Exponential power series expansion for the quantum time evolution operator

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The coordinate matrix element of the time evolution operator, $\exp[-i\hat{H}t/\hbar]$, is determined by expanding (its exponent) in a power series in t. Recursion relations are obtained for the expansion coefficients which can be analytically evaluated for any number of degrees of freedom. Numerical application to the tunneling matrix element in a double well potential and to the reactive flux correlation function for a barrier potential show this approach to be a dramatic improvement over the standard short time approximation for the propagator. Its use in a Feynman path integral means that fewer "time slices" in the matrix product $\exp[(-i/\hbar)\Delta t\hat{H}]^N$, $\Delta t = t/N$, will be required. The first few terms in the present expansion constitute a fully quantum version of the short time propagator recently obtained by us using semiclassical methods [Chem. Phys. Lett. **151**, 1 (1988)].

I. INTRODUCTION

Feynman path integration[1,2] continues to receive considerable attention as a means of describing the dynamics (via the time evolution operator $e^{-iHt/\hbar}$) and statistical mechanics (via the Boltzmann operator $e^{-\beta H}$) of quantum systems. One reason for this attention is that path integrals can be efficiently applied to systems with many degrees of freedom. Another attractive feature is that a "bath" of harmonic degrees of freedom can be integrated out using influence functional methodology,[1] thereby obtaining (without approximation!) a path integral involving only the remaining degrees of freedom of the "system."

In the standard path integral development one obtains the propagator for a net time increment t by multiplying together N propagators each for the shorter time increment $\Delta t \equiv t/N$ (all in the coordinate representation),

$$\langle \mathbf{x}_N|e^{-iHt/\hbar}|\mathbf{x}_0\rangle = \int d\mathbf{x}_{N-1} \cdots \int d\mathbf{x}_1 \prod_{k=1}^{N} \langle \mathbf{x}_k|e^{-iH\Delta t/\hbar}|\mathbf{x}_{k-1}\rangle. \tag{1.1}$$

It is thus necessary to know the (coordinate matrix of the) propagator only for a short time Δt and then to perform the multidimensional integral over all "intermediate" positions. Because the integral will in general be of high dimensionality—particularly so if N is large and the system consists of many degrees of freedom—the only generally feasible approach is some kind of Monte Carlo integration procedure.[3]

It is important to emphasize that Eq. (1.1) is actually exact for any number (N) of time slices; the only thing that requires large N is that the approximation used for the short time, or single step propagator in the integrand of Eq. (1.1),

$$\langle \mathbf{x}_k|e^{-iH\Delta t/\hbar}|\mathbf{x}_{k-1}\rangle, \tag{1.2}$$

be sufficiently accurate. Large N thus means that the single step propagator need be accurate only for a very short time $\Delta t \equiv t/N$. In practice, though, one would like for the single step propagators to be accurate for as long a time Δt as possible, so that N can be taken as small as possible (for a given net time increment t). The (obvious) reason for this is to keep the number of Monte Carlo integration variables as small as possible.

The most commonly used[2] approximation for the short time propagator is obtained from the Trotter formula,[4]

$$\langle \mathbf{x}_k|e^{-iH\Delta t/\hbar}|\mathbf{x}_{k-1}\rangle = \left(\frac{m}{2\pi i\hbar\Delta t}\right)^{(F/2)} \exp\left[\frac{im}{2\hbar\Delta t}|\mathbf{x}_k - \mathbf{x}_{k-1}|^2\right] \times \exp\left\{-\frac{i\Delta t}{2\hbar}[V(\mathbf{x}_k) + V(\mathbf{x}_{k-1})]\right\}, \tag{1.3}$$

where the Hamiltonian has been assumed to be of Cartesian form [see Eq. (2.1) below] for F degrees of freedom. In a preceding Letter[5] we noted that Eq. (1.3) is actually not correct to $O(\Delta t)$, the correct result to this order having the following modification in the exponent of the last factor (i.e., the potential energy part)

$$\tfrac{1}{2}[V(\mathbf{x}_k) + V(\mathbf{x}_{k-1})] \rightarrow \int_0^1 d\xi\, V[\mathbf{x}_{k-1} + (\mathbf{x}_k - \mathbf{x}_{k-1})\xi]. \tag{1.4}$$

This modified, "first order" propagator, which was obtained using semiclassical methods, was shown to be considerably more efficient than the standard one, Eq. (1.3). By more efficient we mean that results to a given level of accuracy are obtained with a smaller value of N. [Both Eq. (1.3) and the modification of Eq. (1.4) give the correct result in Eq. (1.1) in the limit $N \rightarrow \infty$.]

This paper pursues the quest for better short time propagators, i.e., analytically obtainable, easily evaluateable approximations for the single step propagator, Eq. (1.2), that are accurate for as long a time Δt as possible. The basic idea is that used in our earlier paper,[5] namely expanding the exponent of the propagator in a power series in Δt,

$$(\Delta t)^{-F/2}\exp\left[\frac{i}{\hbar}\left(\frac{W_0}{\Delta t} + W_1 + W_2\Delta t + W_3\Delta t^2 + \cdots\right)\right], \tag{1.5}$$

a form suggested to us by the standard short time approximation, Eq. (1.3). (It was our realization that the exponent

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of Eq. (1.3) is not correct through order Δt that led us to search for the propagator that *is* correct to this order, and then also for higher order terms.) The development given in this paper is more general than that in our earlier Letter: it is fully quantum mechanical (rather than semiclassical) and derived for multidimensional systems, and it shows more systematically how terms of arbitrary order can be determined.

The general development is given in Sec. II, and Sec. III shows how these results are modified if there is a vector potential (e.g., from an electromagnetic field) in the Hamiltonian. Section IV shows how the reactive flux correlation function is expressed in terms of this expansion for the propagator. Numerical calculations of tunneling matrix elements in a double well potential and of reactive flux correlation functions for a barrier potential are presented in Sec. V. Results for both the single step propagator itself and path integrals using it show that the number of time slices (N) can be reduced considerably using these new expressions.

Finally, to conclude this introduction it should be noted that other workers have also presented methods for obtaining better short time propagators. We mention specifically the work of Kono, Takasaka, and Lin[6] who have used an expression proposed by Takahashi and Imada.[7] As given, though, this expression applies only to evaluation of the partition function, $\mathrm{tr}(e^{-\beta H})$, and not to general matrix elements. Suzuki[8] has also described ways for correcting the Trotter product formula [i.e., Eq. (1.3)]. Another useful approach is the partial averaging scheme developed by Doll and co-workers,[9] which also has the effect of reducing the number of Monte Carlo integration variables. Schweizer *et al.*[10] have used first order time-dependent perturbation theory and also a variational approximation to improve the standard short time propagator. Also, various semiclassical approximations[11] for the propagator (and for the Boltzmann operator) have been suggested[12] for use as the single step propagator in a path integral.

II. POWER SERIES FOR THE QUANTUM MECHANICAL PROPAGATOR

Throughout this section we consider simple (but multidimensional) Cartesian Hamiltonian operators of the form

$$\hat{H}=\frac{\hat{\mathbf{p}}^2}{2m}+V(\hat{\mathbf{x}}), \tag{2.1}$$

where $\{\hat{\mathbf{x}},\hat{\mathbf{p}}\}=\{\hat{x}_i\equiv x_i,\hat{p}_i\equiv\hbar/i\,\partial/\partial x_i\}$ for $i=1,\ldots,F$. We wish to determine an analytic approximation for the coordinate matrix element of the single step propagator

$$\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}_0\rangle \tag{2.2}$$

for use in Feynman path integrals, as discussed in the Introduction. (With the usual transcription $t\to -i\hbar\beta$, we are also, of course, considering such approximations for the Boltzmann operator $e^{-\beta\hat{H}}$.) The approximation must be correct in the limit $t\to 0$, but for the sake of efficiency in a path integral one would like it to be accurate for as long a time as possible.

In the limit $t\to 0$ one knows the limiting form of the propagator to be

$$\lim_{t\to 0}\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}_0\rangle=\left(\frac{m}{2\pi i\hbar t}\right)^{F/2}\exp\left[\frac{im}{2\hbar t}|\mathbf{x}-\mathbf{x}_0|^2\right], \tag{2.3}$$

so the *ansatz* we choose is

$$\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}_0\rangle=t^{-F/2}e^{(i/\hbar)W(\mathbf{x},t)}, \tag{2.4a}$$

where $W(\mathbf{x},t)$ is expanded as a power series in t as

$$W(\mathbf{x},t)=\frac{1}{t}\sum_{n=0}t^nW_n(\mathbf{x})=\sum_{n=0}t^{n-1}W_n(\mathbf{x}). \tag{2.4b}$$

(W also depends on the initial condition $\mathbf{x}_0$, but to keep the notation simple we do not indicate this explicitly.) In light of Eq. (2.3), we anticipate the form for the first two terms in the expansion (2.4b) to be

$$W_0(\mathbf{x})=\frac{m}{2}|\mathbf{x}-\mathbf{x}_0|^2, \tag{2.5a}$$

$$e^{(i/\hbar)W_1(\mathbf{x})}=\left(\frac{m}{2\pi i\hbar}\right)^{F/2}, \tag{2.5b}$$

so that Eqs. (2.4) and (2.5) may also be combined to read

$$\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}_0\rangle=\langle\mathbf{x}|e^{-i\hat{H}_0t/\hbar}|\mathbf{x}_0\rangle\times\exp\left[\frac{i}{\hbar}\sum_{n=2}t^{n-1}W_n(\mathbf{x})\right], \tag{2.6}$$

where the first factor on the right-hand side is the free particle propagator, Eq. (2.3) (i.e., $H_0=\hat{\mathbf{p}}^2/2m$).

To determine the various terms $\{W_n(\mathbf{x})\}$ in the expansion (2.4b) we use the fact that the propagator satisfies the time-dependent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{x})-i\hbar\frac{\partial}{\partial t}\right]\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}_0\rangle=0, \tag{2.7}$$

where $\nabla^2=\sum_{i=1}^F\partial^2/\partial x_i^2$. Substituting Eq. (2.4) into Eq. (2.7) and equating like powers of t leads in a straightforward way to the following equations for the functions $\{W_n(\mathbf{x})\}$:

$$0=i\hbar\frac{F}{2}\delta_{n,1}+V(\mathbf{x})\delta_{n,2}+(n-1)W_n(\mathbf{x})+\frac{1}{2m}\sum_{n'=0}^{n}\nabla W_{n'}(\mathbf{x})\cdot\nabla W_{n-n'}(\mathbf{x})-\frac{i\hbar}{2m}\nabla^2W_{n-1}(\mathbf{x}), \tag{2.8}$$

for $n=0,1,2,\ldots$ ($W_{-1}\equiv 0$). For $n=0$ and 1 these equations are, respectively,

$$W_0(\mathbf{x})=\frac{1}{2m}|\nabla W_0(\mathbf{x})|^2 \tag{2.9a}$$

$$0=i\hbar\frac{F}{2}+\frac{1}{m}\nabla W_0(\mathbf{x})\cdot\nabla W_1(\mathbf{x})-\frac{i\hbar}{2m}\nabla^2W_0(\mathbf{x}), \tag{2.9b}$$

and one can easily verify that the previously anticipated solutions for $W_0(\mathbf{x})$ and $W_1(\mathbf{x})$, namely Eq. (2.5), do indeed satisfy Eq. (2.9) (noting the fact that $\nabla^2|\mathbf{x}-\mathbf{x}_0|^2=2F$). Using these solutions [Eq. (2.5)] for $W_0(\mathbf{x})$ and $W_1(\mathbf{x})$, Eq. (2.8) then gives the following equations for $W_2(\mathbf{x})$ and for all higher order terms:

$$(\mathbf{x}-\mathbf{x}_0)\cdot\nabla W_2(\mathbf{x})+W_2(\mathbf{x})=-V(\mathbf{x}), \tag{2.10a}$$

$$(\mathbf{x}-\mathbf{x}_0)\cdot\nabla W_n(\mathbf{x}) + (n-1)W_n(\mathbf{x})$$
$$= -\frac{1}{2m}\sum_{n'=2}^{n}\nabla W_{n'}(\mathbf{x})\cdot\nabla W_{n-n'+1}(\mathbf{x}) + \frac{i\hbar}{2m}\nabla^2 W_{n-1}(\mathbf{x}), \tag{2.10b}$$

for $n = 3,4,\ldots$.

Note that Eqs. (2.10) are all linear inhomogeneous first order differential equations of the form

$$(\mathbf{x}-\mathbf{x}_0)\cdot\nabla y(\mathbf{x}) + (n-1)y(\mathbf{x}) = a(\mathbf{x}), \tag{2.11}$$

where the right-hand side $a(\mathbf{x})$ is a known inhomogeneity. One can verify by direct substitution that the solution to Eq. (2.11) is

$$y(\mathbf{x}) = \int_0^1 d\xi\, \xi^{n-2} a(\mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi). \tag{2.12}$$

To show this, note first that

$$\nabla y(\mathbf{x}) \equiv \frac{\partial}{\partial \mathbf{x}} y(\mathbf{x})$$
$$= \int_0^1 d\xi\, \xi^{n-2}\frac{\partial}{\partial \mathbf{x}} a(\mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi)$$
$$= \int_0^1 d\xi\, \xi^{n-1}\frac{\partial}{\partial \mathbf{x}'} a(\mathbf{x}')\Big|_{\mathbf{x}'=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi}, \tag{2.13}$$

so that

$$(\mathbf{x}-\mathbf{x}_0)\cdot\nabla y(\mathbf{x}) = \int_0^1 d\xi\, \xi^{n-1}(\mathbf{x}-\mathbf{x}_0)\cdot\frac{\partial}{\partial \mathbf{x}'} a(\mathbf{x}')\Big|_{\mathbf{x}'=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi} \tag{2.14}$$

But

$$(\mathbf{x}-\mathbf{x}_0)\cdot\frac{\partial}{\partial \mathbf{x}'} a(\mathbf{x}')\Big|_{\mathbf{x}'=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi}$$
$$= \frac{d}{d\xi} a(\mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi), \tag{2.15}$$

so that Eq. (2.14) becomes

$$(\mathbf{x}-\mathbf{x}_0)\cdot\nabla y(\mathbf{x}) = \int_0^1 d\xi\, \xi^{n-1}\frac{d}{d\xi} a(\mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi). \tag{2.16}$$

Integration by parts on the right-hand side of Eq. (2.16) gives

$$\xi^{n-1} a(\mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi)\Big|_0^1$$
$$- \int_0^1 d\xi (n-1)\xi^{n-2} a(\mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi)$$
$$= a(\mathbf{x}) - (n-1)\int_0^1 d\xi\, \xi^{n-2} a(\mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi)$$
$$= a(\mathbf{x}) - (n-1)y(\mathbf{x}),$$

whereby Eq. (2.16) becomes Eq. (2.11), thus verifying that Eq. (2.12) is the solution.

Applying the results of the previous paragraph to Eq. (2.10a) gives the solution for $W_2(\mathbf{x})$ as

$$W_2(\mathbf{x}) = -\int_0^1 d\xi\, V(\mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi), \tag{2.17}$$

and application to Eq. (2.10b) gives an expression for $W_n(\mathbf{x})$ in terms of lower order terms,

$$W_n(\mathbf{x}) = \int_0^1 d\xi\, \xi^{n-2}\Big[\frac{i\hbar}{2m}\nabla^2 W_{n-1}(\mathbf{x}') - \frac{1}{2m}\sum_{n'=2}^{n-2}\nabla W_{n'}(\mathbf{x}')\cdot\nabla W_{n-n'}(\mathbf{x}')\Big]\Big|_{\mathbf{x}'=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi}, \tag{2.18}$$

for $n = 3,4,\ldots$. W_3, W_4,... can thus be determined recursively from Eq. (2.18).

Thus, the explicit solution for $W_3(\mathbf{x})$ is

$$W_3(\mathbf{x}) = \frac{i\hbar}{2m}\int_0^1 d\xi\, \xi \nabla^2 W_2(\mathbf{x}')\Big|_{\mathbf{x}'=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi}, \tag{2.19}$$

with $W_2(\mathbf{x})$ given by Eq. (2.17). Since

$$\nabla^2 W_2(\mathbf{x}') \equiv -\int_0^1 d\xi'\frac{\partial^2}{\partial \mathbf{x}'^2} V(\mathbf{x}_0 + (\mathbf{x}'-\mathbf{x}_0)\xi')$$
$$= -\int_0^1 d\xi'\, \xi'^2 \frac{\partial^2}{\partial \mathbf{x}''^2} V(\mathbf{x}'')\Big|_{\mathbf{x}''=\mathbf{x}_0+(\mathbf{x}'-\mathbf{x}_0)\xi'},$$

Eq. (2.19) becomes

$$W_3(\mathbf{x}) = -\frac{i\hbar}{2m}\int_0^1 d\xi\, \xi \int_0^1 d\xi'\, \xi'^2 \times \frac{\partial^2}{\partial \mathbf{x}''^2} V(\mathbf{x}'')\Big|_{\mathbf{x}''=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi\xi'}.$$

Changing integration variables appropriately allows one of these integrations to be performed, giving finally

$$W_3(\mathbf{x}) = -\frac{i\hbar}{2m}\int_0^1 d\xi\, \xi(1-\xi)\nabla^2 V(\mathbf{x}')\Big|_{\mathbf{x}'=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi}. \tag{2.20}$$

The next term, $W_4(\mathbf{x})$, is then given from Eq. (2.18) as

$$W_4(\mathbf{x}) = \int_0^1 d\xi\, \xi^2\Big[\frac{i\hbar}{2m}\nabla^2 W_3(\mathbf{x}') - \frac{1}{2m}|\nabla W_2(\mathbf{x}')|^2\Big]\Big|_{\mathbf{x}'=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi}. \tag{2.21}$$

Using the previously obtained solutions for W_2 and W_3 and proceeding in a manner similar to the above paragraph, one obtains the following result for W_4:

$$W_4(\mathbf{x}) = -\frac{1}{m}\int_0^1 d\xi \int_0^\xi d\xi'\, \xi'(1-\xi)\nabla V(\mathbf{x}')\cdot\nabla V(\mathbf{x}'') + \frac{\hbar^2}{8m^2}\int_0^1 d\xi\, \xi^2(1-\xi)^2(\nabla^2)^2 V(\mathbf{x}') \tag{2.22}$$

with $\mathbf{x}' = \mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi$ and $\mathbf{x}'' = \mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi'$, and where

$$(\nabla^2)^2 = \Big(\sum_{i=1}^{F}\frac{\partial^2}{\partial \mathbf{x}_i^2}\Big)^2 = \sum_{i,j=1}^{F}\frac{\partial^4}{\partial \mathbf{x}_i^2 \partial \mathbf{x}_j^2}.$$

It is clear that one can continue using Eq. (2.18) to construct higher order terms, though the algebra becomes tedious. If the potential is sufficiently simple (e.g., a polynomial) that the various integrals are doable analytically, then computer algebra manipulators (e.g., MACSYMA or *Mathe-*

matica) can be used to do this very efficiently. This is what has been done, in fact, for the examples discussed in Sec. V to obtain terms up to W_{10}.

It is also possible, of course, to attempt to extend the region of usefulness of the power series expansion for $W(\mathbf{x},t)$ by converting it into a Padé[13] approximant, i.e.,

$$\sum_{n=0}^{L+M} t^n W_n(\mathbf{x}) \to \sum_{n=0}^{L} t^n p_n(\mathbf{x}) \Big/ \left[1 + \sum_{n=1}^{M} t^n q_n(\mathbf{x})\right]. \tag{2.23}$$

There is a well established procedure for determining the $L+M+1$ coefficients $\{p_n(\mathbf{x})\}$, $\{q_n(\mathbf{x})\}$ from the $L+M+1$ coefficients $\{W_n(\mathbf{x})\}$ which is also amenable to computer algebraic manipulation. The results discussed in Sec. V do indeed show that the Padé procedure extends the accuracy of the above propagator to longer times.

Before concluding this section we note that for the case of one dimension ($F=1$) the above integrals can be simplified by integration by parts. Thus, Eqs. (2.17), (2.20), and (2.22) can be written in this case as

$$W_2(x) = -\frac{1}{\Delta x}\int_{x_0}^{x} dx'\, V(x'), \tag{2.24a}$$

$$W_3(x) = -\frac{i\hbar}{2m\Delta x^2}\left[V(x_0) + V(x) - \frac{2}{\Delta x}\int_{x_0}^{x} dx'\, V(x')\right], \tag{2.24b}$$

$$\begin{aligned} W_4(x) = {} & \frac{-1}{2m\Delta x^4}\left\{\Delta x\int_{x_0}^{x} V(x')^2\,dx' - \left[\int_{x_0}^{x} V(x')dx'\right]^2\right\} \\ & - \frac{3\hbar^2}{2m^2\Delta x^4}\left\{V(x_0) + V(x) - \frac{2}{\Delta x}\int_{x_0}^{x} V(x')dx' \right. \\ & \left. - \frac{\Delta x}{6}[V'(x) - V'(x_0)]\right\}, \end{aligned} \tag{2.24c}$$

where $\Delta x = x - x_0$. We note that Eq. (2.24a) for $W_2(x)$ is the same exponent obtained by us previously[5] using semiclassical arguments and also that expansion of the exponential factor involving W_3 of Eq. (2.24b) gives the corresponding Van Vleck determinant. Furthermore, the *first term* of Eq. (2.24c) is the same third order term obtained before semiclassically. In the present fully quantum treatment, though, we obtain a "quantum correction" to this term, the second term of Eq. (2.24c) (which is proportional to $\hbar^2$).

Finally, it is illuminating to see the limiting form taken by the various terms in Eq. (2.24) as $x \to x_0$. It is not hard to show that

$$\lim_{x\to x_0} W_2(x) = -V(x_0), \tag{2.25a}$$

$$\lim_{x\to x_0} W_3(x) = -\frac{i\hbar}{12m}V''(x_0), \tag{2.25b}$$

$$\lim_{x\to x_0} W_4(x) = -\frac{V'(x_0)^2}{24m} + \frac{\hbar^2}{240m^2}V''''(x_0). \tag{2.25c}$$

Thus for the case $t = -i\hbar\beta$, the equilibrium density is given by this single step propagator as

$$\begin{aligned} \langle x|e^{-\beta H}|x\rangle = {} & \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2}\exp\left\{-\beta V(x)\right. \\ & - \frac{\hbar^2\beta^2}{12m}V''(x) + \frac{\hbar^2\beta^3}{24m}\left[V'(x)^2\right. \\ & \left.\left. - \frac{\hbar^2}{10m}V''''(x)\right] + O(\beta^4)\right\}. \end{aligned} \tag{2.26}$$

If one expands the exponential and keeps only the terms through order $\hbar^2$, then one obtains the well-known Wigner[14] correction factor to the classical density,

$$\begin{aligned} \langle x|e^{-\beta H}|x\rangle = {} & \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2} e^{-\beta V(x)} \\ & \times\left[1 - \frac{\hbar^2\beta^2}{12m}V''(x) + \frac{\hbar^2\beta^3}{24m}V'(x)^2\right]. \end{aligned} \tag{2.27}$$

III. HAMILTONIAN WITH VECTOR POTENTIAL

For completeness we show in this section how the results in Sec. II are modified if the Hamiltonian includes a vector potential that arises from an electromagnetic field,[2]

$$\hat{H} = \frac{1}{2m}\left[\hat{\mathbf{p}} - \frac{e}{c}\mathbf{A}(\hat{\mathbf{x}})\right]^2 + \mathbf{V}(\hat{\mathbf{x}}). \tag{3.1}$$

The same *ansatz* as Eq. (2.4) is chosen, and the analogous procedure leads here to the following equations for the functions $\{W_n(\mathbf{x})\}$:

$$\begin{aligned} 0 = {} & i\hbar\frac{F}{2}\delta_{n,1} + (n-1)W_n(\mathbf{x}) - \frac{i\hbar}{2m}\nabla^2 W_{n-1} + \frac{1}{2m}\sum_{n'=0}^{n}\nabla W_{n'}\cdot\nabla W_{n-n'} + \delta_{n,2}\left[V(\mathbf{x}) + \frac{e^2}{2mc^2}|\mathbf{A}(\mathbf{x})|^2\right. \\ & \left. + \frac{i\hbar e}{2mc}\nabla\cdot\mathbf{A}\right] - \frac{e}{mc}\mathbf{A}\cdot\nabla W_{n-1}, \end{aligned} \tag{3.2}$$

$n = 0,1,2,\ldots$ ($W_{-1}\equiv 0$). If the vector potential is set to zero, then Eq. (3.2) reverts to Eq. (2.8).

For $n = 0$ and 1, Eq. (3.2) gives

$$W_0(\mathbf{x}) = \frac{1}{2m}|\nabla W_0|^2, \tag{3.3a}$$

$$0 = i\hbar\frac{F}{2} + \frac{1}{m}\nabla W_0\cdot\nabla W_1 - \frac{i\hbar}{2m}\nabla^2 W_0 - \frac{e}{mc}\mathbf{A}\cdot\nabla W_0. \tag{3.3b}$$

The solution of Eq. (3.3a) for $W_0(\mathbf{x})$ is the same as before, Eq. (2.5a), and Eq. (3.3b) then becomes

$$(\mathbf{x}-\mathbf{x}_0)\cdot\nabla W_1 = \frac{e}{c}(\mathbf{x}-\mathbf{x}_0)\cdot\mathbf{A}(\mathbf{x}). \tag{3.4}$$

Utilizing Eqs. (2.11) and (2.12), the solution to Eq. (3.4) is found to be

$$W_1(\mathbf{x}) = W_1^{(0)} + \frac{e}{c}\int_0^1 d\xi(\mathbf{x}-\mathbf{x}_0)\cdot\mathbf{A}(\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi)$$
$$= W_1^{(0)} + \frac{e}{c}\int_{\mathbf{x}_0}^{\mathbf{x}} d\mathbf{x}'\cdot\mathbf{A}(\mathbf{x}') \tag{3.5}$$

where the constant $W_1^{(0)}$ is the field free result of Eq. (2.5b).

Utilizing the above results for W_0 and W_1, it is not hard to show that for $n = 2,3,4,\ldots$, Eq. (3.2) gives equations *identical* to the field free case, Eq. (2.10); i.e., all terms involving the vector potential cancel out. The solution of Eq. (2.10a) for $W_2(\mathbf{x})$ is thus the same as the field free case, i.e., Eq. (2.17), but the solution for $W_3(\mathbf{x})$ given by Eq. (2.18) for $n = 3$,

$$W_3(\mathbf{x}) = \int_0^1 d\xi\,\xi\left(\frac{i\hbar}{2m}\nabla^2 W_2(\mathbf{x}') - \frac{1}{m}\nabla W_2(\mathbf{x}')\cdot\nabla W_1(\mathbf{x}')\right)\Big|_{\mathbf{x}'=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi}, \tag{3.6}$$

is different from the field free case because here $\nabla W_1(\mathbf{x}) \neq 0$. From Eq. (3.5), in fact, one has

$$\nabla W_1(\mathbf{x}) = \frac{e}{c}\mathbf{A}(\mathbf{x}), \tag{3.7}$$

so that Eq. (3.6) becomes

$$W_3(\mathbf{x}) = W_3^{(0)}(\mathbf{x}) - \frac{e}{mc}\int_0^1 d\xi\,\xi\nabla W_2(\mathbf{x}')\cdot\mathbf{A}(\mathbf{x}')|_{\mathbf{x}'=\mathbf{x}_0+(\mathbf{x}-\mathbf{x}_0)\xi}, \tag{3.8}$$

where $W_3^{(0)}(\mathbf{x})$ is the field free result given by Eq. (2.20). Using the solution for $W_2(\mathbf{x})$, one obtains the following explicit result for W_3:

$$W_3(\mathbf{x}) = W_3^{(0)}(\mathbf{x}) + \frac{e}{mc}\int_0^1 d\xi\int_0^\xi d\xi'\,\frac{\xi'}{\xi}\mathbf{A}(\mathbf{x}')\cdot\nabla V(\mathbf{x}''), \tag{3.9}$$

with $\mathbf{x}' = \mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi$ and $\mathbf{x}'' = \mathbf{x}_0 + (\mathbf{x}-\mathbf{x}_0)\xi'$.

In summary, therefore, the terms $W_0(\mathbf{x})$ are the same as the field-free results of Sec. II, but $W_1(\mathbf{x})$ and $W_3(\mathbf{x})$, given by Eqs. (3.5) and (3.9), have a contribution involving the vector potential. In Eq. (3.5) the well known term that appears in the action for a Lagrangian with a vector potential is recovered.[2,15]

IV. REACTIVE FLUX CORRELATION FUNCTIONS

One potentially powerful use of path integral methodology is to evaluate reactive flux correlation functions, the integral of which gives the thermal [$\beta = (kT)^{-1}$] rate constant for a chemical reaction,

$$k(\beta) = Q_R^{-1}\int_0^\infty dt\, C_f(t), \tag{4.1}$$

where Q_R is the partition function for reactants. The version of the correlation function given by Miller, Schwartz, and Tromp[16] involves the propagator for complex time $t_c = t - i\hbar\beta/2$,

$$C_f(t) = \mathrm{tr}\left[Fe^{iHt_c^*/\hbar}Fe^{-iHt_c/\hbar}\right] \tag{4.2}$$

where F is the flux operator,

$$F = \frac{1}{2m}\left[\delta(\hat{s}-s_0)\hat{p}_s + \hat{p}_s\delta(\hat{s}-s_0)\right]; \tag{4.3}$$

s is the (Cartesian) reaction coordinate, $\hat{p}_s$ its conjugate momentum operator, and $s = s_0$ is the dividing surface that defines reactants and products. Evaluating the trace in a coordinate representation gives the following expression for the correlation function:

$$C_f(t) = \frac{\hbar^2}{2m^2}\int d\mathbf{Q}\int d\mathbf{Q}'\,\mathrm{Re}\Big[\langle s'\mathbf{Q}'|e^{-iHt_c^*/\hbar}|s\mathbf{Q}\rangle^*\frac{\partial^2}{\partial s\partial s'}\langle s'\mathbf{Q}'|e^{-iHt_c/\hbar}|s\mathbf{Q}\rangle$$
$$-\frac{\partial}{\partial s'}\langle s'\mathbf{Q}'|e^{-iHt_c^*/\hbar}|s\mathbf{Q}\rangle^*\frac{\partial}{\partial s}\langle s'\mathbf{Q}'|e^{-iHt_c/\hbar}|s\mathbf{Q}\rangle\Big], \tag{4.4}$$

where Re denotes "real part of," where $s = s' = s_0$ after differentiation, and where $\mathbf{Q}$ are the (Cartesian) coordinates for the degrees of freedom in addition to the reaction coordinate.

Since it is often the case in applications that one needs only the short time behavior of the flux correlation function, we consider in this Section the possibility of using the single step propagator developed in Sec. II to evaluate it. Specializing to the case of one dimension [and thus no coordinate $\mathbf{Q}$ in Eq. (4.4)] and writing the coordinate matrix element of the propagator in the form of Sec. II, i.e.,

$$\langle s'|e^{-iHt_c/\hbar}|s\rangle \equiv \frac{1}{t_c^{1/2}}e^{iW(s,s';t_c)/\hbar}, \tag{4.5}$$

it is not hard to show that Eq. (4.4) becomes

$$C_f(t) = \frac{1}{2m^2|t_c|}e^{-(2/\hbar)\,\mathrm{Im}\,W(0,0;t_c)}\left[-\hbar\,\mathrm{Im}\frac{\partial^2 W(s,s';t_c)}{\partial s\partial s'} - 2\left(\mathrm{Re}\frac{\partial W(s,0;t_c)}{\partial s}\right)^2\right], \tag{4.6}$$

with $s = s' = 0$ after differentiation (where the dividing surface s_0 has been chosen as $s_0 = 0$). Now expanding the exponent

$W(s,s';t_c)$ in a power series as in Eq. (2.4b) gives the final expression

$$C_f(t) = C_f^{(0)}(t)\exp\left[-\frac{2}{\hbar}\,\mathrm{Im}\sum_{n=2} t_c^{n-1} W_n(0,0)\right] \times\left[1-\frac{2|t_c|^2}{m\hbar\beta}\,\mathrm{Im}\sum_{n=2} t_c^{n-1}\frac{\partial^2 W_n(s,s')}{\partial s\partial s'}-\frac{4|t_c|^2}{m\hbar^2\beta}\left(\mathrm{Re}\sum_{n=2} t_c^{n-1}\frac{\partial W_n(s,0)}{\partial s}\right)^2\right], \tag{4.7a}$$

with $s=s'=0$, and where $C_f^{(0)}(t)$ is the free particle correlation function[16]

$$C_f^{(0)}(t) = \frac{kT}{2\pi\hbar}\,\frac{(\hbar\beta/2)^2}{[t^2+(\hbar\beta/2)^2]^{3/2}}. \tag{4.7b}$$

If the standard short time approximation, Eq. (1.3), is used for the propagator, then it is easy to show that Eq. (4.7) gives the free particle correlation function multiplied simply by a classical Boltzmann factor,

$$C_f(t) = C_f^{(0)}(t)e^{-\beta V(0)}. \tag{4.8}$$

Having the propagator expressed as a power series in time, as it is in the present methodology, is especially convenient for Boltzmann correlation functions because complex time is as easily dealt with as real (or pure imaginary) time.

V. APPLICATIONS

We first illustrate the use of the power series expansion of Sec. II, Eq. (2.4) with W_n determined from Eq. (2.18), by calculating the off-diagonal coordinate matrix element of the Boltzmann operator,

$$\langle x_-|e^{-\beta H}|x_+\rangle, \tag{5.1}$$

for the case of an electron in a one-dimensional symmetric double well potential,

$$V(x) = -c_1x^2+c_2x^4. \tag{5.2}$$

This quantity is closely related to the tunneling splitting between the two lowest eigenstates of the double well. The coefficients are chosen so that the barrier height is 4.2 eV and the two minima are located at $x_\pm = \pm 2.65$ Å.

Figure 1 shows the relative error made by truncating Eq. (2.4) at $n_{\max}=6$, 8, and 10, for *a single* (imaginary) *time step*, as a function of the dimensionless quantity $\hbar\omega_{\mathrm{im}}\beta$, where ω_{im} is the imaginary frequency at the top of the barrier. Each successive higher order is seen to reduce the error over a larger range of β. Eventually [i.e., beyond some $\beta_{\max}=\beta_{\max}(n)$], of course, the error begins to grow very rapidly; one would then need to include many more terms in the power series to obtain convergent results, or the series may not converge at all, if β exceeds its radius of convergence. A successful way of overcoming this problem is to use rational expansions such as Padé approximants. As seen in Fig. 1, the [5/3] Padé approximant (computed from the $n=0,\ldots,8$ terms of the Taylor series) converges significantly better over a much broader range of β than the corresponding Taylor expansion. It is thus seen that the recursive evaluation of the propagator according to Eq. (2.18) shows promise for calculating short or intermediate (complex) time dynamics *analytically*. It should then be useful in studying the dynamical (or equilibrium statistical mechanical) properties of *multidimensional* systems in a simple and economical way. Finally, Fig. 1 also shows the error made by using the standard Trotter formula, Eq. (1.3). As anticipated, the error increases *linearly* with β in this case, and very soon grows out of the scale of the figure.

Next, we apply the various approximations discussed above for the short time propagator to the path integral evaluation of the same quantity according to Eq. (1.1). The calculation is performed with fixed $\beta/N\approx\pi/4$. Shown in Fig. 2 are results obtained using the expansion of Eq. (2.4) truncated after the $n=3$ and $n=5$ term. Also shown are results obtained from the corresponding (i.e., of the same order) *semiclassical* expressions derived by us recently,[5] namely the *first* and *third* order propagator. Although no net quantum term appears in the $n=2$ or 3 terms in the present treatment, the effect of retaining the *exponential* form (rather than expanding it to lowest order to produce the Van Vleck determinant of the semiclassical expression) is the reduction of the error roughly by a factor of 2. The semiclassical third order propagator is seen to further reduce the error, and the corresponding quantum version yields results which are essentially indistinguishable from the exact ones within the

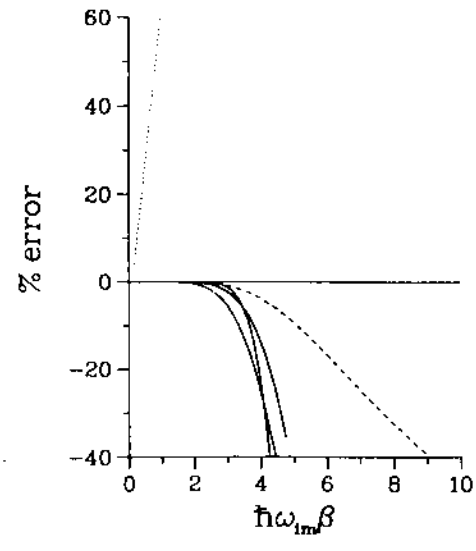

FIG. 1. Percentage error, $100\times$(approximate − exact)/exact, in the tunneling matrix element [Eq. (5.1)] for an electron in a double well potential [Eq. (5.2)], for the single step propagator in pure imaginary time ($t=-i\hbar\beta$). The barrier height is 4.2 eV and the two minima are located at $\pm$ 2.65 Å. The dotted line is the result of the standard short time propagator [Eq. (1.3)], and the solid lines the results of the exponential power series [Eq. (2.4)] for $n_{\max}=6$, 8, and 10. The dashed line is the result of the Padé approximant, Eq. (2.23), with $L=5$, $M=3$. In the abscissa, ω_{im} is the imaginary frequency at the top of the barrier.

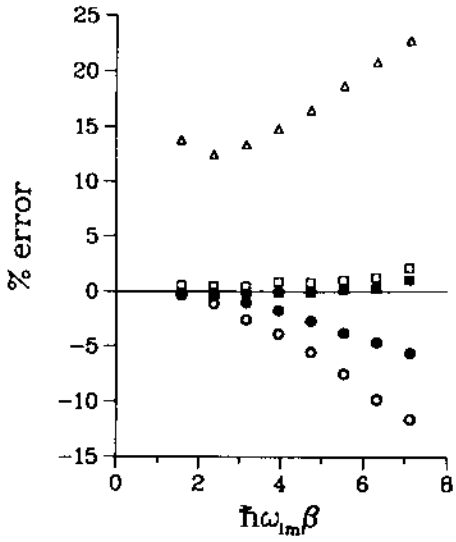

FIG. 2. Percentage error in the path integral evaluation of the off-diagonal coordinate matrix element of the Boltzmann operator, Eq. (5.1), for an electron in a double well potential, with the short time propagator given by the various approximations discussed in Sec. II. The parameters are the same as in Fig. 1. Triangles: Trotter formula; open circles: semiclassical first order propagator; open squares: semiclassical third order propagator; solid circles: quantum version of the first order propagator (terms up to W_1 included in the power series); solid squares: quantum version of the third order propagator (power series with terms up to W_3).

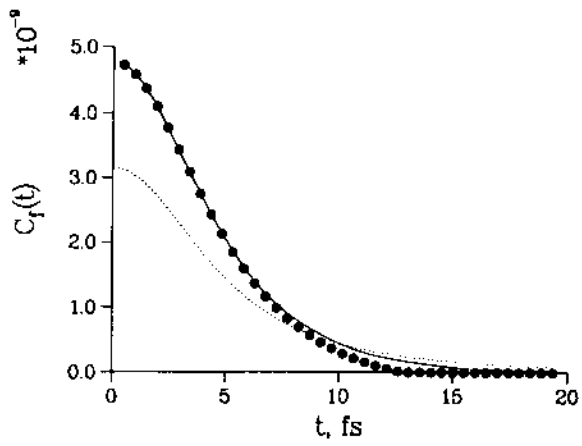

FIG. 3. The flux correlation function, Eq. (4.4), for an Eckart barrier [cf. Eq. (5.3)]. The mass is that of a hydrogen atom, and the temperature is 630 K. The barrier height is 7.5 k cal/mol and the imaginary frequency of the barrier is 1022 cm^{-1}. Solid line: exact results; circles: analytic, single step calculation by power series expansion [cf. Eq. (4.7)], with $n_{\max}=4$; Dotted line: single step evaluation of the flux correlation function using the Trotter formula [cf. Eq. (4.8)].

resolution of the figure. The error made by the Trotter formula [Eq. (1.3)] is again large compared to that of the power series.

Finally, we demonstrate the *analytic* calculation of the reactive flux correlation function as described in Sec. IV using the single step, complex time propagator of Eq. (2.4) for an Eckart barrier,

$$V(x)=\frac{V_0}{\cosh^2(ax)}. \tag{5.3}$$

The mass is taken to be that of a hydrogen atom, the temperature is $T\approx 630$ K ($\beta=500$ h^{-1}), and $V_0=7.5$ kcal/mol, $a=3.15$ Å^{-1} are typical of a hydrogen atom transfer reaction. The Eckart potential is simple enough that the necessary integrations involved in Eq. (2.18) can be performed analytically. However, it is useful to point out that one actually need not carry out all the algebra with the full potential for the flux correlation function. Since the right hand side of Eq. (4.7a) is evaluated at $x=x'=0$, one can readily see that only a *finite* number of terms in the Taylor expansion of the potential contribute to a certain order in t_c. The calculation is thus greatly simplified by expanding the potential as a polynomial, without loss of accuracy for a given order in the complex time. Symbolic algebra programs are particularly efficient in dealing with polynomials, and complex time is no more difficult to manipulate than purely imaginary (or real) time, so that the analytic calculation of the flux correlation function as described above is straightforward and free of numerical errors. The results of this procedure are shown and compared to those obtained by an accurate basis set calculation in Fig. 3. For comparison, the result obtained using the standard short time propagator, i.e., Eq. (4.8), is also shown.

VI. CONCLUDING REMARKS

The exponential power series expansion for the propagator developed in Sec. II is thus seen to be much more accurate than the standard short time approximation, Eq. (1.3), permitting one to use much larger time increments Δt in a path integral, Eq. (1.1). Of course, this more accurate propagator is more difficult to evaluate then Eq. (1.3), but should not be prohibitively so in many situations of practical interest. Padéing the power series extends its range of accuracy to even longer times.

The primary purpose we envision for this single step propagator is as an improved short time propagator for use in a path integral, Eq. (1.1). If time evolution is needed for only relatively short times, however—as is often the case for the reactive flux correlation function of Sec. IV—then it may be possible to use it for the entire time increment. The example treated in Sec. V is very encouraging in this regard. Having the propagator as a power series in time is especially convenient for Boltzmann correlation functions because one is able to deal with complex time ($t-i\hbar\beta/2$) in a very simple way.

By reducing the number of time slices that are required to evaluate a path integral, Eq. (1.1), we believe that the single step propagator described in this paper will significantly increase the feasibility of path integral calculations.

Note added in proof: Since completion of this paper we have become aware of a paper [Y. Fujiwara, T. A. Osborn, and S. F. J. Wilk, Phys. Rev. A 25, 14 (1982)] in which the same kind of exponential expansion of Sec. II has been carried out for the Boltzmann operator $e^{-\beta H}$. Fujiwara *et al.* derived the coefficients $\{W_n\}$ in the expansion by making a perturbation expansion in the potential V and then using a linked-graph method to rearrange the two expansions (one

in Δt, the other perturbation expansion in V). The reader can readily verify that the derivation in Sec. II is considerably simpler. To the best of our knowledge, the present work is the first application of the approach to Feynman path integration and to the evaluation of flux correlation functions. We are grateful to Dr. Weitao Yang for pointing this reference out to us.

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