# Accurate quantum and statistical mechanics from system-specific operator expansions

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An effective and flexible numerical scheme is proposed to calculate the quantum and statistical mechanics of multidimensional systems in a simple economic way. The basic idea is to split the Hamiltonian operator into a reference separable part, whose solution can be obtained by a combination of analytic and numerical techniques, and a term containing nonseparable interactions and then to employ a symmetric decomposition of the time evolution operator, which is exact up to a high order in the time step. The method is applicable to a wide range of coupling potentials and requires numerical effort that scales only linearly with the number of degrees of freedom involved. To verify the utility of the present approach, two model systems with strongly anharmonic mode coupling are considered. The applications show that the method accurately describes the dynamics for fairly long times with moderate coupling strengths and is still much less arduous than a general numerically exact calculation. [S1063-651X(98)03509-0]

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## I. INTRODUCTION

The calculation of quantum and statistical properties of multidimensional systems is one of the central goals of modern theoretical physics. Since exact solutions to the Schrödinger and Fokker-Planck equations are available only for a few simple cases, various analytical methods and numerical schemes have been explored to solve these equations approximately. Both approaches have their own advantages and limitations. Analytical solutions are essential to the conceptual understanding of the behavior of a system, provided the specific assumptions on which they rely are satisfied [1]. Numerical methods are also indispensable since they give detailed solutions. Their utility, however, is strongly limited by the storage requirements and execution time. Efficient schemes for basis set calculations [2–4] and iterative time-propagation methods [5–8] have proved to be extremely valuable for systems with one or two coordinates, but they are not practical for systems with more than three degrees of freedom. The use of a short time propagator [9,10] in conjunction with Monte Carlo integration [11,12] is, at least in principle, the optimal approach. The most appealing feature of this approach is perhaps that it avoids storing large-dimensional Hamiltonian matrices and wave function vectors. Instead, all dynamical (and/or finite temperature) characteristics are included in a discrete path integral representation of the propagator. In this way, the method allows treating truly multidimensional systems, though the practical applicability of numerical methods for evaluation of the discrete path integral depends critically on its dimension. The latter in turn is determined by the dimensionality of the system, as well as the accuracy of the short time propagator used. The higher the accuracy, the smaller the number $N$ of time steps (and therefore Monte Carlo integration variables) required to get convergent results for a given time increment $t$. Unfortunately, most conventional propagators remain correct only for short time steps $\tau = t/N \ll 1$. This limits considerably the time scale of many-body path integral calculations, reducing it to two or so periods of motion of quantum particles in dissipative environments [13]. Another related limitation is the necessity of doing the computations precisely, even if high precision is unwanted. This is because the error made by using standard short time propagators rapidly grows with increasing $\tau$, and beyond some $\tau_{\max}$, which is usually smaller than unity, the propagators fail to provide correct results [10].

An important exception involves problems where an arbitrary one-dimensional system is linearly coupled to a harmonic bath. Makri and co-workers [13,14] suggested a method to deal very efficiently with such situations. The starting point is an improved quasiadiabatic propagator obtained numerically in terms of the Trotter product formula and a basis set method. The approach is particularly attractive for two reasons. First, in many practical applications the quasiadiabatic propagator turns out to be correct for times sufficiently long to observe interesting physical effects. In such cases it can be used for the *entire* time increment $t$. Second, the harmonic bath appears in the path integral expression as a Gaussian integral and therefore can be integrated out *analytically*, giving rise to a nonlocal influence functional and reducing the problem to a path integral for the system coordinate only. In this way the dynamics of system-bath Hamiltonians can be calculated very accurately with *any* number of degrees of freedom for an *arbitrarily long* time increment $t$. More recently the approach was extended to a system coupled *nonlinearly* to a bath of (harmonic or anharmonic) noninteracting degrees of freedom [15]. However, the generalization has appeared to be rather complicated for practical applications.

In this paper we propose an alternative method that preserves the advantages of the aforementioned approach but also easily deals with anharmonic Hamiltonians that cannot

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be expressed in system-bath form. In Sec. II we show how to construct an improved propagator. The basic idea is to split the Hamiltonian operator into one of separable motion and a potential term that mixes the degrees of freedom and then to employ a symmetric decomposition of the evolution operator, which is exact up to a high order in the time step. In Sec. III some calculations that illustrate the idea are presented. The calculations clearly demonstrate that the method leads to a reasonable description of the dynamics already for $N=1$. Finally, in Sec. IV we give our conclusions and indicate directions of future research.

## II. CONSTRUCTION OF IMPROVED PROPAGATORS

In the study of dynamical and statistical properties of quantum systems much information can be found from an investigation of the propagator $\langle \mathbf{x}|e^{-\varepsilon H}|\mathbf{x}^0\rangle$, where $\mathbf{x}=(x_1,\ldots,x_n)$ and $H$ stands for a time-independent Cartesian Hamiltonian operator of the generic form (the summation rule over repeated indices is always implied)

$$H=-\tfrac{1}{2}D_{ii}\partial_{ii}^2+V(\mathbf{x}). \tag{2.1}$$

In the above, $D_{ij}$ is a diagonal matrix with $D_{ii}=\hbar^2/m_i$. Moreover, the parameter $\varepsilon$ entering the evolution operator $e^{-\varepsilon H}$ is either imaginary ($\varepsilon=it/\hbar$) or positive ($\varepsilon=\beta$) depending on whether quantum mechanics or statistics is concerned. Due to the formal similarities of the Schrödinger equation and the Fokker-Planck equation, we are also considering the stochastic dynamics $\langle \mathbf{x}|e^{tL}|\mathbf{x}^0\rangle$ governed by

$$L=\tfrac{1}{2}\partial_i D_{ii}\{\partial_i+[\partial_i U(\mathbf{x})]\}. \tag{2.2}$$

This is because the Fokker-Planck operator (2.2) can always be cast into the Hermitian form (2.1), with the potential $V(\mathbf{x})$ given by

$$V(\mathbf{x})=\tfrac{1}{8}D_{ii}\{[\partial_i U(\mathbf{x})]^2-2\partial_{ii}^2 U(\mathbf{x})\}. \tag{2.3}$$

In our subsequent considerations we set, without loss of generality, $\varepsilon=t$. Then the matrix element of the quantum time evolution operator $\langle \mathbf{x}|e^{-itH/\hbar}|\mathbf{x}^0\rangle$, as well as that of the Boltzmann operator $e^{-\beta H}$, can be obtained from the present treatment by the substitutions $t\to it/\hbar$ and $t\to\beta$, respectively.

The most common procedure of approximating the propagator is based on the partitioning of the Hamiltonian operator into kinetic and potential energy terms

$$H=T+V,\qquad T=-\tfrac{1}{2}D_{ii}\partial_{ii}^2,\quad V=V(\mathbf{x}) \tag{2.4}$$

and employs the Trotter breakup to split the time evolution operator into a product of exactly solvable parts

$$e^{-t(T+V)}=e^{-tV/2}e^{-tT}e^{-tV/2}+O(t^3). \tag{2.5}$$

This leads to a second-order free-particle coordinate representation for the propagator of the form

$$\psi_2^{fp}(\mathbf{x},t|\mathbf{x}^0)=[(2\pi t)^n\det\mathbf{D}]^{-1/2}\exp\{-(2tD_{ii})^{-1}(x_i-x_i^0)^2-\tfrac{1}{2}t[V(\mathbf{x})+V(\mathbf{x}^0)]\}. \tag{2.6}$$

The main disadvantage of the above breakup is that it neglects the commutator of $T$ and $V$, being exact only in the limit of free-particle motion $V(\mathbf{x})=\text{const}$. This neglect is often quite severe and introduces a large error that has to be compensated for by a very small time increment $t$. We will refer to Eqs. (2.5) and (2.6) as the standard Trotter splitting.

Two general approaches to refine the Trotter splitting are possible. First, one can employ an improved zeroth-order representation of the propagator that is accurate for a particular problem, but much better behaved than the standard free-particle basis $e^{-tT}$. It may be noted here that the idea of using a good representation as the zeroth-order description of a problem is not new. It is widely used in perturbation theory [1] and grid and basis set calculations [2,4,7] when the full Hamiltonian can be split into a reference (system) part $H_s$, whose exact solution is easily obtainable by standard techniques, and a correction $\lambda H_c$ reading

$$H=H_s+\lambda H_c, \tag{2.7}$$

where $\lambda$ is a smallness parameter. When inserted into the Trotter product formula, the splitting (2.7) yields a second-order system-specific propagator

$$e^{-t(H_s+\lambda H_c)}=e^{-\lambda tH_c/2}e^{-tH_s}e^{-\lambda tH_c/2}+O(\lambda t^3), \tag{2.8}$$

which in the coordinate representation has the form

$$\psi_2^{ss}(\mathbf{x},t|\mathbf{x}^0)=\int d\mathbf{x}^2 d\mathbf{x}^1\langle \mathbf{x}|e^{-\lambda tH_c/2}|\mathbf{x}^2\rangle\times\langle \mathbf{x}^2|e^{-tH_s}|\mathbf{x}^1\rangle\langle \mathbf{x}^1|e^{-\lambda tH_c/2}|\mathbf{x}^0\rangle. \tag{2.9}$$

It is clear that Eq. (2.9) is more difficult to implement than the standard Trotter splitting. The best zeroth-order propagators cannot be expressed in closed form in general and must therefore be computed *numerically* and stored on grids. By construction, however, they incorporate the exact dynamics of physically motivated reference systems. Therefore, one may expect that in a certain favorable regime of parameter space ($\lambda\lesssim 1$ in the above example) system-specific propagators would allow much larger time increments than Eq. (2.6). Recently, Makri and co-workers [13–15] have implemented this idea to system-bath Hamiltonians with impressive success (see also Refs. [10,16]).

Yet another way to obtain better *analytical* approximations for the propagator consists in using higher-order expansions for the time evolution operator. We mention specifically high-accuracy Trotter-like factorizations [17], power series representations [18,19], extrapolation methods for removing time slice errors [20,21], and cumulant expansions [22]. An extensive study of their relative efficacy can be found in a previous paper [10]. Here we only note that approximate propagators obtained with these methods though more accurate than the standard Trotter splitting are in general correct for short time steps. An exception is the work by Drozdov [19], who elaborated a theory that combines the sum acceleration technique, as well as the power series expansion method by Makri and Miller [18]. The approach distinguishes itself from other methods in that it gives global approximations valid not only for short times, but also in the intermediate and long time domains. However, the efficient evaluation of the power series representation of the propaga-

tor is feasible only when the potential $V(\mathbf{x})$ is simple enough so that the various integrals involved in the expansion coefficients can be evaluated analytically. Otherwise, numerical quadratures are required, making this approach unsuited even for one-dimensional problems.

Instead, we propose an alternative numerical method that combines the spirit of the two kinds of aforementioned approaches so that the resulting propagator includes the commutator of $T$ and $V$ explicitly but is easy to implement regardless of whether or not the Hamiltonian is of the system-bath form. The basic idea is to employ an improved zeroth-order representation along with a fourth-order symmetric decomposition of the time evolution operator designed for solving many-body problems of classical mechanics [23]. When applied to Eq. (2.7), the decomposition reads

$$e^{t(H_s+\lambda H_c)}=e^{\lambda t H_c/6}e^{tH_s/2}e^{tC}e^{tH_s/2}e^{\lambda t H_c/6}+O(\lambda^2 t^5),$$
$$C=\tfrac{2}{3}\lambda H_c+\tfrac{1}{72}\lambda^2 t^2[H_c,[H_s,H_c]], \tag{2.10}$$

where $H_s$ and $H_c$ are two arbitrary noncommuting operators assumed to be bounded on a finite-dimensional Hilbert space. It may be noted that factorizations of this kind have already been used by the authors to construct high-accuracy path integral representations for Fokker-Planck processes with singular diffusion matrices [24]. In such a case, the Fokker-Planck operator cannot in principle be cast into a Hermitian form and the utility of Eq. (2.11) must be studied for each particular system separately. In contrast, its application to Hamiltonian systems is straightforward and does not require an additional analytical work to evaluate the propagator [25]. It is our aim here to show that the use of better zeroth-order systems in Eq. (2.11) leads to improved coordinate propagators that remain accurate for very large time steps.

Of course, when treating truly multidimensional systems, this approach is feasible if and only if the evaluation of the propagators $\langle\mathbf{x}|e^{-th}|\mathbf{x}^0\rangle$ with $h=H_s,\lambda H_c,C$ does not present a major problem. The latter is generally the case for the standard splitting of the Hamiltonian operator (2.4), which immediately yields a fourth-order free-particle representation

$$\psi_4^{fp}(\mathbf{x},t|\mathbf{x}^0)=[(2\pi t)^n\det\mathbf{D}]^{-1}\int d\mathbf{x}^1\ \exp\{-(2tD_{ii})^{-1}\times[(x_i-x_i^1)^2+(x_i^1-x_i^0)^2]-\tfrac{1}{6}t[V(\mathbf{x})+4V(\mathbf{x}^1)+V(\mathbf{x}^0)]-\tfrac{1}{72}t^3D_{ii}[\partial_i V(\mathbf{x}^1)]^2\}. \tag{2.11}$$

Use of Eq. (2.11) in a path integral will require two Monte Carlo samplings of Gaussian variables rather than one, as is the case for Eq. (2.6). However, the resulting error is of order $1/N^4$; consequently, the present factorization allows much larger time steps to be taken than the Trotter breakup for comparable accuracy [25].

An important situation, often met in real physical processes involves problems where the Hamiltonian can be split into one describing separable motion

$$H_s=-\tfrac{1}{2}D_{ii}\partial_{ii}^2+V_i(x_i)=\sum_{i=1}^{n}H_i \tag{2.12}$$

and a potential term $\lambda H_c=\lambda F(\mathbf{x})$, which mixes the degrees of freedom. Here $\lambda$ is the coupling constant. This splitting leads to an improved fourth-order approximation of the form

$$\psi_4^{ss}(\mathbf{x},t|\mathbf{x}^0)=\int d\mathbf{x}^1\langle\mathbf{x}|e^{-tH_s/2}|\mathbf{x}^1\rangle\langle\mathbf{x}^1|e^{-tH_s/2}|\mathbf{x}^0\rangle\times\exp\{-\tfrac{1}{6}\lambda t[F(\mathbf{x})+4F(\mathbf{x}^1)+F(\mathbf{x}^0)]-\tfrac{1}{72}\lambda^2 t^3 D_{ii}[\partial_i F(\mathbf{x}^1)]^2\}, \tag{2.13}$$

where the zeroth-order propagator $\langle\mathbf{x}|e^{-tH_s}|\mathbf{y}\rangle$ is in principle to be evaluated numerically. This is computationally feasible because the reference Hamiltonian $H_s$ is assumed to be separable

$$\langle\mathbf{x}|e^{-tH_s}|\mathbf{y}\rangle=\prod_{i=1}^{n}\langle x_i|e^{-tH_i}|y_i\rangle \tag{2.14}$$

and therefore standard one-dimensional grid or basis set methods can be used to calculate each factor on the right-hand side of Eq. (2.14). Unlike the Trotter-approximated propagator given by Eq. (2.8), which is correct up to $O(\lambda t^3)$, the above approximation is valid up to $O(\lambda^2 t^5)$. The coupling is present in Eq. (2.13) not only through the coupling potential $\lambda F$ but also through the commutator $\lambda^2[F,[H_s,F]]$, which enters this equation as an effective potential. The system-specific propagator by construction is exact for any value of the time increment in the uncoupled limit; one then expects that it will be accurate for fairly long times with moderate coupling strengths.

## III. NUMERICAL RESULTS

Path integral calculations with the improved system-specific propagators suggested in Sec. II will be presented elsewhere. In this section we give two examples illustrating the advantages of Eq. (2.13) when using it as *a single-step propagator*. We consider a simple model of intramolecular nonlinear dynamics as well as a system-bath problem. Both examples involve only two degrees of freedom so that exact results can be generated with the standard split operator fast Fourier transform method [5] in a reasonable amount of time. Our comparison also includes results from the second- and fourth-order free-particle propagators [Eqs. (2.6) and (2.11)]. We have investigated the accuracy of the above-mentioned approximations through the calculation of diagonal and off-diagonal matrix elements of the time evolution operator $\langle xy|e^{-tH}|x_0y_0\rangle$. Calculations were performed in dimensionless units with $m=1$ and $\hbar=1$ over a wide range of coupling potentials.

### A. Modified Hénon-Heiles potential

To begin with, we consider the statistical mechanics in a two-dimensional potential with strongly anharmonic mode coupling. Following Meyer *et al.* [6], our model is described by a modified (bound) Hénon-Heiles Hamiltonian of the form

$$H=-\tfrac{1}{2}(\partial_{xx}^2+\partial_{yy}^2)+\tfrac{1}{2}(x^2+y^2)+\lambda x(y^2-\tfrac{1}{3}x^2)+\tfrac{1}{16}\lambda^2(x^2+y^2)^2. \tag{3.1}$$

The Hénon-Heiles Hamiltonian [26] is a chaotic model that (classically) describes a resonating system and provides a simple example for the study of Poincaré surfaces and trajectories. It has been used as a model for many classical or quantum studies of nonlinear dynamics [27]. The Hénon-Heiles Hamiltonian is also important in numerical analysis. It has frequently been exploited to test the utility of different numerical schemes [3–6] and should present a challenge to our method.

According to the scheme outlined in Sec. II, we split the Hamiltonian (3.1) into a reference part $H_s$ and a correction $\lambda F$ reading

$$H_s = -\tfrac{1}{2}(\partial_{xx}^2+\partial_{yy}^2)+\tfrac{1}{2}(x^2+y^2),$$
$$\lambda F = \lambda x(y^2-\tfrac{1}{3}x^2)+\tfrac{1}{16}\lambda^2(x^2+y^2)^2. \tag{3.2}$$

The reference part is identical to separable motion of two harmonic oscillators; consequently, the respective zeroth-order propagator is obtained analytically to give

$$\langle xy|e^{-tH_s}|x_0y_0\rangle = \psi_{\rm HO}(x,t|x_0)\psi_{\rm HO}(y,t|y_0), \tag{3.3}$$
$$\psi_{\rm HO}(q,t|q_0) = (2\pi \sinh t)^{-1/2} \times \exp\left[\frac{2qq_0-(q^2+q_0^2)\cosh t}{2\sinh t}\right],$$
$$q = x,y.$$

The quantity of interest is the diagonal matrix element

$$\rho = \langle 00|e^{-tH}|00\rangle. \tag{3.4}$$

Since the calculations presented involve only two degrees of freedom, the integrals in Eqs. (2.11) and (2.13) are easily evaluated by quadrature.

Figure 1(a) shows the time evolution, for $\lambda = 0.1$, of the exact diagonal matrix element [Eq. (3.4)] divided by the value of this quantity as obtained from the single-step propagators discussed in Sec. II. As expected, the standard Trotter splitting [Eq. (2.6)] is least accurate. The error made by this propagator increases with $t$ very rapidly and for $t=10$ it overestimates the matrix element by three orders of magnitude. Although no system-specific reference system is used in the fourth-order free-particle approximation [Eq. (2.11)], the effect of taking into account the commutator of $T$ and $V$ is the reduction of the error by two orders of magnitude. The present system-specific propagator [Eq. (2.13)] is seen to further reduce the error roughly by a factor of 8. In Fig. 1(b) we also show the same ratio taken at $t=10$ as a function of the coupling constant $\lambda$. As evidenced by the figure, the error made by the system-specific propagator increases quite slowly with increasing coupling. The excellent agreement demonstrates the potential of the proposed method. It is seen to be able to describe correctly the dynamics of a very anharmonic process over a broad range of $t$.

### B. System-bath Hamiltonian

As a second more sophisticated example, we consider the relaxation dynamics of a one-dimensional system that is coupled nonlinearly to a single harmonic oscillator

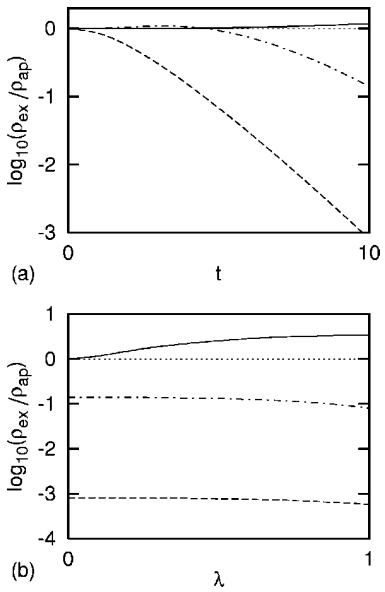


FIG. 1. Exact matrix element $\rho_{\rm ex}$ [Eq. (3.4)] for the modified Hénon-Heiles Hamiltonian [Eq. (3.1)] divided by the value $\rho_{\rm ap}$ of this quantity calculated from the single-step propagator according to the various approximations discussed in Sec. II, as a function of (a) time (at $\lambda=0.1$) and (b) the coupling parameter $\lambda$ (at $t=10$). Dashed lines, standard Trotter splitting, Eq. (2.6); dot-dashed lines, fourth-order free-particle approximation, Eq. (2.11); solid lines, system-specific propagator, Eq. (2.13).

$$H = H_x - \tfrac{1}{2}\partial_{yy}^2 + \tfrac{1}{2}y^2 + \lambda F(x,y). \tag{3.5}$$

The system is described by a double well Hamiltonian

$$H_x = -\tfrac{1}{2}\partial_{xx}^2 + E(x^2-1)^2, \tag{3.6}$$

where $E$ is the height of the potential barrier. The form of the coupling potential is chosen to be nonlinear in both coordinates [15]

$$F(x,y) = -xy\ \exp[-(x^2+y^2)/2\alpha], \tag{3.7}$$

with $\alpha$ being the width of the coupling. The above model, though simple, is of enormous utility in understanding and evaluating the influence of a medium on dynamical processes. It is commonly used in describing varied physical phenomena such as vibrational energy transfer and chemical reactions in the condensed phase [1,2,13–15].

Following the approach described in Sec. II, we take the reference Hamiltonian to be the entire separable part of the full Hamiltonian

$$H_s = H_x - \tfrac{1}{2}\partial_{yy}^2 + \tfrac{1}{2}y^2. \tag{3.8}$$

Then the reference propagator reduces to a product of one-dimensional propagators

$$\langle xy|e^{-tH_s}|x_0y_0\rangle = \psi_x(x,t|x_0)\psi_{\rm HO}(y,t|y_0), \tag{3.9}$$

where $\psi_{\rm HO}(y,t|y_0)$ is given by Eq. (3.3), while $\psi_x(x,t|x_0) = \langle x|e^{-tH_x}|x_0\rangle$ is computed with minimal numerical effort in terms of the eigenstates of the corresponding system Hamiltonian. We set $E=5$ and calculate the off-diagonal matrix element

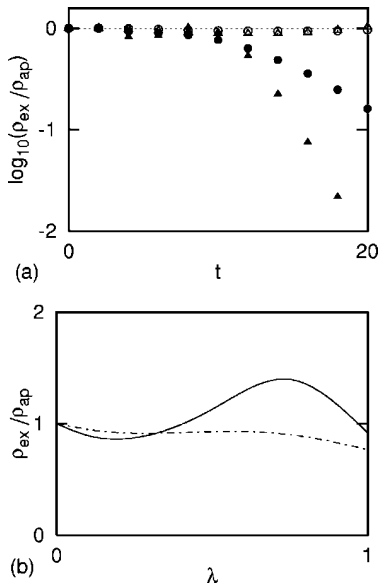


FIG. 2. Exact matrix element $\rho_{ex}$ [Eq. (3.10)] for the system-bath Hamiltonian [Eqs. (3.5)–(3.7)] divided by the value $\rho_{ap}$ of this quantity calculated from the approximate system-specific propagator [Eq. (2.13)], as a function of (a) time and (b) the coupling parameter $\lambda$ (at $t=10$). Open circles, $\lambda=0.1$ and $\alpha=1$; solid circles, $\lambda=0.1$ and $\alpha=5$; open triangles, $\lambda=1$ and $\alpha=1$; solid triangles, $\lambda=1$ and $\alpha=5$; dot-dashed line, $\alpha=1$; solid line, $\alpha=5$.

$$\rho=\langle x_+ y_+|e^{-tH}|x_- y_-\rangle, \tag{3.10}$$

where $x_\pm y_\pm$ are the coordinates of the two potential minima. This quantity is closely related to the tunneling rate [28] and is therefore very sensitive to the coupling term in the Hamiltonian.

In order to understand how dependent the accuracy of the present approach is on the width and the strength of the coupling, we performed the calculations for different values of $\alpha$ and $\lambda$. The results are presented in Fig. 2. It is clear from this figure that the range of applicability is quite robust to variations in the width and the strength of the coupling potential. One would expect the accuracy of Eq. (2.13) to fall off very quickly as $\alpha$ or $\lambda$ went up, but in fact going from a potential of $(\alpha,\lambda)=(1,0.1)$ to one about (5,1), there was almost no decay in the accuracy of the results over a broad range of $t$. Even at the largest values of $\alpha$ and $\lambda$ the system-specific propagator is seen to yield fairly accurate results for $t\lesssim 10$.

Finally, we compare in Fig. 3 the exact off-diagonal matrix element with its approximation calculated in terms of the various single-step propagators discussed in Sec. II. As anticipated, the best agreement is achieved with the present approach. The accuracy of the system-specific propagator deteriorates with $t$ very slowly and for $t=10$ it overestimates the off-diagonal matrix element by 9%. In contrast, the error made by the propagators with the free-particle reference system increases *exponentially* with $t$ and very soon grows out of the scale of the figure. In this case an accuracy of 10% is attainable with the standard Trotter splitting only for $t\lesssim 0.1$.

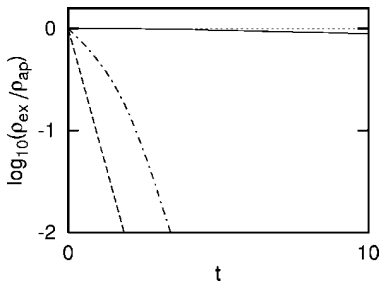


FIG. 3. Same as in Fig. 1(a), but for the off-diagonal matrix element [Eq. (3.10)] of the system-bath Hamiltonian, Eqs. (3.5)–(3.7) with $\lambda=0.1$ and $\alpha=5$.

## IV. CONCLUDING REMARKS

In this paper we have presented a method for accurately solving multidimensional Schrödinger and Fokker-Planck equations in a simple economic way. It is based on splitting the full Hamiltonian into a separable part and a potential term that mixes the degrees of freedom and employing a fourth-order symmetric decomposition of the time evolution operator designed for solving many-body problems of classical mechanics. We have shown that the application of this improved operator expansion to quantum and statistical dynamics is straightforward and does not require a more analytical work to evaluate the propagator than the standard Trotter splitting. Two typical examples, which cover a variety of situations, are used to demonstrate the usefulness and to test the accuracy of the proposed approach. These model systems are chosen to be two dimensional in order to allow a comparison with a conventional grid method without extraordinary computational effort. Because the present operator expansion results in a set of one-dimensional problems, its application to multidimensional systems is not numerically significantly more difficult than in two dimensions and still much less arduous than a general multidimensional calculation. The results obtained are encouraging since the dynamics of very anharmonic processes can be quite accurately described for fairly long times with moderate coupling strengths. The scheme is applicable to the entire time increment if the desired propagation time is not too long or the coupling is not strong. Otherwise, path integral methodology can be employed to correct our representation and systematically extend it to the whole parameter space. Being used in a path integral, the system-specific propagator will allow time steps larger, by two orders of magnitude, than the standard Trotter splitting for comparable accuracy.

Finally, we would like to emphasize that we have not explicitly covered all possible cases to which our approach could be applied. Besides Hamiltonian systems, it can also be applied to Fokker-Planck equations, which do not obey detailed balance and therefore are not reducible to a Hermitian form. The latter are often used in studies of many interesting problems such as molecular dissociation in strongly coupled chemical processes, selective pumps for biological macromolecules, and transport in complex systems as it occurs in glasses. The evaluation of rate constants in these complex opened systems is a daunting problem because even the stationary probability of the underlying multidimensional Fokker-Planck equation is no longer given by the Boltzmann

distribution; it must be determined instead self-consistently from the fluctuating properties [29]. We plan to use our methodology to gain insight into a number of questions related to this problem.

**ACKNOWLEDGMENTS**

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