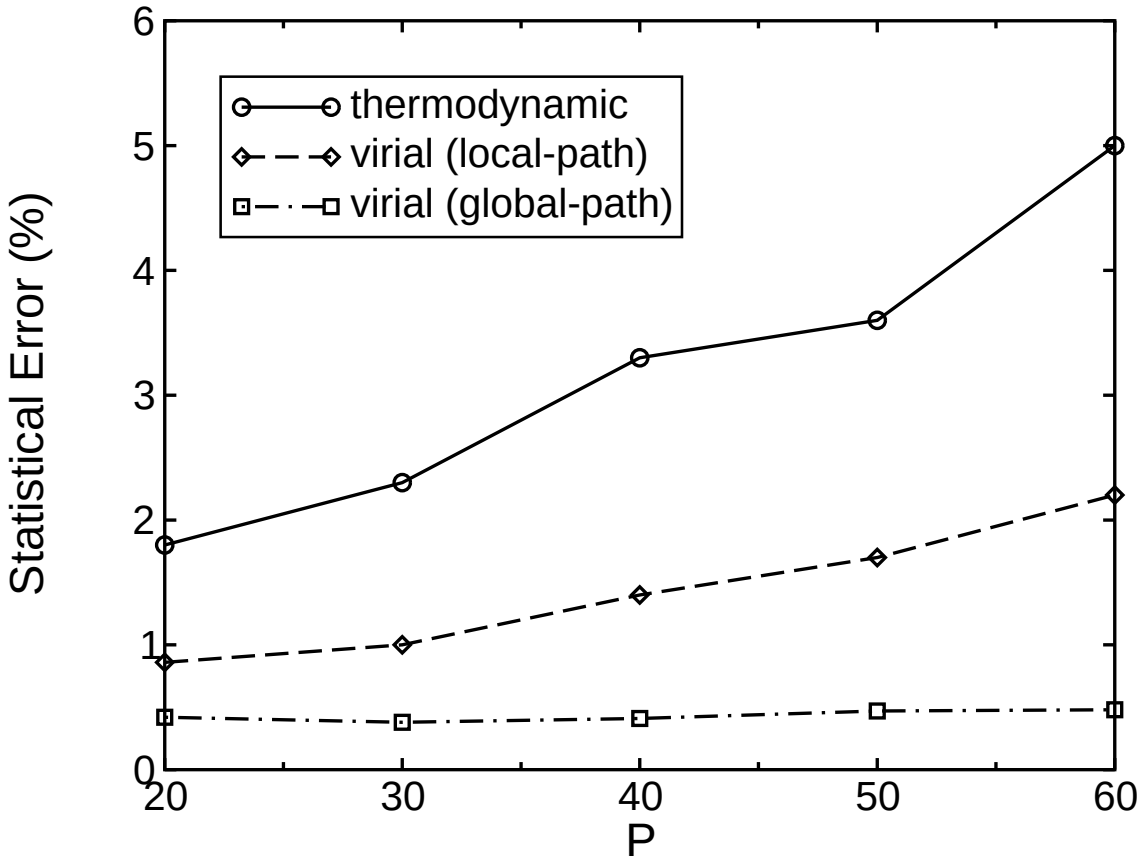
thermodynamic
virial (local-path)
virial (global-path)
Statistical Error (%)
P
0
1
2
3
4
5
6
20
30
40
50
60

Fig. 1 (b)

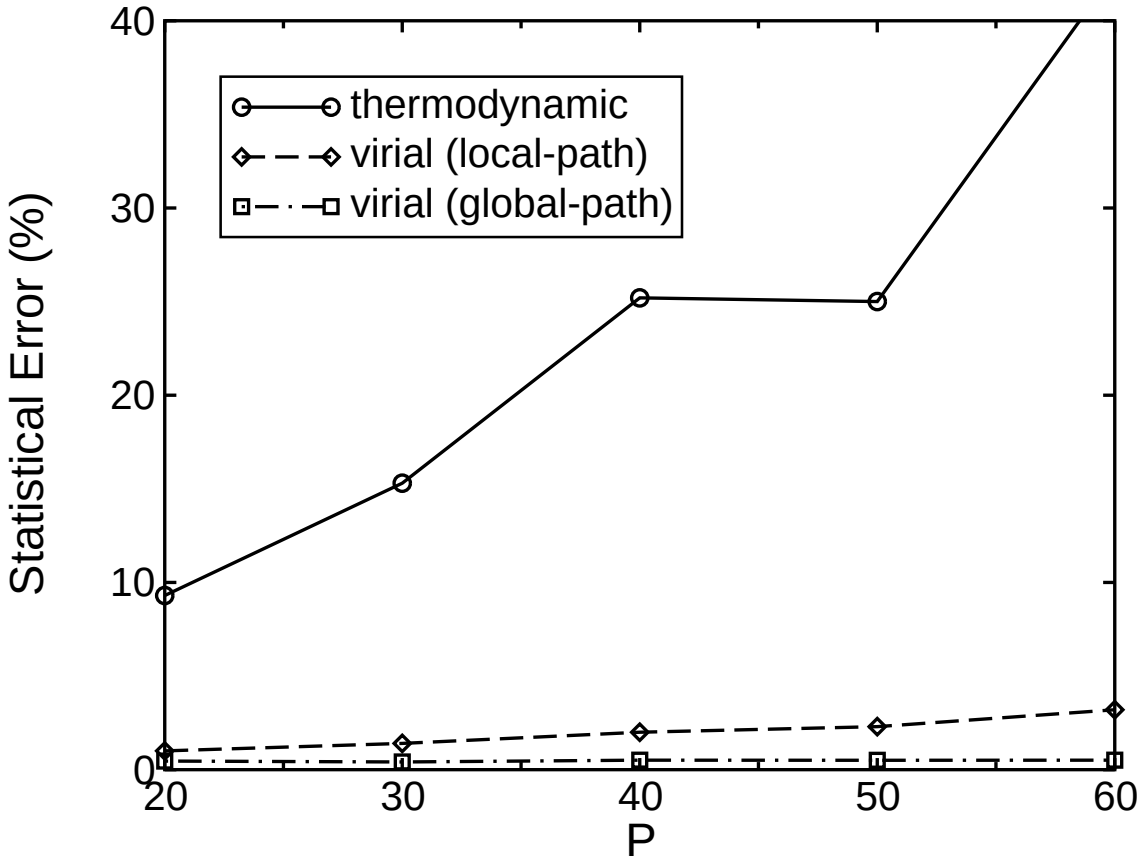
40
30
20
10
0
20
30
40
50
60
P
Statistical Error (%)
thermodynamic
virial (local-path)
virial (global-path)

Fig. 2 (a)

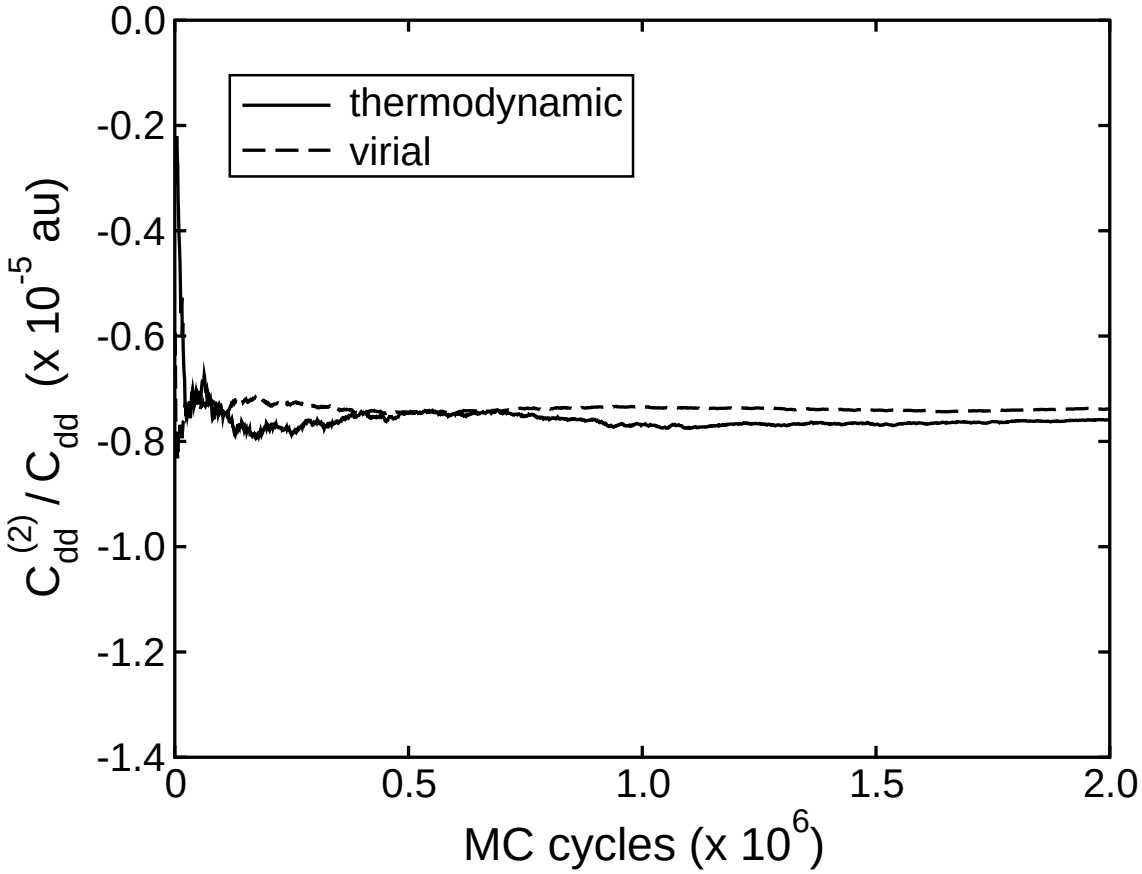
thermodynamic
virial
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
0
0.5
1.0
1.5
2.0
$C_{dd}^{(2)} / C_{dd}$ (x 10^{-5} au)
MC cycles (x 10^{6})

Fig. 2 (b)

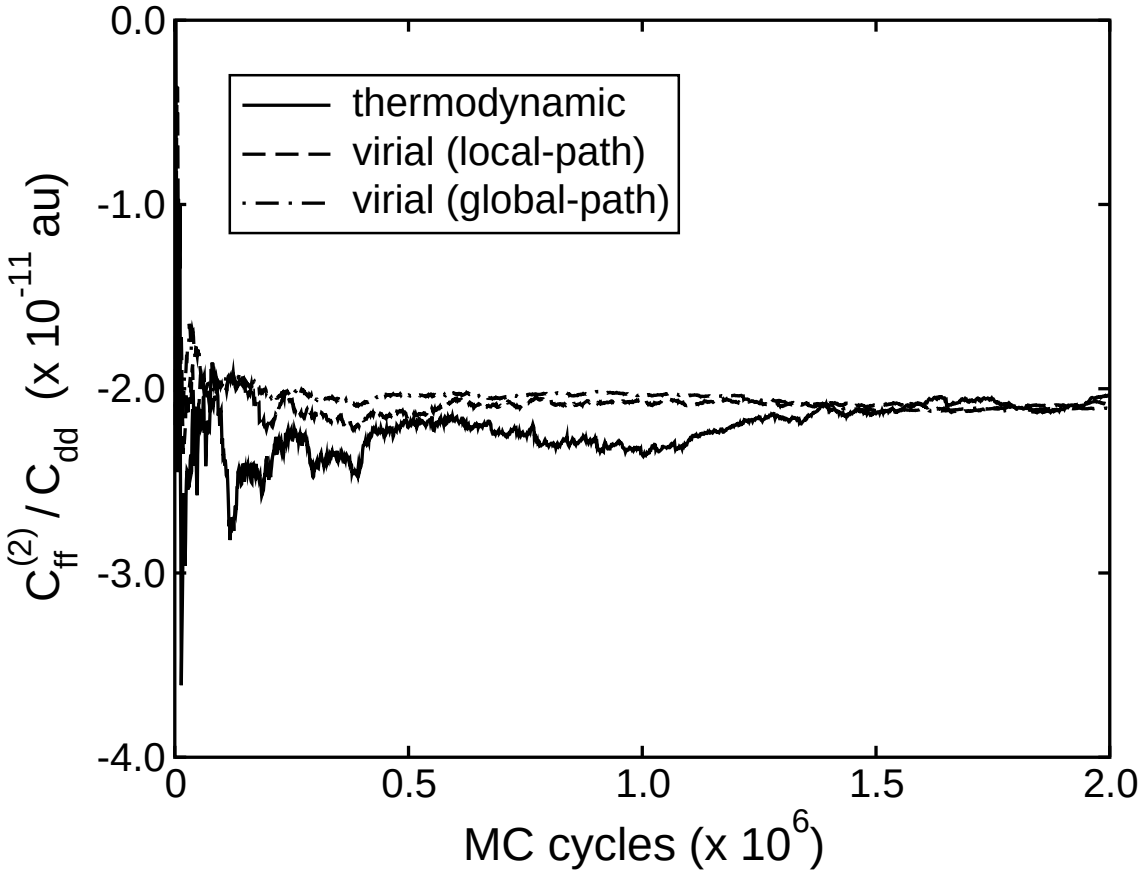
0.0
-1.0
-2.0
-3.0
-4.0
0
0.5
1.0
1.5
2.0
thermodynamic
virial (local-path)
virial (global-path)
$C_{ff}^{(2)} / C_{dd}$ (x 10^{-11} au)
MC cycles (x 10^{6})

Fig. 2 (c)

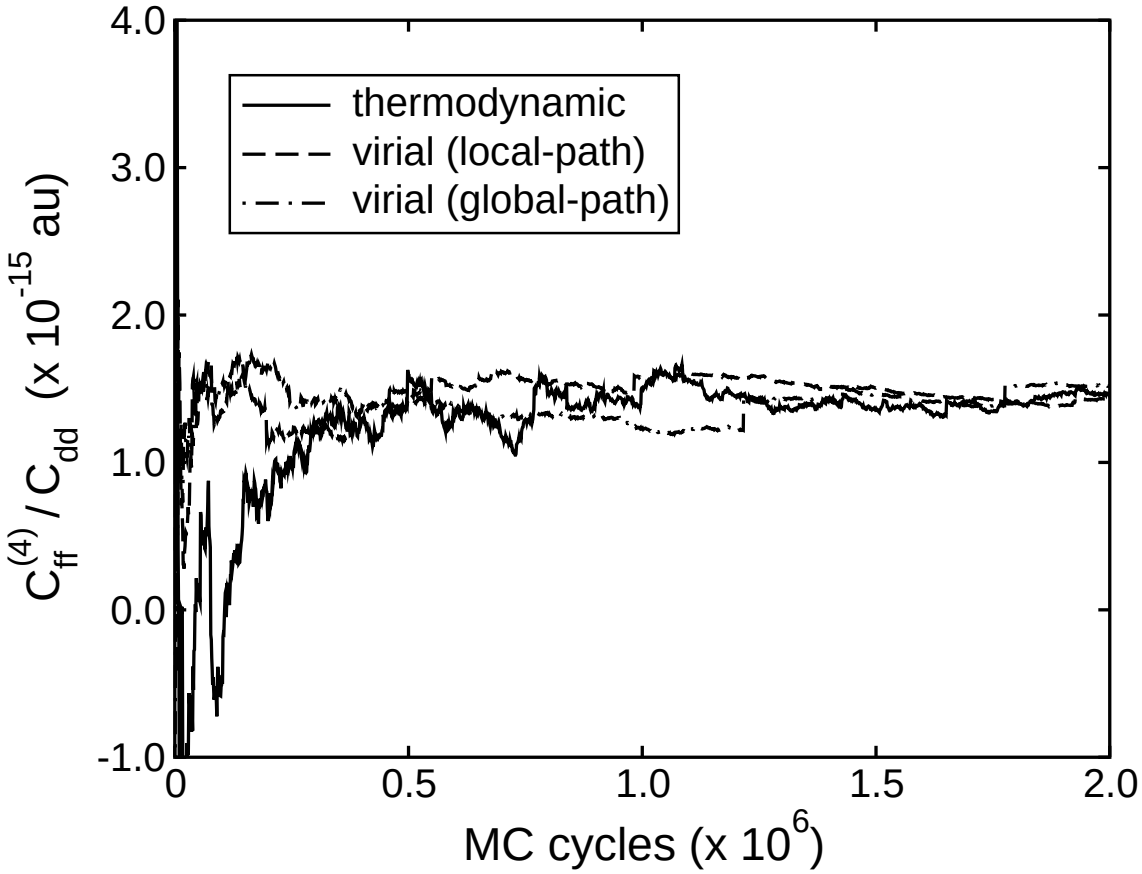
thermodynamic
virial (local-path)
virial (global-path)
4.0
3.0
2.0
1.0
0.0
-1.0
0
0.5
1.0
1.5
2.0
$C_{ff}^{(4)} / C_{dd}$ (x 10^{-15} au)
MC cycles (x 10^{6})

TABLE I: Relative statistical error (%) of the thermodynamic, local-path virial, and global-path virial estimators for the one-dimensional Eckart barrier. One million paths are sampled with 8 and 40 path variables for $T = 1000$ and 200 K, respectively.

	thermodynamic	virial (local-path)	virial (global-path)
		$T = 1000$ K	
$C_{\rm dd}^{(2)}/C_{\rm dd}$	0.5	0.024	0.024
$C_{\rm ff}^{(2)}/C_{\rm dd}$	1.2	0.34	0.012
$C_{\rm ff}^{(4)}/C_{\rm dd}$	2.3	0.33	0.014
$C_{\rm ff}^{(6)}/C_{\rm dd}$	2.6	0.33	0.015
		$T = 200$ K	
$C_{\rm dd}^{(2)}/C_{\rm dd}$	1.1	0.27	0.27
$C_{\rm ff}^{(2)}/C_{\rm dd}$	3.3	1.4	0.41
$C_{\rm ff}^{(4)}/C_{\rm dd}$	8.1	1.7	0.44
$C_{\rm ff}^{(6)}/C_{\rm dd}$	25	2.0	0.51