

Quasi-adiabatic propagator path integral methods. Exact quantum rate constants for condensed phase reactions

Maria Topaler and Nancy Makri

School of Chemical Sciences, University of Illinois, 505 S. Mathews Avenue, Urbana, IL 61801, USA

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We describe an exact quantum-mechanical methodology for calculating Boltzmann-averaged rate constants for a system coupled to a harmonic bath of arbitrary dimensionality. Reactive flux correlation functions are evaluated using the quasi-adiabatic propagator path integral (QUAPI) method. Extremely rapid convergence is achieved; i.e. exact results are obtained with three to five time slices even at temperatures as low as 100 K, and the numerical effort required is essentially independent of the number of bath degrees of freedom. Thus, the proposed method provides an accurate and efficient scheme for studying quantum effects in the low-temperature kinetics of condensed phase reactions.

1. Introduction

The dynamics of a system coupled to a harmonic bath presents a challenging problem of great importance to condensed matter chemistry and physics and has been given a great deal of attention. Among many conceivable theoretical approaches, Feynman's path integral method [1] appears very appealing because it allows the harmonic bath degrees of freedom to be integrated out analytically without introducing approximations. While this procedure reduces the dimensionality of the problem dramatically, it introduces interactions non-local in time into the dynamics of the system so that the latter is no longer solvable by conventional one-dimensional techniques.

In this Letter, we consider the generic system-bath Hamiltonian,

$$\hat{H} = \hat{H}_s + \hat{H}_Q - \sum_{j=1}^n f_j(\hat{s}) \hat{Q}_j. \quad (1a)$$

Here \hat{H}_s describes the anharmonic system,

$$\hat{H}_s = \frac{\hat{p}_s^2}{2m_s} + V_0(\hat{s}), \quad (1b)$$

and

$$\hat{H}_Q = \sum_{j=1}^n \hat{H}_j, \quad \hat{H}_j = \frac{\hat{p}_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \hat{Q}_j^2 \quad (1c)$$

is the Hamiltonian for the n harmonic oscillators $\{\hat{Q}_j\}$ which are linearly coupled to the system and which constitute the bath. Discretization of the propagator in coordinate space leads to the following path integral expression:

$$\langle s_f \mathbf{Q}_f | \exp(-i\hat{H}t/\hbar) | s_0 \mathbf{Q}_0 \rangle = \int ds_1 \dots \int ds_{N-1} \int dQ_{1,1} \dots \int dQ_{1,N-1} \dots \int dQ_{n,1} \dots \int dQ_{n,N-1} \\ \times \prod_{k=1}^N \langle s_k \mathbf{Q}_k | \exp(-i\hat{H}\Delta t/\hbar) | s_{k-1} \mathbf{Q}_{k-1} \rangle, \quad (2)$$

where N is the number of time slices and $\Delta t = t/N$. Use of the conventional Trotter formula [2] (which is based on partitioning the Hamiltonian into kinetic and potential energy terms) to approximate the short time propagators leads to analytic expressions valid over very small time increments, and therefore (for interesting values of the total time t) to a high-dimensional integral, even after the bath coordinates in eq. (2) have been integrated out. Due to the non-local nature of the influence functional that arises from integrating out the bath, the remaining integrations over the $N-1$ system coordinates must then be performed by global (non-iterative) methods. For large-dimensional integrals, one must resort to Monte Carlo techniques [3] which are not well behaved in the case of real time due to the oscillatory character of the coordinate propagator.

Significant advances have been made during the last few years in the development of Monte Carlo methods for evaluating real time path integrals [4–20]. Though fairly successful for sufficiently short time, the algorithms developed converge extremely slowly if longer time information is sought. The convergence problem, known as the “sign problem”, manifests itself as phase interference among *classical* paths in the semiclassical propagator and is inherent in real time quantum dynamics.

A different approach to real time path integration has been proposed recently [19] and applied to model multidimensional problems [20]. The basic idea is to use an improved (compared to the Trotter) splitting of the time evolution operator, based on a physically meaningful reference Hamiltonian. If the dynamics of the reference system is qualitatively similar to that of the full Hamiltonian, the corresponding propagator will be accurate for time increments of considerable length. Use of such improved propagators in the path integral is expected to converge rapidly in that case.

For the system-bath Hamiltonian of eq. (1) a *quasi-adiabatic propagator* has been proposed [5] and found to allow rather large time steps [19,20]. The reference Hamiltonian involves the potential along the adiabatic path and is constructed numerically in terms of the one-dimensional eigenstates of the former, while non-adiabatic effects enter via Franck–Condon factors for displaced bath oscillators. The harmonic bath is then integrated out, leading to an influence functional that incorporates the non-adiabatic corrections to the dynamics along the one-dimensional adiabatic path. Our experience to date has shown that the number of time slices required for convergence is usually very small, leading to efficient quadrature or stable Monte Carlo schemes for evaluating the resulting path integral.

In this Letter, we present a path integral scheme for calculating Boltzmann averaged reaction rate constants for a reaction coordinate coupled to a harmonic bath. The calculation is based on Miller’s reactive flux correlation function [21], whose time integral yields the rate coefficient. In section 2 this correlation function is expressed in path integral form using quasi-adiabatic propagators and the bath is integrated out to yield an influence functional. Section 3 describes a grid Monte Carlo scheme for performing the required integrations over the system path integral variables. Applications presented in section 4 demonstrate the excellent convergence properties of the method. It is shown that with parameters typical of proton transfer reactions in condensed matter the proposed methodology is capable of yielding highly accurate results even at temperatures as low as 100 K, and that the numerical effort required is essentially independent of the number of bath degrees of freedom coupled to the reaction coordinate. Some concluding remarks appear in section 5.

2. Quasi-adiabatic propagator representation of the flux–flux correlation function

The starting point for the calculation of the rate constant is the reactive flux correlation function formalism

of Miller, Schwartz and Tromp [21]. According to the latter, the Boltzmann averaged rate coefficient is given by the time integral of the flux-flux correlation function

$$k = Z^{-1} \int_0^{t_p} C_f(t) dt, \quad (3)$$

where Z denotes the canonical partition function of the reactants, t_p is the conventional "plateau time" [22,23], and the correlation function is defined by

$$C_f(t) = \text{Tr}[\hat{F} \exp(i\hat{H}t_c^*/\hbar) \hat{F} \exp(-i\hat{H}t_c/\hbar)]. \quad (4)$$

Here \hat{F} is the symmetrized flux operator

$$\hat{F} = \frac{1}{2m_s} [\hat{p}_s \delta(\hat{s}) + \delta(\hat{s}) \hat{p}_s], \quad (5)$$

and the "dividing surface" through which the reactive flux is measured is located for notational simplicity as $s=0$. Finally, $t_c = t - i\hbar\beta/2$ is a complex time that arises from combining the time evolution operator with the Boltzmann operator and $\beta = 1/k_B T$.

Evaluating the trace in eq. (4) in the coordinate representation gives

$$C_f(t) = \frac{\hbar^2}{2m_s^2} \text{Re} \int_{-\infty}^{\infty} d^n \mathbf{Q}_0 \left(\frac{\partial^2}{\partial s' \partial s} - \frac{\partial^2}{\partial s'' \partial s} \right) \times \langle \mathbf{Q}_0 | \langle s'' | \exp(i\hat{H}t_c^*/\hbar) | s'' \rangle \langle s' | \exp(-i\hat{H}t_c/\hbar) | s \rangle | \mathbf{Q}_0 \rangle |_{s=s'=s''=0}. \quad (6)$$

Evaluation of the derivatives by finite difference leads to the expression

$$C_f(t) = \frac{\hbar^2}{2m_s^2 s_{\text{FD}}^2} \text{Re} [K(s_{\text{FD}}, s_{\text{FD}}, 0, 0; t_c) - K(0, s_{\text{FD}}, 0, s_{\text{FD}}; t_c) + K(0, 0, 0, s_{\text{FD}}; t_c) - K(s_{\text{FD}}, 0, 0, 0; t_c)], \quad (7)$$

where s_{FD} is a coordinate point sufficiently close to the dividing surface and

$$K(s_0, s_N, s_{N+1}, s_{2N+1}; t_c) \equiv \int_{-\infty}^{\infty} d^n \mathbf{Q}_0 \langle \mathbf{Q}_0 | \langle s_{2N+1} | \exp(i\hat{H}t_c^*/\hbar) | s_{N+1} \rangle \langle s_N | \exp(-i\hat{H}t_c/\hbar) | s_0 \rangle | \mathbf{Q}_0 \rangle. \quad (8)$$

The last two terms in eq. (7) combine to a pure imaginary sum and thus need not be included. However, retaining these two terms gives rise to a smoother integrand in the discretized path integral expression (see below) and therefore enhances the statistics of the Monte Carlo sampling.

Next, the time t_c is divided into N time slices of length Δt and each short time evolution operator is factorized using the quasi-adiabatic propagator splitting [19].

$$\exp(-i\hat{H}\Delta t/\hbar) \approx \exp(-i\hat{H}'_Q \Delta t/2\hbar) \exp(-i\hat{H}'_s \Delta t/\hbar) \exp(-i\hat{H}'_Q \Delta t/2\hbar). \quad (9a)$$

In the last equation \hat{H}'_s is the renormalized system Hamiltonian with $V_0(s)$ replaced by the potential along the adiabatic path,

$$H'_s(\hat{s}, \hat{p}_s) \equiv \frac{\hat{p}_s^2}{2m_s} + V_0(\hat{s}) - \sum_{j=1}^n \frac{f_j(\hat{s})^2}{2m_j \omega_j^2}, \quad (9b)$$

and

$$\hat{H}'_Q \equiv \sum_{j=1}^n H'_j(\hat{Q}_j, \hat{P}_j; \xi) \equiv \sum_{j=1}^n \left[\frac{\hat{P}_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left(\hat{Q}_j - \frac{f_j(\xi)}{m_j \omega_j^2} \right)^2 \right] \quad (9c)$$

is the Hamiltonian for the n adiabatically displaced bath oscillators. Taking advantage of the fact that the shifted bath Hamiltonian depends only parametrically on the system coordinate, eq. (8) takes the form

$$K(s_0, s_N, s_{N+1}, s_{2N+1}; t_c) = \int_{-\infty}^{\infty} ds_1 \dots \int_{-\infty}^{\infty} ds_{N-1} \int_{-\infty}^{\infty} ds_{N+2} \dots \int_{-\infty}^{\infty} ds_{2N} \prod_{k=N+1}^{2N+1} \langle s_k | \exp(i\hat{H}'_s \Delta t_c^*/\hbar) | s_{k-1} \rangle \\ \times \prod_{k=1}^N \langle s_k | \exp(-i\hat{H}'_s \Delta t_c/\hbar) | s_{k-1} \rangle I(s_0, s_1, \dots, s_{N-1}, s_N, s_{N+1}, \dots, s_{2N+1}), \quad (10)$$

where

$$I(s_0, s_1, \dots, s_{N-1}, s_N, s_{N+1}, \dots, s_{2N+1}) = \prod_{j=1}^n I_j(s_0, s_1, \dots, s_{N-1}, s_N, s_{N+1}, \dots, s_{2N+1}), \\ I_j = \int_{-\infty}^{\infty} dQ_{j,0} \langle Q_{j,0} | \exp[i\hat{H}'_j(s_{2N+1}) \Delta t_c^*/2\hbar] \exp[i\hat{H}'_j(s_{2N}) \Delta t_c^*/\hbar] \dots \\ \times \exp[i\hat{H}'_j(s_{N+2}) \Delta t_c^*/\hbar] \exp[i\hat{H}'_j(s_{N+1}) \Delta t_c^*/2\hbar] \exp[-i\hat{H}'_j(s_N) \Delta t_c/2\hbar] \exp[-i\hat{H}'_j(s_{N-1}) \Delta t_c/\hbar] \dots \\ \times \exp[-i\hat{H}'_j(s_1) \Delta t_c/\hbar] \exp[-i\hat{H}'_j(s_0) \Delta t_c/2\hbar] | Q_{j,0} \rangle \quad (11)$$

is an influence functional which incorporates the multidimensional non-adiabatic corrections to the *exact* dynamics along the adiabatic path described by the system propagators of eq. (10).

Eq. (11) is formally identical to the influence function that occurs in the partition function for a forced harmonic oscillator, except that here the time contour F is complex (see fig. 1). Using Feynman's familiar result [24], the influence function becomes

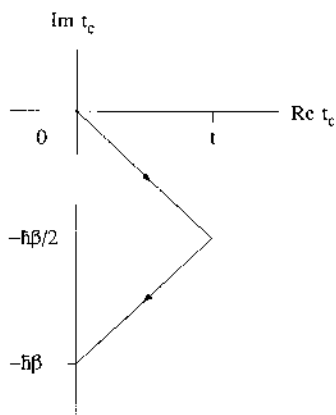


Fig. 1. The time contour F for the path integral of eqs. (10) and (11).

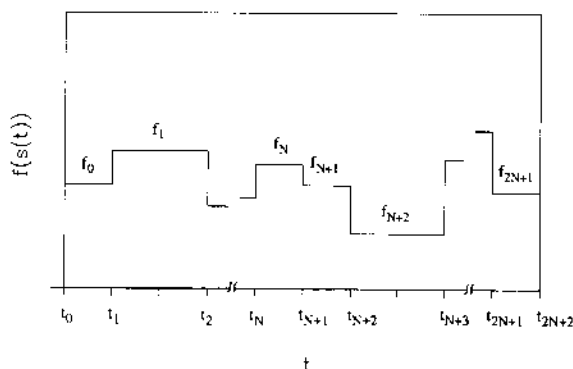


Fig. 2. Schematic plot of the time-dependent force $f(s(t))$ exerted on a bath oscillator along the time contour F with the complex propagation time t_c discretized into N slices; $f_k = f(s(t_k))$.

$$I_j = I_j^0 \exp\left(-\frac{i}{\hbar} \int_{\Gamma} dt' \frac{f_j(t')^2}{2m_j \omega_j^2}\right) \times \exp\left(-\frac{1}{4m_j \omega_j \hbar} \int_{\Gamma'} \int_{\Gamma''} dt' dt'' \frac{\cos[\omega_j(t_b - t_a + i\hbar\beta/2)]}{\sinh(\hbar\omega_j\beta)} f_j(t') f_j(t'')\right), \quad (12)$$

where t_a and t_b are the earlier and later, respectively, of the two times t' and t'' in the positive direction of the time contour Γ . The first factor in the last expression arises from the bath-independent adiabatic renormalization terms of eq. (9c) and I_j^0 is the partition function for the j th oscillator in the absence of coupling. Note that due to the exact treatment of the system propagator (as opposed to a trapezoid rule discretization of the action) the force $f_j(t') \equiv f_j(s(t'))$ exerted on the bath by the system is not a continuous function of time for finite values of N ; rather, this force changes by finite steps that correspond to the coupling at various discrete points of the system coordinate. A related graphical illustration is given in fig. 2.

Because of the step function structure of the time-dependent force, the integrals in eq. (12) can be evaluated exactly to give

$$I_j = I_j^0 \exp\left(-\frac{1}{m_j \omega_j^3 \hbar} \sum_{k=0}^{2N+1} \sum_{k'=0}^{2N+1} \alpha_{kk'}(\omega_j, \Delta t_c) f_j(s_k) f_j(s_{k'})\right), \quad (13)$$

where

$$\alpha_{kk'}(\omega_j, \Delta t_c) = \sin[\omega_j(t_{k+1} - t_k + i\hbar\beta)/2] \sin[\omega_j(t_{k+1} - t_k)/2] / \sinh(\hbar\omega_j\beta/2), \\ \alpha_{kk'}(\omega_j, \Delta t_c) = \cos[\omega_j(t_{k+1} + t_k - t_{k+1} - t_k + i\hbar\beta)/2] \sin[\omega_j(t_{k+1} - t_k)/2] \\ \times \sin[\omega_j(t_{k'+1} - t_{k'})/2] / \sinh(\hbar\omega_j\beta/2), \quad k > k' \quad (14)$$

and t_k is the complex time that corresponds to point s_k on the path (see fig. 1). Finally, if the coupling functions have a simple analytic form, e.g., if

$$f_j(s) = \sum_{r=0}^{r_{\max}} b_{jr} s^r, \quad (15)$$

the exponentials corresponding to the various bath oscillators can be combined to yield a compact expression for the total influence functional:

$$I = \prod_{j=1}^n I_j^0 \exp\left(-\frac{1}{\hbar} \sum_{k=0}^{2N+1} \sum_{k'=0}^{2N+1} \sum_{r=0}^{r_{\max}} \sum_{r'=0}^{r_{\max}} A_{kk'rr'}(\Delta t_c) s_k^r s_{k'}^{r'}\right), \quad (16a)$$

where the coefficients are given by the relation

$$A_{kk'rr'}(\Delta t_c) = \sum_{j=1}^n \alpha_{kk'}(\omega_j, \Delta t_c) \frac{b_{jr} b_{j r'}}{m_j \omega_j^3}, \quad (16b)$$

Eq. (10), with the influence functional given by eqs. (16), is the main result of this section. The path integral is expressed in terms of system propagators that describe the *exact* dynamics along the adiabatic path, with an influence functional that incorporates the effects of coupling to the bath on the dynamics of the one-dimensional system. These effects enter via Franck-Condon-type factors, as is seen from eqs. (16). Note that the coefficients $A_{kk'rr'}$ are independent of the integration variables s_k and therefore can be computed and stored at the beginning of the calculation. As a consequence, the numerical effort required to evaluate the path integral expression, eq. (10), is essentially independent of the dimensionality of the bath.

Finally, the infinite n limit can be taken easily from eqs. (16). In that limit the bath is described by a continuous spectral density which for bilinear coupling $f_i(s) = c_i s$ is defined as

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{-c_j^2}{m_j \omega_j} \delta(\omega - \omega_j) . \quad (17)$$

It is easy to show that the influence functional is still given by an equation of the form of eq. (16a),

$$I = I^0 \exp\left(-\frac{1}{\hbar} \sum_{k=0}^{2N+1} \sum_{k'=0}^{2N+1} B_{kk'}(\Delta t_c) s_k s_{k'}\right) , \quad (18a)$$

where I^0 is the partition function for the uncoupled bath and the coefficients are obtained from integrals of the bath spectral density:

$$B_{kk'}(\Delta t_c) = \frac{2}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \alpha_{kk'}(\omega, \Delta t_c) . \quad (18b)$$

Finally, the reactant partition function Z is given by identical expressions but with the time contour being a straight line from 0 to $-i\hbar\beta$ along the imaginary time axis.

3. Exact system propagators and Monte Carlo sampling

The $2N-2$ integrations that appear in the path integral expression for the flux correlation function are performed using Monte Carlo sampling. The one-dimensional propagator for the adiabatically rescaled system Hamiltonian is computed numerically in terms of the eigenfunctions Φ_i and eigenvalues E_i of H'_s and stored as an $M \times M$ complex-valued matrix on an M -point grid that spans the s coordinate [19]:

$$\langle s'' | \exp(-i\hat{H}'_s \Delta t_c / \hbar) | s' \rangle = \sum_i \Phi_i(s') \Phi_i^*(s'') \exp(-iE_i \Delta t_c / \hbar) . \quad (19)$$

The Monte Carlo random walk is performed *on a grid* as described in ref. [19]. Specifically, the value of the s coordinate is incremented by randomly selected multiples of the grid spacing Δs , rather than in a continuous fashion.

The absolute value ρ of the integrand of eq. (7) with the various propagator terms given by eqs. (10) and (16) is used as the (un-normalized) sampling function, thus,

$$C_f(t) = D_\rho \int_{-\infty}^{\infty} ds_1 \dots \int_{-\infty}^{\infty} ds_{N-1} \int_{-\infty}^{\infty} ds_{N+2} \dots \int_{-\infty}^{\infty} ds_{2N} [D_\rho^{-1} \rho(s_1, \dots, s_{N-1}, s_{N+2}, \dots, s_{2N})] \\ \times S(s_1, \dots, s_{N-1}, s_{N+2}, \dots, s_{2N}) , \quad (20)$$

where S is the sign of the real part of the integrand and D_ρ is the normalization integral, i.e. the integral of the sampling function ρ . The normalization integral is calculated by a separate Monte Carlo procedure with the absolute value σ of one of the system propagator products as the sampling function,

$$D_\rho = D_\sigma \int_{-\infty}^{\infty} ds_1 \dots \int_{-\infty}^{\infty} ds_{N-1} \int_{-\infty}^{\infty} ds_{N+2} \dots \int_{-\infty}^{\infty} ds_{2N} [D_\sigma^{-1} \sigma(s_1, \dots, s_{N-1}, s_{N+2}, \dots, s_{2N})] \\ \times \frac{\rho(s_1, \dots, s_{N-1}, s_{N+2}, \dots, s_{2N})}{\sigma(s_1, \dots, s_{N-1}, s_{N+2}, \dots, s_{2N})} , \quad (21)$$

where

$$\sigma(s_1, \dots, s_{N-1}, s_{N+2}, \dots, s_{2N}) = \prod_{k=N+1}^{2N+1} |\langle s_k | \exp(i\hat{H}'_k \Delta t_c / \hbar) | s_{k-1} \rangle| \prod_{k=1}^N |\langle s_k | \exp(-i\hat{H}'_s \Delta t_c / \hbar) | s_{k-1} \rangle|,$$

and

$$s_0 = s_N = s_{FD}, \quad s_{N+1} = s_{2N+1} = 0.$$

Finally, the second normalization integral that appears in eq. (21) involves the one-dimensional system propagator and is computed by matrix multiplication [25]. The results presented in section 4 were obtained with two million Monte Carlo passes for each integration variable and the calculation took up to several hours of CPU time on an IBM RISC 6000/350 workstation.

4. Application

We demonstrate the stability and convergence properties of the methodology described in sections 2 and 3 by applying it to calculate reaction rate constants for a model symmetric double well system coupled to a continuous bath. This model combines a number of interesting effects, such as competition between coherent tunneling and dissipation typical of two-level systems [26], and also allows thermally activated processes to take place. Consequently, a number of interesting questions concerning the kinetics of such a model may be addressed by performing accurate multidimensional quantum calculations; for the sake of brevity, however, we reserve those issues for another article, and present only a few sample calculations here that illustrate the technical advantages of our method.

The parameters of the one-dimensional double well are chosen such that the barrier height is approximately 7.8 kcal/mol and the mass is that of a hydrogen atom. The coupling is bilinear and the spectral density of the bath has the form

$$J(\omega) = \eta \omega^3 \exp(-\omega/\omega_c), \quad (22)$$

with $\omega_c = 50 \text{ cm}^{-1}$ and $\eta = 10^8 \text{ au}$. The cubic spectral density at low frequencies is typical of three-dimensional solids.

In the absence of coupling to the bath, the system exhibits coherent tunneling oscillations and does not display rate dynamics. Accordingly, the flux-flux correlation function does not decay to zero and no rate constant can be extracted. Rate kinetics are observed at finite values of the coupling due to the dissipative role of the bath and the flux-flux correlation function decays to zero at a certain plateau time, such that its integral yields the rate constant. Thus, the effect that we are calculating is entirely due to multidimensional dissipation and therefore this model provides a challenging test to our method.

Fig. 3 shows the flux-flux correlation function at 100 K, as obtained from the path evaluation of eq. (7), with the propagators given by eqs. (10) and (18). This low temperature, which corresponds to deep tunneling, is chosen to provide a challenge to our method. For $N > 3$ the integrals over the $2N-2$ system variables were calculated by the Monte Carlo scheme described in section 3, while direct quadrature was used for $N \leq 3$. The results are presented for various numbers of time slices and the Monte Carlo error bars are indicated. These error bars are not easily discernible in the figure, though, because they are smaller than or equal to the size of the markers.

It can be shown that the single-step quasi-adiabatic propagator yields the exact one-dimensional (coherent) dynamics along the adiabatic path in this case, and thus the $N=1$ flux correlation function does not decay to zero. It is seen that the convergence of the correlation function with N is very rapid: the results are converged to about 10% already at $N=3$, and fully converged results are obtained with just five time slices. This very fast convergence is due to the use of quasi-adiabatic propagators based on a physically meaningful reference Hamiltonian. Furthermore, the use of exact eigenstates to construct the one-dimensional system propagator results

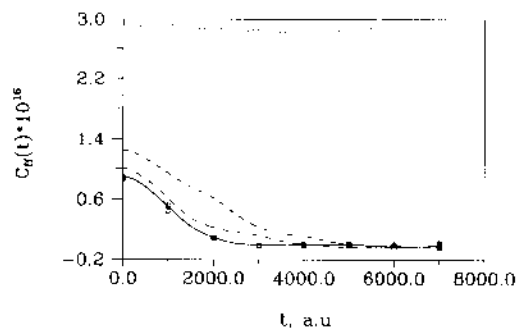


Fig. 3. The flux-flux correlation function for the double well potential discussed in section 4 at $T = 100$ K for various numbers of time slices N . The path integral was evaluated by quadrature for $N \leq 3$ and by Monte Carlo for $N \geq 4$. (---) $N = 1$; (---) $N = 2$; (---) $N = 3$; (\square) $N = 5$; (\triangle) $N = 6$; (\bullet) $N = 7$.

in an integrand which contains true dynamical information; thus, the sampling function is optimal, and minimal phase cancellation takes place, leading to small statistical error in the Monte Carlo results. Thus, we conclude that the methodology described in this Letter provides a powerful scheme for calculating reaction rate constants in tunneling-dominated condensed matter systems *exactly*, i.e. without introducing any uncontrolled approximations.

5. Concluding remarks

We have described an exact, fully quantum-mechanical methodology for calculating thermally averaged rate constants for condensed phase reactions. The quasi-adiabatic propagator representation of the path integral leads to convergence with large time steps and allows optimal Monte Carlo sampling, thus permitting evaluation of the resulting integral with small statistical error. The derived influence functional expressions incorporate non-adiabatic effects due to the multidimensional nature of the problem and are easily evaluated both for a continuous and for a discrete bath. In the latter case the required numerical effort is essentially independent of the number of coupled bath degrees of freedom, and thus this methodology is convenient for performing calculations in cases where the phonon spectrum and coupling functions are obtained numerically from a normal mode analysis of a finite lattice cluster.

To our knowledge, the numerical application presented in section 4 represents the first exact treatment of the rate kinetics in the case of a continuous coordinate coupled to a dissipative bath at low temperature. The rapid convergence observed is very encouraging. We believe that the QUAPI methodology for rate constants described in this Letter offers a very useful tool for answering a number of intriguing questions concerning chemical reaction dynamics in the condensed phase, and we are in the process of investigating various such questions.

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References

- [1] R.P. Feynman, *Rev. Mod. Phys.* 20 (1948) 367;
R.P. Feynman and A.R. Hibbs, *Quantum mechanics and path integrals* (McGraw-Hill, New York, 1965).

- [2] L.S. Schulman, *Techniques and applications of path integration* (Wiley, New York, 1981).
- [3] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, H. Teller and E. Teller, *J. Chem. Phys.* 21 (1953) 1087;
J.P. Valleau and S.G. Whittington, in: *Modern theoretical chemistry*, Vol. 5, B.J. Berne, ed. (Plenum Press, New York, 1977) pp. 137-168;
K. Binder and D.W. Heermann, *Monte Carlo simulation in statistical physics* (Springer, Berlin, 1988).
- [4] D. Thirumalai and B.J. Berne, *Chem. Phys. Letters* 116 (1985) 471; *Ann. Rev. Phys. Chem.* 37 (1986) 401.
- [5] E.C. Behrman, G.A. Jongeward and P.G. Wolynes, *J. Chem. Phys.* 79 (1983) 6277;
E.C. Behrman and P.G. Wolynes, *J. Chem. Phys.* 83 (1985) 5863;
R.E. Cline Jr. and P.G. Wolynes, *J. Chem. Phys.* 88 (1988) 4334;
B.A. Mason, K. Hess, R.E. Cline and P.G. Wolynes, *Superlattices and microstructures* 3 (1987) 421.
- [6] J.D. Doll, *J. Chem. Phys.* 81 (1984) 3536;
J.D. Doll and D.L. Freeman, *Science* 234 (1986) 1356;
J.D. Doll, R.D. Coalson and D.L. Freeman, *J. Chem. Phys.* 87 (1987) 1641.
- [7] J. Chang and W.H. Miller, *J. Chem. Phys.* 87 (1987) 1648.
- [8] V.S. Filinov, *Nucl. Phys. B* 271 (1986) 717.
- [9] N. Makri and W.H. Miller, *Chem. Phys. Letters* 139 (1987) 10; *J. Chem. Phys.* 89 (1988) 2170.
- [10] J.D. Doll and D.L. Freeman, *Advan. Chem. Phys.* 73 (1988) 120;
J.D. Doll, D.L. Freeman and M.J. Gillan, *Chem. Phys. Letters* 143 (1988) 277;
J.D. Doll, T.L. Beck and D.L. Freeman, *J. Chem. Phys.* 89 (1988) 5753;
T.L. Beck, J.D. Doll and D.L. Freeman, *J. Chem. Phys.* 90 (1989) 3181.
- [11] J.D. Doll, D.L. Freeman and T.L. Beck, *Advan. Chem. Phys.* 78 (1990) 61.
- [12] N. Makri, *Comput. Phys. Comm.* 63 (1991) 389.
- [13] C. Mak and D. Chandler, *Phys. Rev. A* 41 (1990) 5709; *Phys. Rev. A* 44 (1991) 2352.
- [14] A.M. Amini and M.F. Herman, *J. Chem. Phys.* 96 (1992) 5999.
- [15] C.H. Mak, *Phys. Rev. Letters* 68 (1992) 899.
- [16] N. Makri, *Chem. Phys. Letters* 159 (1989) 489.
- [17] O.A. Sharafeddin, D.J. Kouri, N. Nayar and D. Hoffman, *J. Chem. Phys.* 95 (1991) 3224;
D.K. Hoffman, N. Nayar, O.A. Sharafeddin and D.J. Kouri, *J. Phys. Chem.* 95 (1991) 8299;
D.K. Hoffman and D.J. Kouri, *J. Phys. Chem.* 96 (1992) 1179.
- [18] N. Makri, *J. Phys. Chem.*, in press.
- [19] N. Makri, *Chem. Phys. Letters* 193 (1992) 435.
- [20] M. Topaler and N. Makri, *J. Chem. Phys.* 97 (1992) 9001;
N. Makri, in: *Time-dependent quantum molecular dynamics*, eds. J. Broeckhove and L. Lathouwers (Plenum Press, New York, 1992) p. 209.
- [21] W.H. Miller, S.D. Schwartz and J.W. Tromp, *J. Chem. Phys.* 79 (1983) 4889.
- [22] R. Kapral, S. Hudson and J. Ross, *J. Chem. Phys.* 53 (1970) 4387.
- [23] D. Chandler, *Introduction to modern statistical mechanics* (Oxford Univ. Press, Oxford, 1987).
- [24] R.P. Feynman, *Statistical mechanics* (Addison-Wesley, Reading, 1972).
- [25] D. Thirumalai, E.J. Bruskin and B.J. Berne, *J. Chem. Phys.* 79 (1983) 5063.
- [26] A.J. Leggett, S. Chakravarty, A.T. Dorsey, M.P. Fisher, A. Garg and W. Zwerger, *Rev. Mod. Phys.* 59 (1987) 1.