A 'path-by-path' monotone extrapolation sequence for Feynman path integral calculations of quantum mechanical free energies

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Abstract

Feynman path integral methods based on the Trotter approximation represent paths by a set of P discrete points. We prove that the M-point partition function is an upper bound of the P-point one if M is a divisor of P. Also for this case, we show that, during calculations using P-point paths, it is possible – at negligible additional cost – to obtain M-point estimators of the partition function that, for *each individual path*, converge monotonically. This permits accurate extrapolation to infinite P, which greatly improves the accuracy of calculations of thermodynamic quantities.
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1. Introduction

Feynman path integral techniques [1–3], especially when coupled with Monte Carlo integration, are a powerful approach for the calculation of thermodynamic quantities such as partition functions and free energies. The most commonly implemented approach – the trapezoidal Trotter (TT) scheme – converges as $O(1/P^2)$, where P is the number of points used in the discretization of the paths [4,5]. In order to minimize the computa-tional costs, considerable efforts have been directed toward developing higher-order methods [6–14] or approximate schemes [15–25]. Another approach is to use extrapolation [26–28] to estimate the infinite-P limit using several small values of P. In previous work, we have presented accurate extrapolation schemes for Fourier path integral (FPI) methods [27] and Fourier analogs of discrete path integral (DPI) methods [28] which rely on the use of a correlated sequence of paths to reduce statistical errors. We will now extend this work by showing a new approach for extrapolating with Trotter-based methods that is both cheaper and more accurate than our earlier methods; it is equally applicable with either the widely used DPI formalism or the more recent 'Fourier analog'

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[28,29] methods. In particular, for an appropriate choice of P, the new method allows one to construct, on a 'path-by-path' basis, a monotonically decreasing sequence of estimates for the partition function that have highly systematic errors, and hence may be extrapolated with high accuracy.

2. Theory

The P-point discretized representation of the trapezoidal Trotter approximation of the partition function is commonly written [2] as

$$Q^{[P]}(T) = \left(\frac{mP}{2\pi\beta\hbar^2} \right) \int dx_1 \, dx_2 \cdots dx_P \\ \times \exp(-\beta\Phi_P(x_1, x_2, \ldots, x_P; \beta)), \qquad (1)$$

where

$$\Phi(x_1, x_2, \ldots, x_P; \beta) = \frac{mP}{2\beta^2\hbar^2} \sum_{i=1}^{P} (x_i - x_{i+1})^2 \\ + \frac{1}{P} \sum_{i=1}^{P} V(x_i), \qquad (2)$$

where T is the temperature, m is the mass, $\hbar$ is Plank's constant divided by 2π, β is $1/kT$, k is Boltzmann's constant, $V(x)$ is the potential energy, and $x_{i+P} = x_i$. Each point, x_i, is a (possibly multi-dimensional) configuration space point and the ordered set of $(x_1, x_2, \ldots, x_P)$, which we will denote $\mathbf{s}$, constitutes a discretization of a particular closed Feynman path.

At first glance, extrapolation of the partition function with respect to P would seem complicated by the fact that both the kinetic and potential energy terms have an explicit P dependence; fortunately, the situation is not as complicated as it seems. Coalson [29] has shown that the P-point TT scheme is isomorphic to a P-point trapezoidal rule integration over an infinite-dimensional path. Thus, the *same* paths (with the same weightings) can be used with several different values of P to obtain a sequence of estimates of the $P = \infty$ partition function, and these may be readily extrapolated. In the TT scheme of Eqs. (1) and (2), we only know the locations of P points on the paths,

so we can obtain simultaneous estimates of $Q^{[M]}(T)$ only for cases where M is a divisor of P.

Eq. (1) can be put into a form more appropriate for Monte Carlo sampling by restricting the centroids of the paths to lie within a finite domain D, having a volume, V^D, which is sufficient to contain all physically relevant configurations, and then multiplying and dividing the right-hand side by the P-point free-particle partition function (i.e., an expression identical to that of Eqs. (1) and (2) but with $V(x) = 0$). We then analytically evaluate the free-particle expression in the numerator to obtain

$$Q^{[P]}(T) \\ = \frac{Q^{fp}(T) \int dx_1 \, dx_2 \cdots dx_P \exp(-\beta\Phi_P[x_1, x_2, \ldots, x_P; \beta])}{\int dx_1 \, dx_2 \cdots dx_P \exp\left(-\frac{mP}{2\beta\hbar^2} \sum_{i=1}^{P} (x_i - x_{i+1})^2 \right)}, \qquad (3)$$

where $Q^{fp}(T)$ denotes the analytic form of the free-particle partition function within domain D – which is independent of P – and is given by

$$Q^{fp}(T) = V^D \left(\frac{m}{2\pi\beta\hbar^2} \right)^{N/2}, \qquad (4)$$

where N is the dimension of the configuration space. We can conveniently rewrite this as

$$Q^{[P]}(T) = Q^{fp}(T) \langle q^{[P]}(\mathbf{s}) \rangle_{fp} \equiv \langle \phi(P, P, 1, \mathbf{s}) \rangle_{fp}, \qquad (5)$$

where $\langle \cdots \rangle_{fp}$ denotes an average over paths, $\mathbf{s}$, selected from the free-particle distribution,

$$q^{[P]}(\mathbf{s}) = \exp\left(-\frac{\beta}{P} \sum_{i=1}^{P} V(x_i; \mathbf{s}) \right), \qquad (6)$$

the arguments of V denote point i on path $\mathbf{s}$, and

$$\phi(M, P, i, \mathbf{s}) = Q^{fp}(T) \exp\left(-\frac{\beta}{M} \sum_{j=1}^{M} V(x_{i+jP/M}; \mathbf{s}) \right). \qquad (7)$$

Note that $\phi(P, P, 1, \mathbf{s})$ is the P-point estimate of the contribution of the particular path $\mathbf{s}$ to the partition function $Q^{[P]}(T)$.

During a P-point calculation, one can also get M-point results, if M is a divisor of P, via

$$Q^{[M]}(T) = Q^{[M;P]}(T) = \langle \phi(M, P, 1, \mathbf{s}) \rangle_{fp}, \qquad (8)$$

where (since it will be useful below) we write $Q^{[M]}$ as $Q^{[M;P]}$ when we obtain it during a P-point calculation. We have previously shown [28] that Monte Carlo calculations using Eq. (8) have much higher *relative* errors (i.e., the magnitude of the error divided by the magnitude of the quantity) for quantities like $Q^{[P]}(T) - Q^{[M]}(T)$ than for the $Q^{[P]}(T)$, and this poses a problem during extrapolation. An alternative approach is to use

$$Q^{[M]}(T) = Q^{[M;P]}(T) = \langle\langle\phi(M,P,i,\mathbf{s})\rangle_i\rangle_{\mathrm{fp}}, \qquad (9)$$

where $\langle\ldots\rangle_i$ denotes an average over all (P/M) possible M-point trapezoidal rule integrations of the path $\mathbf{s}$. An application of Gibb's inequality [2], i.e.,

$$\langle\exp(x)\rangle \geqslant \exp(\langle x\rangle), \qquad (10)$$

which is just a special case of Jensen's inequality [30,31], to Eq. (7) is sufficient to show that

$$\langle\phi(M,P,i,\mathbf{s})\rangle_i \geqslant \phi(P,P,1,\mathbf{s}). \qquad (11)$$

Additionally, if M' is a divisor of both M and P, then P/M invocations of Gibb's inequality are sufficient to show that

$$\langle\phi(M',P,i,\mathbf{s})\rangle_i \geqslant \langle\phi(M,P,i,\mathbf{s})\rangle_i. \qquad (12)$$

Thus, when using Eq. (9) for certain sequences of discretizations, the calculated partition functions will converge monotonically, and furthermore, this monotonic convergence will occur on a 'path-by-path' basis. Eq. (11) constitutes a formal proof that

$$Q^{[M]}(T) \geqslant Q^{[P]}(T) \qquad (13)$$

if M is a divisor of P, which is a result that has previously been proven [32,33] to hold only for the special case where P (and thus M) is a power of 2. For some special cases, such as harmonic potentials, where analytic expressions are readily available [2], one can see that Eq. (13) holds for the more general case of any $M < P$, but it is easy to see that this more general result does *not* hold on a path-by-path basis (for example, if we let $\mathbf{s}$ be a path such that $V(x) = 0$ on the first half of $\mathbf{s}$ and $V(x) = 1$ on the second half of $\mathbf{s}$, it is easy to see that $\langle\phi(2,P,i,\mathbf{s})\rangle_i$ is *less* than $\langle\phi(3,P,i,\mathbf{s})\rangle_i$). We conjecture that there is a wide class of 'sufficiently well-behaved' potentials for which this more gen-

eral monotonic convergence of the $Q^{[P]}(T)$ holds. The present results are, however, of more than formal interest, since we will see that when using Eq. (9) to calculate a sequence of estimates of the partition function, the various values may be more accurately extrapolated than if they had been calculated using Eq. (8).

3. Numerical examples and discussion

In order to demonstrate the efficacy of the new extrapolation approach we will consider some numerical results for a simple yet realistic model problem – the HCl molecule – which has also been used in previous studies [28,34]. We remove the center-of-mass motion analytically, which leaves three coupled degrees of freedom (two rotations and one vibration, but we use Cartesian coordinates and do not explicitly treat vibrations and rotations as vibrations and rotations).

All of our calculations used 2×10^7 sample paths with each path chosen independently from the free-particle distribution using our TT-FPI algorithm [28,35], and the remaining numerical parameters were taken to be identical to those used in previous calculations on this system [28]. The use of uncorrelated samples in our algorithm (as opposed to the more popular Metropolis walk, which is a correlated Markov process) allows easy and accurate estimates of the statistical uncertainties.

We will consider three different extrapolation schemes. The first will be called the primitive same path (PSP) approach and is given by Eq. (8). The second will be denoted the enhanced same path (ESP) scheme and is given by Eq. (9). The third approach, the similar Fourier expansion (SFE) method, was explored previously [28], and is only applicable when the paths are sampled via a re-weighted Fourier approach of Coalson [29]. In the SFE scheme a number of different TT-FPI paths of varying expansion length are generated using a common set of random numbers. This approach yields a set of infinite-dimensional paths (where only the nodes needed for trapezoidal integration are specified) which have similar low-order Fourier expansions. A disadvantage of this approach is

that these paths have no quadrature points in common.

In each of these three extrapolation approaches, several different estimates of the partition function are generated simultaneously. We also accumulate statistics on *differences* like

$$\Delta Q(M, M', P) \equiv Q^{[M;P]}(T) - Q^{[M';P]}(T), \qquad (14)$$

where M and M' are both divisors of P. The accumulation of differences on a path-by-path basis allows us to obtain accurate estimates of the statistical uncertainty of such differences. We expect that the statistical uncertainty of the individual $Q^{[M]}(T)$ will be essentially the same for each of the three different approaches; in particular, no improvement is expected in the ESP scheme from averaging the P/M estimates of the contribution from a particular path since these estimates are highly correlated. In practice, our calculations confirm these expectations. However, the uncertainties for the $\Delta Q(M, M', P)$ are found to vary markedly with the method employed, and thus the accuracy of extrapolations varies significantly as well.

Table 1 lists the partition function as a function of P for a temperature of 300 K; the converged result of 1.651×10^{-2} was obtained by eigenvalue summation [34]. Table 2 gives examples of the magnitudes and relative statistical uncertainties of the $\Delta Q(M, M', P)$ for each of the three extrapolation methods. The table also includes a 'relative

Table 1
Partition function and statistical errors for HCl as a function of discretization size

P	$Q^{[P]}(T)$	Uncertainty	
		2σ	2σ in %[a]
30	1.768×10^{-2}	3.55×10^{-5}	0.201
40	1.718×10^{-2}	3.48×10^{-5}	0.202
60	1.682×10^{-2}	3.43×10^{-5}	0.204
80	1.669×10^{-2}	3.41×10^{-5}	0.204
120	1.660×10^{-2}	3.39×10^{-5}	0.204
240	1.655×10^{-2}	3.39×10^{-5}	0.205
∞	1.651×10^{-2}		

[a] Relative to $Q^{[P]}(T)$.

Table 2
Statistical errors for correction terms calculated for three different extrapolation schemes[a]

Scheme	M	M'	P	$\Delta Q(M, M', P)$	2σ in %[b]	RVMF[c]
ESP	240	30	240	-1.14×10^{-3}	0.190	0.90
	120	30	240	-1.08×10^{-3}	0.193	0.93
	120	30	120	-1.08×10^{-3}	0.206	1.05
	80	30	240	-9.92×10^{-4}	0.201	1.01
	60	30	240	-8.66×10^{-4}	0.208	1.07
	60	30	120	-8.66×10^{-4}	0.223	1.23
	60	30	60	-8.67×10^{-4}	0.276	1.85
	40	30	240	-5.06×10^{-4}	0.322	2.57
	40	30	120	-5.06×10^{-4}	0.373	3.44
PSP	240	30	Any	-1.14×10^{-3}	0.997	22.97
	120	30	Any	-1.09×10^{-3}	1.021	24.09
	80	30	Any	-9.98×10^{-4}	1.201	33.36
	60	30	Any	-8.73×10^{-4}	1.141	30.09
	40	30	Any	-5.11×10^{-4}	2.639	161.08
SFE	240	30	Any	-1.14×10^{-3}	0.424	4.21
	120	30	Any	-1.09×10^{-3}	0.438	4.49
	80	30	Any	-9.96×10^{-4}	0.464	5.03
	60	30	Any	-8.71×10^{-4}	0.507	6.01
	40	30	Any	-5.09×10^{-4}	0.713	11.92

[a] All results in the table were calculated by the TT-FPI scheme [28].
[b] This column is relative to $\Delta Q(M, M', P)$.
[c] The relative variance magnification factor, see text.

variance magnification factor' (RVMF) which is calculated as the square of the ratio of the relative statistical uncertainty of the $\Delta Q(M, M', P)$ to the relative statistical uncertainty of the $Q^{[M]}(T)$. (A RVMF of 10 means that we would have required 10 times as many samples to obtain $\Delta Q(M, M', P)$ with the same relative uncertainty as has already been obtained for $Q^{[M]}(T)$.)

We see that the RVMFs for the PSP scheme are all very large, which means that the approach would yield poor extrapolation results. The RVMFs of our previous [28] SFE approach are much less than those of the PSP scheme, but are still significant. The ESP scheme yields the lowest RVMFs and is thus the most accurate approach. The RVMFs for the ESP scheme decrease slightly with increasing P, but the improvement is fairly modest and is not sufficient to motivate using larger values of P than would otherwise be necessary.

It is interesting to note that the RVMF for $\Delta Q(80, 30, 240)$ calculated with the ESP scheme is quite small even though 30 is not a divisor of 80. This indicates that working with means of the quadrature estimates of each path decreases the statistical errors of difference terms like the $\Delta Q(80, 30, 240)$ even when the strict path-by-path monotonic property does not apply.

4. Concluding remarks

The present Letter is stated in terms of partition functions, but the reader will recall that partition functions yield free energies directly and all other thermodynamic functions indirectly. Thus the conclusions have broad applicability to computational thermochemistry.

We have demonstrated that it is possible to simultaneously obtain lower-order estimates $Q^{[M]}(T)$ of partition functions during calculations of higher-order estimates $Q^{[P]}(T)$, where M is a divisor of P, that may be more accurately extrapolated than previously available estimators to the infinite-P limit. These lower-order estimates and the associated extrapolation are virtually cost free (compared to more time-consuming computational steps like path sampling and evaluation of the potential energy), so the approach should be of widespread utility in Feynman path integral calculations of quantum mechanical free energies. We have also provided a proof that $Q^{[M]}(T) \geqslant Q^{[P]}(T)$ if M is a divisor of P, which is a generalization of a previously known result, and have further shown that this monotonic convergence property holds also for the contributions of each individual path.

We note that the algorithms discussed in this Letter yield absolute free energies, not just relative ones, but the speedup that we achieve for absolute free energies can also be obtained in the same way for various kinds of relative free energy calculations.

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