



# Information guided noise reduction for Monte Carlo integration of oscillatory functions

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## Abstract

A simple procedure for decreasing the statistical error associated with Monte Carlo integration of oscillatory functions is presented. The method uses available information about the integral of a similar oscillatory function to correlate the estimates of the positive and negative components of the integral. Numerical tests show that information guided noise reduction (IGNoR) leads to substantial decrease of the statistical error, allowing meaningful results to be obtained with a fraction of the cost required to attain similar precision from the raw Monte Carlo estimate.

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## 1. Introduction

Since its inception, the Metropolis Monte Carlo method [1] has revolutionized molecular simulation. Rather than using spatial grids, whose size grows exponentially with the dimension of the function of interest, Monte Carlo methods estimate integrals by sampling the integrand at randomly selected values of the integration variables subject to an appropriate probability distribution. As a result, such stochastic integration methods are capable of arriving at meaningful results even when the dimension of the integral is very large. Because of the relatively slow increase of computational cost with integral dimension, the Monte Carlo has become one of an extremely valuable technique for simulating the properties of large ensembles of particles [2].

The rapid convergence mentioned above is characteristic of smooth functions that do not change sign. Many physical situations conform to these requirements. For example, the canonical ensemble is characterized by

the Boltzmann distribution, whose classical and quantum path integral representations give rise to high-dimensional integrands of positive-definite functions. Similar descriptions are possible for ensembles of identical particles obeying Bose statistics. By contrast, the treatment of identical fermions requires an exchange operation associated with a sign change, violating the positivity requirement. Further, quantum dynamical properties are associated with rapidly varying phase factors. Such situations present enormous challenges to Monte Carlo methods, known as ‘the sign problem’. To date, accurate quantum mechanical calculations in real time, as well as equilibrium simulations of fermion systems, are feasible either by restricting the number of treated particles or by introducing assumptions that lead to approximate solutions.

The reason for the failure of the powerful Monte Carlo method in cases where the integrand changes sign is extreme cancellation. Even when a function appears mildly non-positive in one-dimension, in many physical problems multiplication of small negative lobes with large positive ones in higher dimension leads to a hopeless situation, where the positive and negative parts occupy nearly equal volumes. Suppose the integral of the

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positive areas of a function is equal to  $J_p$ , and that of the negative areas is  $J_n$ . Direct evaluation of the integral by a Monte Carlo procedure is equivalent to estimating separately  $J_p$  and  $J_n$ , and adding these estimates. Because estimation of each of these integrals is associated with statistical uncertainties of order  $\sigma$ , the actual figures for the positive and negative integrals given by the Monte Carlo procedure typically are in the range  $J_p \pm \sigma$  and  $J_n \pm \sigma$ . As a result, the statistical uncertainty in the Monte Carlo estimate of the desired integral  $J_p + J_n$  is  $\sqrt{2}\sigma$ . While the relative Monte Carlo uncertainty  $\sigma/J_p$  (or  $\sigma/|J_n|$ ) typically increases slowly with the dimension of the function, the growth of the negative domains of the function relative to the positive area usually causes the ratio  $(J_p + J_n)/J_p$  to decrease *exponentially* with integral dimension. As soon as  $J_p + J_n \approx \sigma$ , the estimate of the desired integral is meaningless.

The present Letter describes a simple procedure for reducing the magnitude of the statistical error in Monte Carlo evaluations of non-positive functions. The method is based on correlating the estimates of the positive and negative areas of the function by exploiting information about a related function whose integral is available. Because correlated errors are not random, partial error cancellation is achieved. As a result, information guided noise reduction (IGNoR) allows a significant increase in precision of the desired integral, compared to the raw estimate obtainable from the same Monte Carlo random walk.

Section 2 describes the IGNUOR procedure. Two numerical examples that illustrate the convergence properties of the method are presented in Section 3. Finally, Section 4 presents some concluding remarks about potential applications of IGNUOR, with particular emphasis on time correlation function expressions of rate constants.

## 2. The method

Consider an integral of the type

$$J = \int f(x)g(x) dx, \quad (2.1)$$

over a particular domain. It is assumed that the function  $g$  is easy to integrate by Monte Carlo methods (subject to a suitable sampling function), while the function  $f$  is oscillatory, such that evaluation of its integral requires an unrealistically large number of Monte Carlo samples. For example, the function  $g$  may be a smooth, positive definite function, although deviations from this behavior are acceptable as long as the above assumptions are satisfied. Throughout the Letter, it is assumed that both functions are real-valued, and the sampling function required for the random walk is incorporated in  $f$ . Extension

to integrals of complex functions is straightforward by splitting the product into its real and imaginary parts.

To proceed, consider the integrals of the positive and negative parts of the oscillatory function  $f$  separately

$$\begin{aligned} I_p &= \int f(x)\theta(f(x)) dx, \\ I_n &= \int f(x)\theta(-f(x)) dx, \end{aligned} \quad (2.2)$$

where  $\theta$  is the Heavyside step function,  $\theta(x) = 1$  if  $x > 0$  and  $\theta(x) = 0$  otherwise. Let  $\langle I_p \rangle$  and  $\langle I_n \rangle$  be the Monte Carlo estimates of these integrals, which differ from the exact values by the amounts

$$\sigma_p = \langle I_p \rangle - I_p, \quad \sigma_n = \langle I_n \rangle - I_n. \quad (2.3)$$

The statistical errors  $\sigma_p$  and  $\sigma_n$  approach zero slowly (as  $\sqrt{M}$ ) as the number  $M$  of Monte Carlo samples increases. Because the integrands of  $I_p$  and  $I_n$  do not alternate in sign, the statistical errors in these integrals may be positive or negative with magnitudes typical of Monte Carlo integration with smooth, positive definite functions. Since the Monte Carlo errors  $\sigma_p$  and  $\sigma_n$  are uncorrelated, the error in the sum  $\langle I_p \rangle + \langle I_n \rangle$  often exceeds  $\sigma_p$  (or  $\sigma_n$ ). (Note that the term ‘error’ is used in the present context as the actual difference of the integral estimated in a particular calculation from its exact value, and not as the standard deviation of the Monte Carlo result, which is referred to as ‘statistical uncertainty’ throughout the manuscript.) The well-known ‘sign problem’ occurs because the integral  $I = I_p + I_n$  of the entire function  $f$  is often much smaller than the statistical errors of its positive and negative parts, causing the estimate of the integral

$$\langle I \rangle = \langle I_p \rangle + \langle I_n \rangle = I_p + I_n + \sigma_p + \sigma_n \quad (2.4)$$

to be meaningless. Similar remarks apply to the Monte Carlo estimation of the desired integral  $J$ .

Much progress can be made if the integral of the oscillatory function  $f$  is known *exactly*. This is often the case in quantum or statistical mechanical calculations, because this function reduces to the integrand of a zeroth-order quantity that can be obtained analytically (see Section 3 for examples). Since the exact value of the integral  $I$  is available, the statistical errors of the positive and negative integrals need not be uncorrelated but can be made to cancel. This is achieved by defining a ‘corrected’ value of the negative integral

$$\tilde{I}_n \equiv I - \langle I_p \rangle. \quad (2.5)$$

For the given value of the positive part of  $f$  estimated by the Monte Carlo procedure, the corrected negative integral is obtained using the knowledge of the exact value of the sum. This way the Monte Carlo error on the corrected negative integral  $\tilde{\sigma}_n = \tilde{I}_n - I_n$  equals  $\sigma_p$ , and the two errors cancel by construction.

The corrected negative integral  $\tilde{J}_n$  is now used to estimate the desired integral  $J$  with much higher precision than possible from the raw Monte Carlo result.

To this end, the integrals

$$J_p = \int f(x)g(x)\theta(f(x)) dx, \quad \text{and}$$

$$J_n = \int f(x)g(x)\theta(-f(x)) dx \quad (2.6)$$

of the product function  $fg$  within the positive and negative domains of  $f$  are estimated from the same Metropolis random walk performed to obtain the corresponding integrals of  $f$ . Calling the Monte Carlo estimates  $\langle J_p \rangle$  and  $\langle J_n \rangle$ , the ratios

$$\kappa_p = \frac{\langle J_p \rangle}{\langle I_p \rangle} \quad \text{and} \quad \kappa_n = \frac{\langle J_n \rangle}{\langle I_n \rangle} \quad (2.7)$$

are calculated. These ratios describe how much (and in which direction) the factor  $g(x)$  modifies the volumes of the positive and negative domains of  $f$ . Because all Monte Carlo results include statistical error, the ratios estimated by Eq. (2.7) differ from the exact values by factors  $\alpha_p$  and  $\alpha_n$ , such that

$$\frac{J_p}{I_p} = \alpha_p \kappa_p \quad \text{and} \quad \frac{J_n}{I_n} = \alpha_n \kappa_n. \quad (2.8)$$

The procedure of calculating the integrals  $I_p$  and  $J_p$  from the same Monte Carlo samples implies that the corresponding estimates  $\langle J_p \rangle$  and  $\langle I_p \rangle$  are correlated, leading to a reduction of statistical uncertainty in their ratio. The two integrands differ by the factor  $g(x)$ , whose behavior determines the extent of this correlation. (For example, the two estimates are perfectly correlated if  $g(x) = 1$ , and completely uncorrelated if  $g$  is a wildly varying function; for smooth positive functions these integrals are often sufficiently correlated to allow a significant reduction of the statistical error in the ratio  $\kappa_p$ .) As a result, the factors  $\alpha_p$  and  $\alpha_n$  approach unity much faster than the raw statistical errors  $\sigma_p$  and  $\sigma_n$  approach zero, as long as  $g(x)$  is a smooth function. The amount of correlation of these Monte Carlo estimates can be quantified by blocking the collected samples.

Based on the above, IGNoR proceeds by ignoring the Monte Carlo estimate of the negative integral  $\langle J_n \rangle$ , replacing it by a corrected value  $\tilde{J}_n$  determined from the corrected value of  $\tilde{J}_n$  and the estimated ratio:

$$\tilde{J}_n \equiv \kappa_n \tilde{J}_n. \quad (2.9)$$

Thus, the IGNoR prescription for estimating the desired integral is

$$J \approx \langle J_p \rangle + \tilde{J}_n. \quad (2.10)$$

It is not hard to show that the prescription of Eq. (2.10) will generally give an improved estimate of the desired integral. From Eqs. (2.7), (2.3) and (2.8), one has

$$\langle J_p \rangle = \langle I_p \rangle \kappa_p = (I_p + \sigma_p) \kappa_p = \alpha_p^{-1} J_p + \sigma_p \kappa_p \quad (2.11)$$

and

$$\tilde{J}_n = \kappa_n (I_n - \sigma_p) = \alpha_n^{-1} J_n - \kappa_n \sigma_p. \quad (2.12)$$

From these, the IGNoR prescription is

$$\begin{aligned} \langle J_p \rangle + \tilde{J}_n &= \alpha_p^{-1} J_p + \sigma_p \kappa_p + \alpha_n^{-1} J_n - \kappa_n \sigma_p \\ &= \alpha_p^{-1} J_p + \alpha_n^{-1} J_n + (\kappa_p - \kappa_n) \sigma_p. \end{aligned} \quad (2.13)$$

It is easy to see from this form that the IGNoR result approaches faster the exact value of the integral  $J = J_p + J_n$  than the raw Monte Carlo estimate  $\langle J_p \rangle + \langle J_n \rangle$ . First, as argued above,  $|\alpha_p^{-1} J_p - J_p| \ll \sigma_p$ , such that the sum of the first two terms in the IGNoR estimate approaches rapidly the exact value  $J$  of the desired integral. The second source of error in Eq. (2.13) is  $(\kappa_p - \kappa_n) \sigma_p$ . (Note the absence of the statistical error  $\sigma_n$  from Eq. (2.13).) If the function  $g$  is scaled such that the magnitude of  $J_p$  (or  $J_n$ ) is similar to the magnitude of  $I_p$  (or  $I_n$ ), then the ratios  $\kappa_p$  and  $\kappa_n$  are of order 1, and their difference, thus the error given by the last term in Eq. (2.13), is much smaller than  $\sigma_p$ . Thus, a sufficiently precise estimate of the desired integral can be obtained with a number of Monte Carlo samples that may be too small for the raw estimate of the integral to be meaningful.

### 3. Numerical examples

The noise reduction achievable with IGNoR is illustrated with two numerical examples. In the first example the statistical error is examined as a function of integral dimension for a complex-valued Gaussian integrand. The second example involves application of IGNoR to the path integral representation of the survival probability in a one-dimensional system.

#### 3.1. Multi-dimensional Gaussian integral

The integrand is chosen as the product of the  $N$ -dimensional functions

$$f(x_1, \dots, x_N) = \prod_{k=1}^N e^{-ax_k^2} \cos bx_k, \quad g(x_1, \dots, x_N) = \prod_{k=1}^N e^{-cx_k^2} \quad (3.1)$$

with  $a = 1$ ,  $b = 1.8$  and  $c = 0.1$ . The integral of the function  $f$  is available analytically, inviting application of IGNoR as described in Section 2. In this case the form of  $g$  is chosen such that the desired integral  $J$  is also known analytically for comparison. This function is mildly oscillatory in one-dimension, but the negative lobes become very prominent as the dimension  $N$  is increased, occupying comparable volume with that of

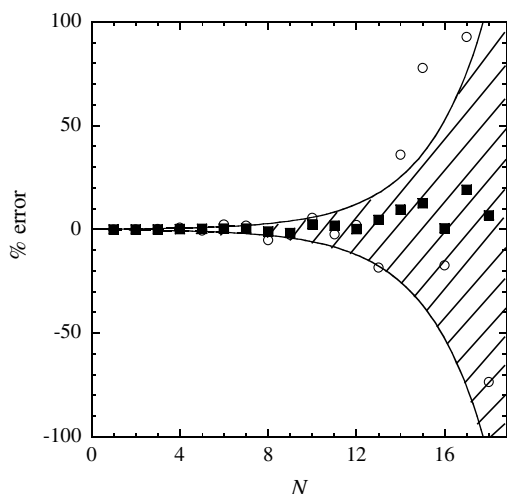


Fig. 1. Percent error for the integral specified by (3.1) as a function of dimension.  $\circ$ , raw Monte Carlo estimates;  $\blacksquare$ , IGNoR-corrected results. The shaded area shows statistical uncertainty (corresponding to one standard deviation) of the percent error given by the raw Monte Carlo estimate.

the positive lobes. This behavior results in dramatic cancellation that leads to large statistical error. The calculations presented below were performed with  $M = N \times 10^6$  Monte Carlo samples.

Fig. 1 shows the percent error of the raw Monte Carlo evaluation of the integral (along with its statistical error) and the percent error of the IGNoR procedure as a function of integral dimension. It is seen that the raw Monte Carlo estimate results in large statistical errors which grow exponentially as the integral dimension is increased. By contrast, the IGNoR-corrected results provide much better estimates. Even though the statistical error of the IGNoR results also grows exponentially with dimension, the rate of this increase is considerably slower, allowing reliable estimation of the integral at higher dimension.

### 3.2. Real-time path integral

As a second example relevant to quantum mechanical calculations I treat here the quantum mechanical expression for the survival probability of a pure state  $\Psi_0$  under propagation in a one-dimensional harmonic oscillator Hamiltonian. The survival probability defined as the absolute square of the survival amplitude  $\langle \Psi_0 | e^{-i\hat{H}t/\hbar} | \Psi_0 \rangle$ , which can be brought into the form of a path integral [3] by splitting the time evolution operator into  $N$  time slices of length  $\Delta t = t/N$ . In order to produce a more general expression applicable to the expectation value of an operator  $\hat{O}$  with respect to a mixed state (e.g., a thermal ensemble), the survival probability is written below in the form of a (discretized) double path integral

$$\begin{aligned}
 P(t) &= \langle \Psi_0 | e^{i\hat{H}t/\hbar} | \Psi_0 \rangle \langle \Psi_0 | e^{-i\hat{H}t/\hbar} | \Psi_0 \rangle \\
 &= \int dx_0^- \cdots \int dx_N^- \int dx_0^+ \cdots \int dx_N^+ \Psi_0(x_0^-) \\
 &\quad \times \langle x_0^- | e^{i\hat{H}\Delta t/\hbar} | x_1^- \rangle \cdots \langle x_{N-1}^- | e^{i\hat{H}\Delta t/\hbar} | x_N^- \rangle \langle x_N^- | \hat{O} | x_N^+ \rangle \\
 &\quad \times \langle x_N^+ | e^{-i\hat{H}\Delta t/\hbar} | x_{N-1}^+ \rangle \cdots \langle x_1^+ | e^{-i\hat{H}\Delta t/\hbar} | x_0^+ \rangle \Psi_0(x_0^+).
 \end{aligned} \tag{3.2}$$

Eq. (3.2) becomes the survival probability with the choice  $\hat{O} = |\Psi_0\rangle\langle\Psi_0|$  but can also be used to evaluate expectation values of other operators.

Evaluation of Eq. (3.2) by Monte Carlo methods requires a weight function for all integration variables. The traditional Trotter product approximation to the short time propagator has the form of a pure phase and thus does not provide a suitable weight function (unless filtering procedures are used). An attractive alternative is offered by effective system-specific propagators [4], which are constructed numerically by expanding the time evolution operator in terms of low-lying eigenstates of an appropriate reference Hamiltonian  $\hat{H}_0$

$$\langle x'' | e^{-i\hat{H}_0\Delta t/\hbar} | x' \rangle = \sum_{n=0}^{n_{\max}} \Phi_n(x') \Phi_n(x'') e^{-iE_n\Delta t/\hbar}, \tag{3.3}$$

where  $\Phi_n$  and  $E_n$  are the eigenfunctions and eigenvalues of  $\hat{H}_0$ . Eq. (3.3) converges to the exact quantum mechanical propagator in the limit  $n_{\max} \rightarrow \infty$ . The useful feature of this form is that its use in the path integral expression results in exponential convergence with the number  $n_{\max}$  of eigenfunctions. At the same time, the resolution of the propagator in terms of a finite number of states leads to a form that decays with the coordinates of *both* endpoints [5], providing a natural weight function for Monte Carlo integration. Finally, the construction of propagators based on exact information for a suitable zeroth-order Hamiltonian often allows time steps that are much larger than those possible with primitive propagators. For the purpose of illustrating the advantages of IGNoR on a one-dimensional example an effective propagator is obtained from the eigenstates of the entire Hamiltonian, i.e.,  $\hat{H}_0 = \hat{H}$ ; the resulting propagator is exact for any value of the time step. (Clearly, the chosen short time propagator contains all information necessary to evaluate the survival probability in a single time step with minimal numerical effort; the purpose of the calculation presented below is solely to illustrate the convergence properties of IGNoR on an integrand relevant to quantum mechanical propagation.)

Eq. (3.2) is used to construct a short-time propagator on a coordinate grid. The various functions defined in Section 2 are chosen as

$$\begin{aligned}
f(x_0^-, \dots, x_N^-, x_0^+, \dots, x_N^+) &= \Psi_0(x_0^-) \Psi_0(x_0^+) \\
&\times \langle x_0^- | e^{i\hat{H}\Delta t/\hbar} | x_1^- \rangle \\
&\dots \langle x_{N-1}^- | e^{i\hat{H}\Delta t/\hbar} | x_N^- \rangle \\
&\times \langle x_N^+ | e^{-i\hat{H}\Delta t/\hbar} | x_{N-1}^+ \rangle \\
&\dots \langle x_1^+ | e^{-i\hat{H}\Delta t/\hbar} | x_0^+ \rangle \quad (3.4)
\end{aligned}$$

and

$$g(x_N^-, x_N^+) = \langle x_N^- | \hat{O} | x_N^+ \rangle. \quad (3.5)$$

Monte Carlo sampling is performed with the absolute value of  $f$  as the sampling function. The required normalization integral is evaluated by matrix multiplication.

The initial state is chosen as a Gaussian with a width equal to four times that of the ground state wavefunction, centered at the potential minimum. The path integral expression, Eq. (3.2), was evaluated at  $\omega t = 1$  with  $N = 4$  time slices, resulting in a 10-dimensional integral. The truncated propagator used in the path integral expression is shown in Fig. 2. Clearly, the negative parts of the integrand are sizable, and obtaining converged results is an extremely difficult task when several time slices are used. A new random number seed was used in each Monte Carlo run in order to prevent the use of identical random number blocks in successive integral estimates, which would result in correlated data.

The convergence of the calculation with the number of Monte Carlo points per integration variable is shown in Fig. 3. The raw Monte Carlo estimate is accompanied by large statistical uncertainty and requires over three million samples per integration variable to bring the statistical error within 5% of the exact value. By contrast, the IGNoR-corrected estimate converges much faster, achieving this goal with about one million samples. In fact, the IGNoR results are consistently

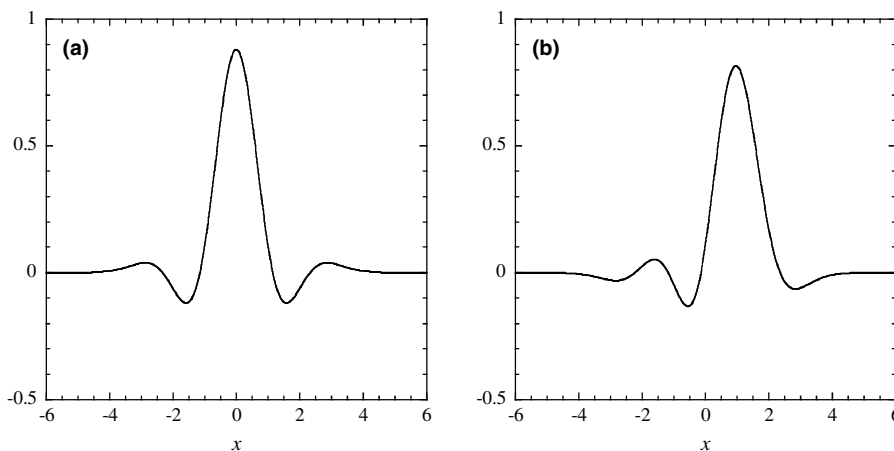


Fig. 2. The real part of the short time propagator  $\langle x' | e^{-i\hat{H}\Delta t/\hbar} | x \rangle$  calculated from Eq. (3.3) for  $\Delta t = 0.25\omega^{-1}$  as a function of  $x$  for (a)  $x' = 0$  and (b)  $x' = 1$ .

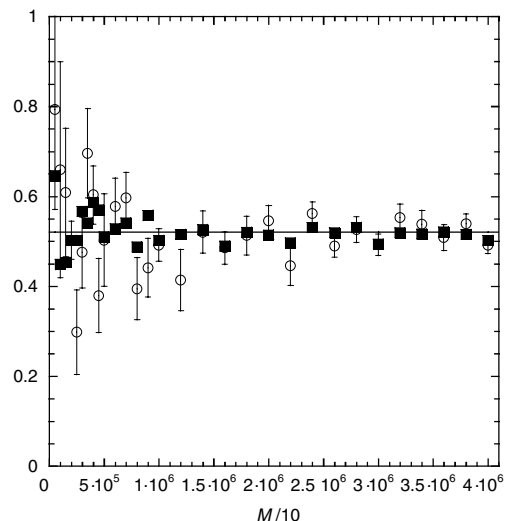


Fig. 3. Survival probability at  $t = \omega^{-1}$  for a harmonic oscillator evaluated from Eq. (3.2) with  $N = 4$  as a function of the number of Monte Carlo points per integration variable employed in each calculation. The raw Monte Carlo estimates are shown as  $\circ$ , along with error bars corresponding to one standard deviation. The  $\blacksquare$  show results corrected with IGNoR. The solid line shows the exact result.

within 14% of (and generally much closer to) the exact value for all calculations performed with  $10^5$  or more Monte Carlo samples, while the raw Monte Carlo results are in error almost by a factor of two at the low end of this range.

#### 4. Concluding remarks

Unlike smooth positive-definite functions, integrands with negative domains present extremely severe chal-

enges to Monte Carlo methods. This is so because the fractional statistical error of the positive and negative areas remains the same or grows, while their relative difference decreases exponentially with the number of integration variables. As a result, preventing the relative statistical error of the result from growing requires an exponential increase of the number of Monte Carlo points with the dimension of the integral.

The present Letter presented a simple procedure that leads to a substantial decrease of statistical error. To achieve this, IGNoR refrains from adding the Monte Carlo estimates of the positive and negative areas of the integrand. Guided by the known integral of a similar function, IGNoR replaces the negative integral by a corrected estimate whose error is, by construction, correlated with the statistical error of the positive integral. The resulting partial error cancellation allows significant gains in precision without an increase of the computational cost incurred in a given calculation. Even though the statistical error of the IGNoR estimate is also likely to increase exponentially with the number of integration variables, the analysis given in Section 2 and the numerical examples presented in Section 3 show that this increase typically occurs much slower compared to the error of the raw Monte Carlo procedure. This fact implies that integrals of much higher dimension can be performed with a given amount of numerical effort if the IGNoR correction is employed.

IGNoR works best if the integrand of interest differs by that of an integrable function by a smooth, positive multiplicative factor. While this restriction prevents straightforward application of the method to certain desirable integrals, there are still many situations in theoretical chemical physics where the procedure is applicable. A particularly favorable situation is offered by the quantum mechanical expression for the rate constant of a reactive process, which can be written in terms of the following correlation function [6]:

$$k = \lim_{t \rightarrow \infty} \frac{d}{dt} C(t), \quad (4.1)$$

$$C(t) = Z_R^{-1} \text{Tr} \left( \theta(-\hat{s}) e^{i\hat{H}t_c/\hbar} \theta(\hat{s}) e^{-i\hat{H}t_c/\hbar} \right) \quad (4.2)$$

Here  $Z_R = \text{Tr}[\theta(-\hat{s})e^{-\beta\hat{H}}]$  is the reactant partition function,  $\hat{F}$  is the flux operator,  $t_c = t - i\hbar\beta/2$  is a ‘complex time’ that combines the real time with the inverse temperature  $\beta = 1/k_B T$ , and the ‘dividing surface’ in Eq. (4.1) is defined by the plane  $s = 0$ . Representing each of the propagators by  $N$  path integral slices  $\Delta t_c = t_c/N$ , the correlation function for a multi-dimensional system described by the reaction coordinate  $s$  and orthogonal degrees of freedom  $\mathbf{x}$  takes the form

$$\begin{aligned} C(t) &= Z_R^{-1} \int ds_0 \int ds_1^\pm \cdots \int ds_{N-1}^\pm \int ds_N \int d\mathbf{x}_0 \\ &\times \int d\mathbf{x}_1^\pm \cdots \int d\mathbf{x}_{N-1}^\pm \int d\mathbf{x}_N \theta(-s_N) \\ &\times \langle s_N \mathbf{x}_N | e^{iH\Delta t_c/\hbar} | s_{N-1}^- \mathbf{x}_{N-1}^- \rangle \\ &\cdots \langle s_1^- \mathbf{x}_1^- | e^{iH\Delta t_c/\hbar} | s_0 \mathbf{x}_0 \rangle \times \theta(s_0) \langle s_0 \mathbf{x}_0 | e^{-iH\Delta t_c/\hbar} | s_1^+ \mathbf{x}_1^+ \rangle \\ &\cdots \langle s_{N-1}^+ \mathbf{x}_{N-1}^+ | e^{-iH\Delta t_c/\hbar} | s_N \mathbf{x}_N \rangle, \end{aligned} \quad (4.3)$$

where  $\Delta t_c = t_c/N$ . To apply the IGNoR procedure to this expression, one defines

$$\begin{aligned} f(s_0, s_1^\pm, \dots, s', \mathbf{x}_0, \mathbf{x}_1^\pm, \dots, \mathbf{x}_N) \\ = \theta(-s_N) \langle s_N \mathbf{x}_N | e^{iH\Delta t_c/\hbar} | s_{N-1}^- \mathbf{x}_{N-1}^- \rangle \cdots \langle s_1^- \mathbf{x}_1^- | e^{iH\Delta t_c/\hbar} | s_0 \mathbf{x}_0 \rangle \\ \times \langle s_0 \mathbf{x}_0 | e^{-iH\Delta t_c/\hbar} | s_1^+ \mathbf{x}_1^+ \rangle \cdots \langle s_{N-1}^+ \mathbf{x}_{N-1}^+ | e^{-iH\Delta t_c/\hbar} | s_N \mathbf{x}_N \rangle \end{aligned} \quad (4.4)$$

and

$$g(s_0, s_1^\pm, \dots, s', \mathbf{x}_0, \mathbf{x}_1^\pm, \dots, \mathbf{x}_N) = \theta(s_0). \quad (4.5)$$

It is easy to show that the required integral of  $f$  equals the reactant partition function  $Z_R$ . The sampling function may be chosen as

$$\begin{aligned} \rho(s_0, s_1^\pm, \dots, s', \mathbf{x}_0, \mathbf{x}_1^\pm, \dots, \mathbf{x}_N) \\ = \theta(-s_N) \langle s_N \mathbf{x}_N | e^{-\beta/2N} | s_{N-1}^- \mathbf{x}_{N-1}^- \rangle \cdots \langle s_1^- \mathbf{x}_1^- | e^{-\beta/2N} | s_0 \mathbf{x}_0 \rangle \\ \times \langle s_0 \mathbf{x}_0 | e^{-\beta/2N} | s_1^+ \mathbf{x}_1^+ \rangle \cdots \langle s_{N-1}^+ \mathbf{x}_{N-1}^+ | e^{-\beta/2N} | s_N \mathbf{x}_N \rangle. \end{aligned} \quad (4.6)$$

The integral of this, which provides the normalization factor for the Monte Carlo results, is also equal to  $Z_R$ . Using these observations, the IGNoR procedure for the rate constant takes the form

$$k = \lim_{t \rightarrow \infty} \frac{d}{dt} \left[ \langle J_P \rangle_{\rho_{\text{norm}}} - \kappa_n \left( 1 - \langle I_P \rangle_{\rho_{\text{norm}}} \right) \right], \quad (4.7)$$

where the subscript  $\rho_{\text{norm}}$  is used to indicate the average with respect to the normalized sampling function that is given by the Monte Carlo calculation without multiplication by a normalizing factor. Notice that the reactant partition function has cancelled out; in this form, the required normalization integral of  $f$  is unity, and thus is available free of statistical uncertainty.

The use of IGNoR is also attractive in many other situations. For example, Kubo-type correlation functions [7] may be cast in a path integral form suitable for straightforward application of the method. Further, semiclassical calculations, which encounter difficulties due to the presence of the rapidly oscillatory semiclassical phase, will benefit from the use of IGNoR. Work along these lines is in progress.

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