CORRECT SHORT TIME PROPAGATOR FOR FEYNMAN PATH INTEGRATION BY POWER SERIES EXPANSION IN Δt

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The most commonly used short time propagator in a discretized Feynman path integral (and also several more sophisticated "improved" ones) is not correct through first order in the time increment Δt. The correct result for the phase (i.e. the action) of the short time propagator is developed in this paper as a power series in Δt, explicit expressions being given for the terms of order Δt^{-1}, Δt^1, and Δt^3. Test applications to the standard harmonic oscillator and also to a double well potential (typical for intramolecular H-atom transfer) show the first-order propagator (i.e. the correct result through order Δt) to be a significant improvement over previous ones; inclusion of the third-order term gives considerable additional improvement (i.e. faster convergence).

1. Introduction

Feynman path integration [1] has proved to be a powerful technique for evaluating equilibrium statistical mechanical properties, and it shows great promise for studying the real time dynamics of chemical systems. Its power lies in the fact that, unlike basis set methods, it can be used effectively to deal with systems of many degrees of freedom. Another attractive feature is that harmonic "bath" type degrees of freedom (which occur in many areas of chemical physics) can be integrated out *exactly* using the influence functional theory [1] of the path integral formalism.

Numerical evaluation of a path integral, however, requires that a discretized representation be used. One "slices" the total time t into N segments, each with time increment $\Delta t = t/N$:

$$\langle x_N|\exp(-\mathrm{i}Ht/\hbar)|x_0\rangle = \int \mathrm{d}x_{N-1} \dots \int \mathrm{d}x_1 \prod_{k=1}^{N} \langle x_k|\exp(-\mathrm{i}H\Delta t/\hbar)|x_{k-1}\rangle \tag{1}$$

and uses some short time approximation for each factor in the integrand of the above equation. (At present we are considering a one-dimensional system with a standard Cartesian Hamiltonian $\hat{H} = \hat{p}^2/2m + V(\hat{x}) \equiv \hat{T} + \hat{V}$.) The most popular approximation for the short time propagator, which results from use of the Trotter product formula [2–4], is

$$\langle x_k|\exp(-\mathrm{i}H\Delta t/\hbar)|x_{k-1}\rangle = \left(\frac{m}{2\pi \mathrm{i}\hbar\Delta t}\right)^{1/2} \exp\left(\frac{\mathrm{i}m}{2\hbar\Delta t}(x_k - x_{k-1})^2 - \frac{\mathrm{i}\Delta t}{\hbar}\frac{V(x_k) + V(x_{k-1})}{2}\right). \tag{2}$$

Eq. (2), substituted in eq. (1), has been extensively used for numerical evaluation of path integrals. Another choice that has been used [1] corresponds to replacing the average potential by the potential at the average position,

$$\tfrac{1}{2}[V(x_k) + V(x_{k-1})] \to V(\tfrac{1}{2}(x_k + x_{k-1})), \tag{3}$$

in eq. (2). There are a number of other, more sophisticated (and thus more difficult to apply) short time approximations that have also been suggested [5–10].

The purpose of this paper is to point out that even though eqs. (2) and (3) and other previously suggested short time propagators all give the correct $N\to\infty$ limit in eq. (1), *none* of them are actually correct through first order in Δt for finite N. In this paper we consider the exponent of the short time propagator as a power series in Δt, with terms of order Δt^{-1}, Δt^{1}, Δt^{3}, ..., and derive the correct coefficients of these various orders. Neither eqs. (2) and (3), nor any of the other more sophisticated approximations (that we are aware of) have even the first-order term correct. The pre-exponential factor is also modified in our result. (The reason that eqs. (2) and (3) and others give the correct $N\to\infty$ limit is because the first term in the exponent, the kinetic energy term, effectively restricts $x_k - x_{k-1}$ in the integration in eq. (1) to be of order $\Delta t^{1/2}$. In our treatment, though, we consider x_k and x_{k-1} to be independent variables.)

Apart from this formal improvement, though, the practically significant feature is that our short time approximation converges to the correct result more rapidly with increasing N in eq. (1), and it is still simple and thus directly amenable to Monte Carlo integration methodology. Section 2 derives the new expressions, which are illustrated with some numerical applications in section 3.

2. Power series expansion for the short time propagator

The derivation in this section will be presented for the real time propagator, $\exp(-iHt/\hbar)$. All results are readily generalizable to complex time (for example, the corresponding expression for the Boltzmann operator is obtained by setting $it/\hbar=\beta$). We will consider first a system of one degree of freedom, with a Cartesian Hamiltonian

$$\hat{H}=\frac{\hat{p}^2}{2m}+V(\hat{x})\equiv\hat{T}+\hat{V}.$$

For short time the propagator is given by the semiclassical expression [2]

$$\langle x_f|\exp(-iH\Delta t/\hbar)|x_0\rangle=\left(-\frac{\partial^2 S/\partial x_0\,\partial x_f}{2\pi i\hbar}\right)^{1/2}\exp(iS/\hbar), \tag{4}$$

where $S=S(x_f, x_0; \Delta t)$ is the action along the classical trajectory from x_0 to x_f in time Δt [11],

$$S(x_f, x_0; \Delta t)=\int_0^{\Delta t}[\tfrac{1}{2}m\dot{x}(t)^2-V(x(t))]\,dt. \tag{5}$$

(Here there is no sum over different classical trajectories that go from x_0 to x_f, as usually appears semiclassically [12], because only one trajectory contributes in the limit $\Delta t\to 0$.) Our plan is to express $S(x_f, x_0; \Delta t)$ as a power series in Δt and then use eq. (4) to obtain the short time propagator. Because of time reversal symmetry, i.e.

$$\langle x_f|\exp(-iH\Delta t/\hbar)|x_0\rangle^*=\langle x_f|\exp(iH\Delta t/\hbar)|x_0\rangle, \tag{6}$$

the action contains no even powers in Δt. (This is also true for the matrix elements of the Boltzmann operator, as follows by analytic continuation of the real time expressions.)

We have carried out the derivation several ways. The one presented here is the simplest algebraically, though it is specialized to one-dimensional systems. We will comment on the multidimensional generalization below. The action can be expressed (for the one-dimensional case) as

$$S(x_f, x_0; \Delta t)=\Phi(E)-E\Delta t, \tag{7a}$$

$$\Phi(E)=\int_{x_0}^{x_f}\{2m[E-V(x)]\}^{1/2}\,dx, \tag{7b}$$

where the energy E is determined implicitly by the equation

$$\Phi'(E) = \Delta t. \tag{8}$$

Expanding Φ in a Taylor series in $V(x)$ gives the following equations which correspond to eqs. (7) and (8):

$$\Phi(E) = (2m)^{1/2} \sum_{n=0}^{\infty} \binom{\frac{1}{2}}{n} (-1)^n E^{1/2-n} \int_{x_0}^{x_f} V(x)^n \, dx, \tag{9}$$

$$S(x_f, x_0; \Delta t) = (2m)^{1/2} \sum_{n=0}^{\infty} \binom{\frac{1}{2}}{n} (\tfrac{1}{2}+n)(-1)^n E^{1/2-n} \int_{x_0}^{x_f} V(x)^n \, dx, \tag{10a}$$

$$E^{1/2} = \frac{(2m)^{1/2}}{\Delta t} \sum_{n=0}^{\infty} \binom{\frac{1}{2}}{n} (\tfrac{1}{2}-n)(-1)^n E^{-n} \int_{x_0}^{x_f} V(x)^n \, dx. \tag{10b}$$

Combining eqs. (10a) and (10b) gives

$$S(x_f, x_0; \Delta t) = \frac{2m}{\Delta t} \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \binom{\frac{1}{2}}{n} \binom{\frac{1}{2}}{n'} (\tfrac{1}{2}-n)(\tfrac{1}{2}+n')(-1)^{n+n'} E^{-n-n'} \int_{x_0}^{x_f} V(x)^n \, dx \int_{x_0}^{x_f} V(x)^{n'} \, dx. \tag{11}$$

Solving eq. (10b) through $\mathcal{O}(\Delta t^2)$ by successive iteration and substituting into eq. (11) gives the following result for the action through third order in Δt:

$$S(x_f, x_0; \Delta t) = \frac{m}{2\Delta t} \Delta x^2 - \Delta t \langle V \rangle - \frac{\Delta t^3}{2m\Delta x^2} (\langle V^2 \rangle - \langle V \rangle^2) + \mathcal{O}(\Delta t^5), \tag{12a}$$

where

$$\Delta x = x_f - x_0, \tag{12b}$$

$$\langle V^n \rangle = \frac{1}{\Delta x} \int_{x_0}^{x_f} V(x)^n \, dx, \qquad n = 1,2. \tag{12c}$$

We note that the averages of the potential (and its square) in eq. (12c) can also be written as

$$\langle V^n \rangle = \frac{1}{\Delta t} \int_0^{\Delta t} V(x_0 + (x_f - x_0) t/\Delta t)^n \, dt, \tag{13a}$$

which emphasizes that they are time averages over the straight line, constant velocity trajectory from x_0 to x_f; in dimensionless form this becomes

$$\langle V^n \rangle = \int_0^1 V((1-\xi)x_0 + \xi x_f)^n \, d\xi. \tag{13b}$$

Consider now the *first-order propagator*, i.e. eq. (4) with S given by the first two terms of eq. (12a),

$$S(x_f, x_0; \Delta t) = \frac{m}{2\Delta t} \Delta x^2 - \Delta t \langle V \rangle. \tag{14}$$

It is not hard to show that the Van Vleck determinant is given by

$$-\frac{\partial^2 S}{\partial x_0\,\partial x_f}=\frac{m}{\Delta t}+\Delta t\int_0^1 \xi(1-\xi)\,V''((1-\xi)x_0+\xi x_f)\,d\xi; \tag{15a}$$

integration by parts (twice) allows the second term also to be written as

$$\int_0^1 \xi(1-\xi)\,V''((1-\xi)x_0+\xi x_f)\,d\xi=\frac{2}{\Delta x^2}\{\tfrac{1}{2}[V(x_0)+V(x_f)]-\langle V\rangle\}. \tag{15b}$$

It is also easy to see how this first-order propagator is related to other simple approximations for the short time propagator. Eq. (2), for example, corresponds to the two-point approximation (the trapezoid rule) for the potential energy integral,

$$\langle V\rangle\to\tfrac{1}{2}[V(x_0)+V(x_f)], \tag{16a}$$

and eq. (3) to the one-point approximation to the integral,

$$\langle V\rangle\to V(\tfrac{1}{2}(x_f+x_0)). \tag{16b}$$

Not surprisingly, therefore, eq. (16a) has been seen in practice [10,13] to work much better than eq. (16b). As will be seen, though, eq. (14) itself is better still. This comparison also makes it clear that both of these approximations approach the correct first-order propagator as $\Delta x\to 0$.

Finally, we note that the multidimensional version of eqs. (14) and (15) is of the same form, i.e. the action is the time integral over a straight line trajectory,

$$S(\boldsymbol{x}_f,\boldsymbol{x}_0;\Delta t)=\frac{m}{2\Delta t}|\Delta\boldsymbol{x}|^2-\Delta t\int_0^1 V((1-\xi)\boldsymbol{x}_0+\xi\boldsymbol{x}_f)\,d\xi, \tag{17a}$$

where $\Delta\boldsymbol{x}=\boldsymbol{x}_f-\boldsymbol{x}_0$ and the Van Vleck determinant is

$$\det\left(-\frac{\partial^2 S}{\partial x_0^i\,\partial x_f^j}\right)=\det\left(\frac{m}{\Delta t}\delta_{ij}+\Delta t\int_0^1 \xi(1-\xi)\,\frac{\partial^2 V}{\partial x_i\,\partial x_j}[(1-\xi)\boldsymbol{x}_0+\xi\boldsymbol{x}_f]\,d\xi\right). \tag{17b}$$

The first-order propagator for an F-dimensional Cartesian Hamiltonian is then

$$\langle\boldsymbol{x}_f|\exp(-iH\Delta t/\hbar)|\boldsymbol{x}_0\rangle=\left(\frac{\det(-\partial^2 S/\partial\boldsymbol{x}_f\,\partial\boldsymbol{x}_0)}{(2\pi i\hbar)^F}\right)^{1/2}\exp(iS/\hbar), \tag{17c}$$

with S given by eq. (17a).

3. Applications

We illustrate the ideas discussed in section 2 by presenting the path integral evaluation of the Boltzmann operator in the coordinate representation for a harmonic potential and a double well potential.

3.1. Harmonic potential

With $V(x)=\frac{1}{2}m\omega^2x^2$, eqs. (4), (14) and (15) give the following result for the first-order propagator:

$$\langle x_f|\exp(-iH\Delta t/\hbar)|x_0\rangle=\left(\frac{m}{2\pi i\hbar\Delta t}\right)^{1/2}(1+\tfrac{1}{6}\omega^2\Delta t^2)^{1/2}\exp\left(\frac{im}{2\hbar\Delta t}\Delta x^2-\tfrac{1}{6}i\Delta t\,m\omega^2(x_f^2+x_fx_0+x_0^2)\right). \tag{18}$$

In contrast, the "trapezoid rule" form of the Trotter product formula (eq. (2)) gives

$$\langle x_f|\exp(-iH\Delta t/\hbar)|x_0\rangle=\left(\frac{m}{2\pi i\hbar\Delta t}\right)^{1/2}\exp\left(\frac{im}{2\hbar\Delta t}\Delta x^2-\tfrac{1}{4}i\Delta t\, m\omega^2(x_f^2+x_0^2)\right). \tag{19}$$

One can readily check that eq. (18) is the correct expansion through order Δt of the exact propagator for the harmonic oscillator [1],

$$\langle x_f|\exp(-iH\Delta t/\hbar)|x_0\rangle=\left(\frac{m\omega}{2\pi i\hbar\sin\omega\Delta t}\right)^{1/2}\exp\left(\frac{im\omega}{2\sin\omega\Delta t}\left[(x_f^2+x_0^2)\cos\omega\Delta t-2x_f x_0\right]\right), \tag{20}$$

while eq. (19) is not [a1]. We point out that Doll et al.'s [5,6] short time propagator, obtained according using the partial averaging methodology (eq. (6.5) of ref. [6]), is not (in spite of the authors' claim) correct through $\mathcal{O}(\Delta t^2)$.

We now use the various short time approximations for the propagator in the discretized path integral, eq. (1), to obtain the coordinate matrix element of the propagator for time $t=N\Delta t$. By straightforward algebra, it is possible to show that use of the Trotter product formula, eq. (19), gives for $x_0=x_N=0$:

$$\langle 0|\exp(-iHt/\hbar)|0\rangle=\left(\frac{m}{2\pi i\hbar t}\right)^{1/2}\prod_{k=1}^{N-1}\left(1-\frac{\omega^2t^2}{4N^2\sin^2(k\pi/2N)}\right)^{-1/2}. \tag{21}$$

On the other hand, the first-order propagator of eq. (18) gives

$$\langle 0|\exp(-iHt/\hbar)|0\rangle=\left(\frac{m}{2\pi i\hbar t}\right)^{1/2}\left(1+\frac{\omega^2t^2}{6N^2}\right)^{N/2}\prod_{k=1}^{N-1}\left[\cot^2\left(\frac{k\pi}{2N}\right)-\frac{\omega^2t^2}{6N^2}-\frac{\omega^2t^2}{12N^2}\csc^2\left(\frac{k\pi}{2N}\right)\right]^{-1/2}, \tag{22}$$

and inclusion of the third term in the action, i.e. the *third-order propagator*, gives

$$\langle 0|\exp(-iHt/\hbar)|0\rangle=\left(\frac{m}{2\pi i\hbar t}\right)^{1/2}\left(1+\frac{\omega^2t^2}{6N^2}+\frac{7\omega^4t^4}{360N^4}\right)^{N/2}$$

$$\times\prod_{k=1}^{N-1}\left[\cot^2\left(\frac{k\pi}{2N}\right)-\frac{\omega^2t^2}{6N^2}-\frac{7\omega^4t^4}{360N^4}-\left(\frac{\omega^2t^2}{12N^2}+\frac{\omega^4t^4}{360N^4}\right)\csc^2\left(\frac{k\pi}{2N}\right)\right]^{-1/2}. \tag{23}$$

Fig. 1 compares the relative error given by eqs. (21), (22), and (23) for the case of imaginary time $t=-i\hbar\beta$, as a function of N, the number of time "slices". The dimensionless imaginary time is $\hbar\omega\beta=\pi$. One sees that the results given by the first-order propagator converge to the correct value considerably faster than those of

[a1] It was this observation, that the standard short time approximation, eq. (19), is not correct to order Δt even for the harmonic oscillator, that led us to search for the correct result.

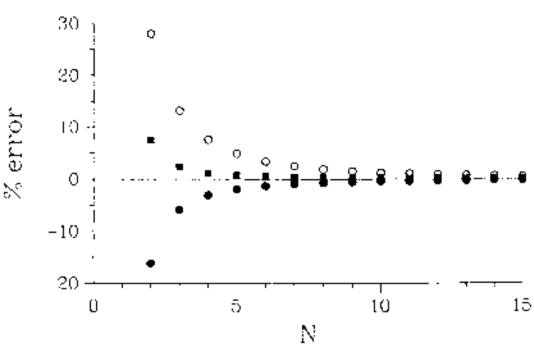

Fig. 1. The relative error, (approximate − exact)/exact, made by the three propagators discussed in section 2 for the 0–0 coordinate matrix element of the Boltzmann operator with a harmonic potential for the value of $\hbar\omega\beta=\pi$, as a function of N (cf. eqs. (21), (22), and (23)). Open circles: Trotter product formula, eq. (21). Solid circles: first-order propagator, eq. (22). Squares: third-order propagator, eq. (23).

the conventional Trotter product, requiring only about half as large a value of N to reduce the error to a few percent. The third-order propagator gives still faster convergence, requiring only about half the value of N as the first-order result.

3.2. Double well potential

For a general potential function, one must evaluate the many-dimensional integral of eq. (1) numerically. For the case of imaginary time this is straightforward to do using Monte Carlo methods [14]. Moreover, procedures have recently been developed [15–17] whereby Monte Carlo methods can be effectively used to evaluate the real time propagator, for which the integrand is oscillatory. Since the goal of the present paper is to estimate the success of the new short time propagators obtained in section 2, we consider imaginary time applications in the remainder of this section.

With the standard Trotter product formula, the path integral representation for the imaginary time propagator becomes

$$\langle x_N|\exp(-\beta H)|x_0\rangle = \left(\frac{mN}{2\pi\hbar^2\beta}\right)^{N/2} \int_{-\infty}^{\infty} \mathrm{d}x_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}x_{N-1} \exp\left(-\frac{mN}{2\hbar^2\beta}\sum_{k=1}^{N}(x_k-x_{k-1})^2 - \frac{\beta}{2N}\sum_{k=1}^{N}[V(x_k)+V(x_{k-1})]\right). \tag{24}$$

Exactly equivalent to this is Coalson's [13] quasi-Fourier representation,

$$\langle x_N|\exp(-\beta H)|x_0\rangle = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2} \exp\left(-\frac{m}{2\hbar^2\beta}(x_N-x_0)^2\right) \times \int_{-\infty}^{\infty} \mathrm{d}a_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}a_{N-1} \exp\left(-\pi\sum_{k=1}^{N-1} a_k^2 - \frac{\beta}{2N}\sum_{k=1}^{N}[V(x_k)+V(x_{k-1})]\right), \tag{25}$$

where

$$x_k = x_0 + (x_N - x_0)\frac{k}{N} + \left(\frac{\pi\hbar t}{m}\right)^{1/2} \frac{1}{N}\sum_{k'=1}^{N-1} a_{k'} \frac{\sin(\pi k k'/N)}{\sin(\pi k'/2N)}, \tag{26}$$

i.e. eq. (25) is obtained from (24) simply by changing integration variables from $\{x_k\}$ to $\{a_k\}$ according to eq. (26). It is useful to carry out the Monte Carlo integration in the $\{a_k\}$ variables because the kinetic energy part of the action is diagonal in them.

The path integral expression corresponding to eq. (25) that results from using the first- (or third-) order short time propagator of section 2 is obtained simply by replacing the average potential $\frac{1}{2}[V(x_k)+V(x_{k-1})]$ in eq. (25) by the corresponding corrected expressions derived in section 2. and also multiplying the integrand by the factor that arises from the Van Vleck determinants. For the first-order short time propagator, for example. the replacement in eq. (25) is

$$\tfrac{1}{2}[V(x_k)+V(x_{k-1})] \rightarrow \frac{1}{x_k - x_{k-1}} \int_{x_{k-1}}^{x_k} V(x)\,\mathrm{d}x \tag{27a}$$

and the extra factor arising from the Van Vleck determinants is

$$\prod_{k=1}^{N-1}\left[1-\left(\frac{\hbar\beta}{N}\right)^2 \frac{1}{2m(x_k-x_{k-1})^2}\left(\tfrac{1}{2}[V(x_k)+V(x_{k-1})] - \frac{1}{x_k-x_{k-1}}\int_{x_{k-1}}^{x_k} V(x)\,\mathrm{d}x\right)\right]^{1/2}. \tag{27b}$$

Since the Monte Carlo integration over the variables $\{a_k\}$ in eq. (25) – either as it stands or with the mod-

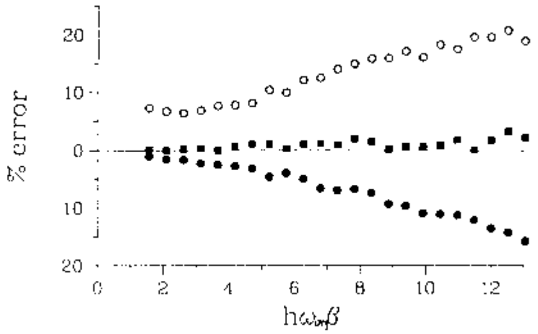

Fig. 2. Same as fig. 1, but for the off-diagonal coordinate matrix element of the Boltzmann operator for a double well potential (cf. eq. (28)). The imaginary frequency at the top of the barrier is $\omega_{im} = 1140\ cm^{-1}$. The "step size" is fixed to the value of $\hbar\omega_{im}\beta/N = \pi/6$. Open circles: Trotter product formula. Solid circles: first-order propagator. Squares: third-order propagator. The Monte Carlo statistical error bars are of the order of the size of the marker points.

ifications given by eq. (27) – is an un-normalized Monte Carlo average, one must use the charging algorithm [14,18] as before [16] to carry out the calculation.

The application we have made is to the symmetric double well potential,

$$V(x) = -c_1 x^2 + c_2 x^4, \tag{28}$$

with the coefficients chosen so that the barrier height is 7.8 kcal/mol and the minima are located at $x_{\pm} = \pm 0.53$ Å. The mass is chosen to be that of a hydrogen atom. These parameters correspond roughly to the potential for H-atom transfer in malonaldehyde [19].

Fig. 2 compares the results for the off-diagonal element of the Boltzmann operator,

$$\langle x_- | \exp(-\beta H) | x_+ \rangle, \tag{29}$$

obtained by the three short time propagators discussed above as a function of $\hbar\omega_{im}\beta$ with fixed β/N, where ω_{im} is the imaginary frequency at the top of the barrier. This quantity is closely related to the tunneling splitting between the two nearly degenerate eigenstates of the double well [20]. The first-order propagator is clearly superior to the Trotter product formula, in particular for small values of β (high temperatures); the third-order propagator gives essentially exact results (within the Monte Carlo error bars) for all values of β considered.

4. Concluding remarks

The short time propagators developed in section 2, eq. (12) together with eq. (4), are thus seen to be a significant improvement over the conventional one. The first-order propagator requires calculation of the average of the potential over the time increment, and the third-order one requires in addition the variance of the potential. If the potential function is not too complicated, this is only a modest increase in complexity compared to the conventional procedure. We thus believe that these new short time propagators will find utility in numerical path integral calculations.

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Note added

Since completion of this work we have become aware that the first term in the power series expansion of the propagator derived in section 2 is the same as that obtained previously by Fujiwara, Osborn and Wilk [21]. To our knowledge, the present paper is the first use of this type of short time approximation in a Feynman path integral.

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