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Citation: [The Journal of Chemical Physics](#) **98**, 6975 (1993); doi: 10.1063/1.464739

View online: <http://dx.doi.org/10.1063/1.464739>

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An approximate discretized real time path integral simulation method for nearly classical systems

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(Received 6 July 1992; accepted 28 January 1993)

A new approximate technique for real time discretized path integral simulations is introduced. The technique transforms the oscillatory integrands into nonoscillatory functions for accurate Metropolis Monte Carlo evaluation. The method is applied to a system containing a Br_2 diatomic in two Ar atoms. The vibrational transition probability of finding the diatomic in its ground vibrational state is calculated at time t . The diatomic is initially in its first vibrational state. Computations are carried out for two different times and the results are compared to the previously published results of full discretized path integral calculation. The convergence of the technique is tested as a function of the number of points in the discretized solvent path.

I. INTRODUCTION

Applications of discretized path integral Monte Carlo methods to time dependent multicoordinate systems are rare largely due to the highly oscillatory real time propagators describing the system. The local averaging techniques¹⁻⁸ introduced by Filonov,^{7,8} and developed by Freeman and Doll,⁴⁻⁶ and Miller and Makri^{2,3} offer a possible means of reducing these oscillations. However, because of the practical limitations on the width of the functions used for local averaging, the effectiveness of the method is reduced due to residual long-wavelength oscillations.

In this paper, we introduce a new technique which works well for nearly classical systems at relatively short simulation times. This technique eliminates the imaginary exponent of the product of the real time path integral propagator and its conjugate. Therefore, it transforms the time dependent oscillatory integrand of interest into a nonoscillating function which can be evaluated accurately by a Monte Carlo technique.

Our interest is in the evaluation of the transition probabilities. The transition probability contains the product of two transition amplitudes. Each transition amplitude can be expressed as a matrix element of a time dependent propagator. Therefore, the transition probability involves two path integrals and can be expressed as a functional integration over two paths for the evolution of the system. The technique introduced in this paper involves defining the coordinates of the two paths in terms of an average path and a difference path (δ_k) coordinates. Then an expansion of the action terms from the propagators is carried out through first order in δ_k , about the point $\delta_k=0$. In this case, the δ_k integral can be carried out analytically.

The vibrational transition probability is expressed as the ratio of two integrals⁹ $P'_{fi}(t)/Q$, where Q is the canonical density partition function, and $P'_{fi}(t)$ the unnormalized probability. The δ_k integrations in the numerator and denominator yield delta functions which are not suitable functions for Metropolis Monte Carlo evaluation. We are able to broaden the delta functions without significantly

changing the ratio, by multiplying the integrands with the Gaussian function $\exp(-\Sigma \epsilon \delta_k^2)$. This eliminates the numerical difficulties associated with delta functions obtained when $\epsilon=0$. It can be shown that the dependence of the probability on ϵ is linear for small ϵ values. Therefore, the probability is obtained by a linear extrapolation of ϵ to zero.

To test whether these approximations provide accurate results we apply the technique to a system of Br_2 in two Ar atoms and calculate the solvent-induced vibrational transition probability of finding the diatomic Br_2 in its ground vibrational state at time t , provided it is in its first vibrational state at $t=0$. The full quantum calculations of the solvent-induced vibrational transition probability, $P_{fi}(t)$, is presented elsewhere for this system.⁹

The vibrational wave functions are evaluated in the adiabatic representation in the calculations presented in this work and in our earlier quantum calculations.⁹⁻¹¹ The comparatively slowly moving Ar coordinates as well as the center of mass of the diatomic are gathered into a vector \mathbf{R} . The fast moving vibrational coordinates is called r . The rotational degrees of freedom are frozen in the calculations presented here, as well as in the previous full quantum calculations.⁹ There are semiclassical calculations which indicate that the rotational degrees of freedom play a small role in the vibrational relaxation of this system.¹² The solvent-diatomic potential energy terms are expanded through first order in r around the equilibrium bond length r_e . This enables us to employ the Feynman's forced oscillator propagator¹³ by which the vibrational contribution to the transition amplitude can be obtained in closed form.⁹ The resulting vibrational transition amplitudes depend on the solvent path only. A high temperature approximation to the canonical density function is assumed. This is an accurate approximation for this system. The vibrational potential is treated as harmonic, and the solvent-solvent, and solvent-diatomic potentials are approximate by Lennard-Jones potentials. This paper is outlined as follows: Section II contains mathematical modeling of the vibra-

tional transition probability problem. The results are given in Sec. III, and Sec. IV contains the conclusion.

II. THEORY

The real time propagator employed in path integral simulations contains an imaginary exponent that makes it an oscillatory function. Averaging over such rapidly oscillating functions is an extremely difficult task for Monte Carlo procedures. Local averaging of the oscillating function is an approach that minimizes the problem.¹⁻⁸ We have successfully employed such a technique to calculate the vibrational transition probabilities of Br₂ in Ar.⁹ However, this approach can be CPU intensive, since it involves taking the derivatives of the oscillating function. Moreover long range oscillations can remain after the local averaging, reducing the effectiveness of the method.

The probability that the system with the diatomic initially in the first excited vibrational state is in the ground vibrational state at time t is formally given by the expression,⁹

$$P_{10}(t) = Q^{-1} \int d\mathbf{R}_{ia} d\mathbf{R}_{ib} d\mathbf{R}_f \langle 0(\mathbf{R}_f) | e^{-i\hat{H}t/\hbar} | 1(\mathbf{R}_{ia}) \rangle \times \langle 1(\mathbf{R}_{ia}) | e^{-\beta\hat{H}} | 1(\mathbf{R}_{ib}) \rangle \langle 1(\mathbf{R}_{ib}) | e^{i\hat{H}t/\hbar} | 0(\mathbf{R}_f) \rangle, \quad (1)$$

where $|n(\mathbf{R})\rangle \equiv \psi_n^v(r, \mathbf{R})$ is the n th vibrational wave function, $\langle \dots \rangle$ is a matrix element involving integration only over the r coordinate. The real time propagators, e.g., $\langle 0(\mathbf{R}_f) | e^{-i\hat{H}t/\hbar} | 1(\mathbf{R}_{ia}) \rangle$, are in the adiabatic state representation for the vibrational degree, and coordinate representation for the solvent degrees of freedom. And Q is the partition function give by

$$Q = \text{Tr } \rho_{11} = \int d\mathbf{R} \langle 1(\mathbf{R}) | e^{-\beta\hat{H}} | 1(\mathbf{R}) \rangle. \quad (2)$$

As seen from Eq. (1), $P_{10}(t)$ contains a product of two propagators, each of which can be expressed as a Feynman path integral. Therefore, $P_{10}(t)$ can be expressed as an integral over two paths for the system. The two paths (a and b) start at different points in space, \mathbf{R}_{ia} and \mathbf{R}_{ib} , but end at the same point \mathbf{R}_f after some time t . If the system is nearly classical, the initial configurations of the two paths are very close since they are connected by the canonical density function, $\langle 1(\mathbf{R}_{ia}) | e^{-\beta\hat{H}} | 1(\mathbf{R}_{ib}) \rangle$. The high temperature approximation to this density function is employed, and should provide a good approximation for this system. We suggest that, for a nearly classical system, pairs of paths which remain close for the entire time should dominate in the calculation of the transition probability. This approximation enables us to simplify the mathematics. The resulting expression for the vibrational transition probability becomes a real function. Therefore, the CPU intensive local averaging technique can be completely eliminated.

Much of the mathematical detail concerning the calculation of the vibrational transition probability is the same as has been presented previously.⁹ The system em-

ployed consists of a diatomic molecule (Br₂) and two solvent atoms (Ar), the total potential is given by

$$V(r, \mathbf{R}) = V_d(r) + V_{sd}(r, \mathbf{R}) + V_{ss}(\mathbf{R}) + V_{\text{ext}}(\mathbf{R}^{\text{c.m.}}), \quad (3)$$

where r is the diatomic bond length, and \mathbf{R} is a vector containing the solvent coordinates (that is, Br₂ center of mass and Ar coordinates). $V_d(r)$ is the vibrational potential, $V_{sd}(r, \mathbf{R})$ and $V_{ss}(\mathbf{R})$ are solvent-diatomic and solvent-solvent potentials, respectively. The $V_{\text{ext}}(\mathbf{R}^{\text{c.m.}})$ is a harmonic potential employed to hold the cluster together. $\mathbf{R}^{\text{c.m.}}$ is the distance between an Ar atom and the center of mass of the diatomic.

To obtain the solvent dependent vibrational wave functions, $\psi_n^v(r, \mathbf{R})$, we employ the adiabatic representation.⁹⁻¹¹ This is analogous to the Born-Oppenheimer approximation.^{14,15} The vibrational wavefunctions are eigenfunctions of the fixed solvent vibrational Hamiltonian

$$\hat{H}_v = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r, \mathbf{R}), \quad (4)$$

where μ is the reduced mass of the diatomic. The total Hamiltonian is $\hat{H} = \hat{T}_s + \hat{H}_v$, where the solvent kinetic energy is given by

$$\hat{T}_s = -\sum_{j=1}^3 \frac{\hbar^2}{2m_j} \nabla_j^2 \quad (5)$$

and the sum is over the two Ar atom ($j=1,2$) and the center of mass ($j=3$).

The time dependent transition amplitude, $\langle 0(\mathbf{R}_f) | e^{-i\hat{H}t/\hbar} | 1(\mathbf{R}_i) \rangle$, is given by

$$T_{fi}(\mathbf{R}_f, \mathbf{R}_i, t) = \int dr_f dr_i \psi_f(r_f, \mathbf{R}_f) \times K(r_f, \mathbf{R}_f, r_i, \mathbf{R}_i, t) \psi_i(r_i, \mathbf{R}_i), \quad (6)$$

where K is the Feynman propagator¹³ given by

$$K(r_f, \mathbf{R}_f, r_i, \mathbf{R}_i, t) = \int D[r(\tau)] D[\mathbf{R}(\tau)] \exp \left(\frac{i}{\hbar} \int_0^t L d\tau \right) \quad (7)$$

and L is the Lagrangian of the system. The bond length coordinate, $r(t)$ vibrates over a small range. This suggests that a linear expansion of the $V_{sd}(r, \mathbf{R})$ around r_e , the equilibrium bond length, is a good approximation to this potential. Furthermore, the diatomic potential, $V_d(r)$, can be approximated by a harmonic potential, since we are interested in a low lying transition. Making these approximations the total potential has the form,

$$V(r, \mathbf{R}) = \frac{\mu\omega^2}{2} (r - r_e)^2 + \left(\frac{\partial V_{sd}(r, \mathbf{R})}{\partial r} \right)_{r=r_e} (r - r_e) + V_s(\mathbf{R}), \quad (8)$$

where $V_s(\mathbf{R}) = V_{sd}(r_e, \mathbf{R}) + V_{ss}(\mathbf{R}) + V_{\text{ext}}(\mathbf{R}^{\text{c.m.}})$. By substituting these approximations into the Lagrangian of Eq. (7), one can carry out the $D[r(t)]$ integrations in closed form.⁹ After this has been performed, we have

$$K(r_f, \mathbf{R}_f, r_b, \mathbf{R}_b, t) = \int D[\mathbf{R}(\tau)] K_V[r_b, r_f, \mathbf{R}(\tau), t] \times \exp\left(\frac{i}{\hbar} \int_0^t L_s d\tau\right), \quad (9)$$

where $L_s = \hat{T}_s + V_s$ and K_V is the forced harmonic oscillator propagator corresponding to the $D[r(\tau)]$ integration. It is given by Feynman and Hibbs.¹³ The time dependent force is $f(\tau) = -(\partial V_{sd}(r_e, \mathbf{R})/\partial r)$. The integrals of Eq. (6) over r_i and r_f can be obtained in closed form.⁹ ψ_f and ψ_i are harmonic oscillator wave functions centered around r_m , which is the \mathbf{R} dependent minimum in the potential energy with respect to the vibrational coordinate r ,

$$r_m = r_e - \left(\frac{\partial V_{sd}(r, \mathbf{R})}{\partial r}\right)_{r=r_e} / \mu\omega^2. \quad (10)$$

The adiabatic energies are given by

$$H_V \psi_n^V(r, \mathbf{R}) = E_n^V(\mathbf{R}) \psi_n^V(r, \mathbf{R}). \quad (11)$$

For the potential (8) they have the form

$$E_n^V(\mathbf{R}) = (n + 1/2)\hbar\omega + V_s(\mathbf{R}) - \left(\frac{\partial V_{sd}(r_e, \mathbf{R})}{\partial r}\right)^2 / 2\mu\omega^2. \quad (12)$$

Employing (9), the transition amplitude, Eq. (6), has the form,

$$T_{fi}(\mathbf{R}_b, \mathbf{R}_f, t) = \int D[\mathbf{R}(t)] T_{fi}^V[\mathbf{R}(t), t] \times \exp\left(\frac{i}{\hbar} \int_0^t L_s dt\right), \quad (13)$$

where T_{fi}^V is the vibrational contribution to the transition amplitude given by

$$T_{fi}^V[\mathbf{R}(t), t] = \int dr_i dr_f \psi_f(r_f, \mathbf{R}_f) \times K_V(r_b, r_f, \mathbf{R}(\tau), t) \psi_i(r_b, \mathbf{R}_i). \quad (14)$$

The transition probability, Eq. (1), can be rewritten as

$$P_{10}(t) = Q^{-1} \int d\mathbf{R}_{ia} d\mathbf{R}_{ib} d\mathbf{R}_f T_{fi}(\mathbf{R}_{ia}, \mathbf{R}_f, t) \times \rho_{11}(\mathbf{R}_{ia}, \mathbf{R}_{ib}, \beta) T_{fi}^*(\mathbf{R}_{ib}, \mathbf{R}_f, t). \quad (15)$$

In discretized path integral approximation T_{fi} has the form,¹⁶

$$T_{fi}(\mathbf{R}_b, \mathbf{R}_f, t) = \int d\mathbf{R}_1 d\mathbf{R}_2 \cdots d\mathbf{R}_{N-1} \times \exp\left[\frac{i}{\hbar} \sum_{K=1}^N \left\{ \frac{m}{2t/N} (\mathbf{R}_K - \mathbf{R}_{K-1})^2 - \frac{t}{2N} [V_s(\mathbf{R}_K) + V_s(\mathbf{R}_{K-1})] \right\}\right] T_{fi}^V[\mathbf{R}(t), t]. \quad (16)$$

Analytical expressions for $T_{fi}^V[\mathbf{R}(t), t]$ are provided elsewhere.⁹

The canonical density function, $\rho_{11} = \langle 1(\mathbf{R}_{ia}) | e^{-\beta \hat{H}} | 1(\mathbf{R}_{ib}) \rangle$ is evaluated using the diabatic representation, that is, $V_{sd}(r, \mathbf{R}) \approx V_{sd}(r_e, \mathbf{R})$. The use of the diabatic representation rather than the adiabatic representation somewhat simplifies the calculation of ρ_{11} without significantly altering the results. However, it is important to employ the adiabatic representation in the evaluation of the transition amplitudes, since the linear coupling in $r - r_e$ in Eq. (8) is ignored in the diabatic representation. It is this coupling which induces the vibrational transitions. Since T_s and H_v commute in the diabatic representation and $\hat{H} = \hat{T}_s + \hat{H}_v$, ρ_{11} has the form

$$\langle 1(\mathbf{R}_{ia}) | e^{-\beta \hat{H}} | 1(\mathbf{R}_{ib}) \rangle = \langle \mathbf{R}_{ia} | e^{-\beta \hat{H}_s} | \mathbf{R}_{ib} \rangle, \quad (17)$$

where $\hat{H}_s = \hat{T}_s + V_s + 3\hbar\omega/2$. Since the calculations are performed at $T = 300$ K, a high temperature approximation to ρ_{11} can be used. The canonical partition function can be evaluated from $Q = \text{Tr } \rho_{11}$, where Tr is the trace over solvent coordinates. This is discussed in more detail below.

The expression for the transition probability, Eq. (15), can be written as

$$P_{10}(t) = Q^{-1} \int d\mathbf{R}_{ia} d\mathbf{R}_{ib} d\mathbf{R}_f \prod_{K=1}^{N-1} d\mathbf{R}_{Ka} \prod_{K=1}^{N-1} d\mathbf{R}_{Kb} \times A \exp[\phi_T(\mathbf{R}_{ia}, \mathbf{R}_{1a}, \dots, \mathbf{R}_f) + \phi_T^*(\mathbf{R}_{ib}, \mathbf{R}_{1b}, \dots, \mathbf{R}_f) + \phi_\rho(\mathbf{R}_{ia}, \mathbf{R}_{ib})], \quad (18)$$

where ϕ_T is the contribution to the exponent from T_{fi} (including terms from T_{fi}^V), ϕ_ρ is the contribution from the canonical density, and A is the product of the prefactors for the transition amplitudes and the canonical density. The function ϕ_T has real and imaginary parts, while ϕ_ρ is real. In our calculations we employ the Fourier representation of the paths, defined by^{13,17-21}

$$\mathbf{R}(\tau) = \mathbf{R}_i + (\mathbf{R}_f - \mathbf{R}_i)\tau/t + \sum_{K=1}^{N-1} \mathbf{C}_K \sin \frac{K\pi\tau}{t}. \quad (19)$$

In this case each path, a and b , is described by $\mathbf{R}_b, \mathbf{R}_f$, and the Fourier coefficients $\mathbf{C}_1, \dots, \mathbf{C}_{N-1}$, rather than by $\mathbf{R}_b, \mathbf{R}_f, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N-1}$.

The difference between the two paths, $\mathbf{R}_a(\tau) - \mathbf{R}_b(\tau)$, is a measure of the quantum uncertainty in the system. In a classical system, the system evolves along a single classical path. The complex nature of the exponent causes the double path integral to oscillate, leading to extensive cancellation. Since the solvent coordinates correspond to heavy particle motions, we might expect a nearly classical behavior and the dominant contribution to the double path integration to come from regions where the two paths are nearly identical. In order to take advantage of this idea, we describe the two paths by the mean path, represented by $\bar{\mathbf{R}}_b, \mathbf{R}_f, \bar{\mathbf{C}}_1, \bar{\mathbf{C}}_2, \dots, \bar{\mathbf{C}}_{N-1}$, and the difference between the paths, $\delta_0, \delta_1, \delta_2, \dots, \delta_{N-1}$, where

$$\bar{\mathbf{R}}_i = (\mathbf{R}_{ia} + \mathbf{R}_{ib})/2, \quad (20a)$$

$$\bar{\mathbf{C}}_K = (\mathbf{C}_{Ka} + \mathbf{C}_{Kb})/2, \quad (20b)$$

$$\delta_0 = \mathbf{R}_{ia} - \mathbf{R}_{ib}, \quad (20c)$$

$$\delta_K = \mathbf{C}_{Ka} - \mathbf{C}_{Kb}. \quad (20d)$$

In these expressions \mathbf{C}_{Ka} and \mathbf{C}_{Kb} are the values of \mathbf{C}_K for the a and b paths, respectively. Since regions of the integration domain for which δ_0 and the δ_K 's are small are expected to dominate, we expand ϕ , the exponent of Eq. (18), about $\delta_0 = \delta_1 = \dots = \delta_{N-1} = 0$. This yields¹⁶

$$\phi = [2 \operatorname{Re}(\phi_T) + \phi_\rho]_{\delta=0} + \sum_{K=0}^{N-1} \delta_K \cdot \frac{\partial}{\partial \delta_K} (\phi_{Ta} + \phi_{Tb}^*)|_{\delta=0} - \frac{m}{2\hbar^2\beta} \delta_0^2 + \text{higher order terms}, \quad (21)$$

where $\phi_{Ta} = \phi_T(\mathbf{R}_{ia}, \mathbf{R}_{1a}, \dots, \mathbf{R}_f)$ and $\phi_{Tb} = \phi_T(\mathbf{R}_{ib}, \mathbf{R}_{1b}, \dots, \mathbf{R}_f)$, and $\delta=0$ indicates that the term is evaluated for $\delta_0 = \delta_1 = \dots = \delta_{N-1} = 0$. If $\delta=0$, then $\phi_{Ta} = \phi_{Tb} = \phi_T$. The term $(\partial/\partial \delta_K)(\phi_{Ta} + \phi_{Tb}^*)|_{\delta=0}$ is easily shown to be purely imaginary. It is also readily shown that all terms in the expansion which contain an even number of δ 's are real and all terms containing an odd member of δ 's are imaginary.

If the expansion is truncated after the linear terms, and the δ dependence of the prefactors is ignored, then the δ_K integrations yield a product of Dirac delta functions. These delta functions provide conditions that must be satisfied by the mean path. In order to avoid the numerical difficulties associated with searching for the paths which satisfy these conditions, we alter the integrand by multiplying it by Gaussian functions of the δ_K 's¹⁶

$$P_\epsilon(t) = Q^{-1} \int d\bar{\mathbf{R}}_i d\mathbf{R}_f d\bar{\mathbf{C}}_1 \dots d\bar{\mathbf{C}}_{N-1} d\delta_0 d\delta_1 \dots d\delta_{N-1} \times A \exp \left\{ \phi|_{\delta=0} + \sum_{K=0}^{N-1} \frac{\partial \phi}{\partial \delta_K} \Big|_{\delta=0} \cdot \delta_K - \sum_{K=1}^{N-1} \epsilon_K \delta_K^2 - \frac{m}{2\hbar^2\beta} \delta_0^2 \right\}. \quad (22)$$

We have used the quadratic term for δ_0 from the kinetic energy term in ρ_{11} , since it is readily available. All other quadratic terms, however, involve second derivatives of the potential. It is numerically advantageous to devise a calculation method which avoids the evaluation of these terms. This is accomplished by the introduction of the $\exp(-\epsilon_K \delta_K^2)$ factors.

Ignoring the δ dependence of the prefactor A , the δ integrations yield¹⁶

$$P_\epsilon(t) = Q^{-1} \int d\bar{\mathbf{R}}_i d\mathbf{R}_f d\bar{\mathbf{C}}_1 \dots d\bar{\mathbf{C}}_{N-1} \left(\frac{2\pi\hbar^2\beta}{\mu} \right)^{M/2} \times \prod_{K=1}^{N-1} \left(\frac{\pi}{\epsilon_K} \right)^{M/2} A_0 \times \exp \left\{ \phi_{\delta=0} - \sum_{K=1}^{N-1} \phi_K^2 / 4\epsilon_K - \frac{\hbar^2\beta}{2m} \phi_0^2 \right\}, \quad (23)$$

where M is the number of solvent coordinates, A_0 denotes A evaluated at $\delta=0$, and $\phi_K = -i(\partial\phi/\partial\delta_K)|_{\delta=0}$ for $K=0, 1, \dots, N-1$. The factor of $-i$ is included in the definition of ϕ_K so that ϕ_K is real. [Recall $(\partial\phi/\partial\delta_K)|_{\delta=0}$ is imaginary.] For simplicity we choose all ϵ_K 's to have the same value in a given calculation. In the limit as $\epsilon \rightarrow 0$ the delta function conditions on the mean path are recovered. For positive values of ϵ , the points in path space which satisfy these conditions are broadened into Gaussian regions. As we show below, this leads to a computationally feasible Monte Carlo procedure which avoids the problems presented by the $\epsilon=0$ integral.

To better understand the effect that the Gaussian factors have on the value of the integral, the prefactor A_0 can be expanded about a path which satisfies the conditions $\phi_K=0$ for $K=1, 2, \dots, N-1$. Near this path ϕ_K can be approximated as a linear function of the variables describing the mean paths, $\mathbf{R}_p, \mathbf{R}_f, \bar{\mathbf{C}}_1, \bar{\mathbf{C}}_2, \dots, \bar{\mathbf{C}}_{N-1}$. We denote the set of these variables by $\{\xi_j\}$. The linear expansion of ϕ_K about the path satisfying $\phi_K=0$ has the form

$$\phi_K \approx \sum_j \frac{\partial \phi_K}{\partial \xi_j} (\xi_j - \xi_{j_0}). \quad (24)$$

The expansion of the prefactor, through quadratic terms, is

$$A_0 = A_0(\xi_0) + \sum_j \frac{\partial A_0}{\partial \xi_j} (\xi_j - \xi_{j_0}) + \frac{1}{2} \sum_{j,k} \frac{\partial^2 A_0}{\partial \xi_j \partial \xi_k} (\xi_j - \xi_{j_0})(\xi_k - \xi_{k_0}). \quad (25)$$

Substituting Eqs. (24) and (25) into Eq. (23), and performing the integrations demonstrates that $P_\epsilon(t)$ has the form

$$P_\epsilon(t) \approx a + b\epsilon \quad (26)$$

through first order in ϵ . Therefore, the $\epsilon \rightarrow 0$ result can be obtained by linear extrapolation of results for positive ϵ .

In order to implement a Monte Carlo procedure, it is very helpful if P_{10} can be expressed as the ratio of two integrals with the same set of integration variables and the same integration domain. This is readily accomplished by writing Q as

$$Q = \operatorname{Tr} \rho_{11} = \int d\mathbf{R} \langle 1(\mathbf{R}) | e^{-\beta \hat{H}_s} | 1(\mathbf{R}) \rangle = \int d\mathbf{R} \langle 1(\mathbf{R}) | e^{-i\hat{H}_s t/\hbar} e^{\beta \hat{H}_s} e^{-i\hat{H}_s t/\hbar} | 1(\mathbf{R}) \rangle = \int d\mathbf{R}_{ia} d\mathbf{R}_{ib} \langle 1(\mathbf{R}_f) | e^{-i\hat{H}_s t/\hbar} | 1(\mathbf{R}_{ia}) \rangle \times \langle 1(\mathbf{R}_{ia}) | e^{-\beta \hat{H}_s} | 1(\mathbf{R}_{ib}) \rangle \langle 1(\mathbf{R}_{ib}) | e^{i\hat{H}_s t/\hbar} | 1(\mathbf{R}_f) \rangle. \quad (27)$$

As before, $\langle n_1(\mathbf{R}_1) | \dots | n_2(\mathbf{R}_2) \rangle$ denotes a matrix element in the coordinate representation for the solvent coordinates and in the vibrational state representation for the vibrational coordinate. Because it simplifies the calculations

slightly without introducing significant errors, we evaluate Eq. (27) in the diabatic representation, which is obtained by neglecting the linear term in $r-r_e$ in Eq. (8), rather than the adiabatic representation. In inserting the resolution of the identity in the last line of Eq. (27), there should formally be a summation over vibrational states. Since \hat{H}_s is the diabatic Hamiltonian, the summations over vibrational states are reduced to the single term shown in Eq. (27) involving the $n=1$ state. Expression (27) for Q can be written as an integration over two paths, analogous to the integration in Eq. (18). This expression can then be written in terms of the mean path and the difference in the paths. The integrand can be written as a prefactor, multiplied by an exponential function, and the exponent can be expanded about its value when the two paths are equal. Finally, the integrand can be multiplied by a Gaussian function in the variables $\delta_0, \delta_1, \dots, \delta_{N-1}$, describing the difference between the paths, and the integrations over $\delta_0, \delta_1, \dots, \delta_{N-1}$ can be performed. All this is analogous to the manipulations outlined in Eqs. (18) through (23).

The transition probability can now be written as

$$P_{10}(t) = \frac{\int d\xi F(\xi)}{\int d\xi G(\xi)} = \frac{\int d\xi \rho(\xi) F(\xi)/P(\xi)}{\int d\xi \rho(\xi) G(\xi)/P(\xi)} = \frac{\langle F/P \rangle_\rho}{\langle G/P \rangle_\rho}, \quad (28)$$

where $\rho(\xi)$ is a normalized weighing function proportional to $P(\xi)$, and ξ represents the complete set of integration variables, $\bar{\mathbf{R}}, \mathbf{R}_f, \bar{\mathbf{C}}_1, \dots, \bar{\mathbf{C}}_{n-1}$. $F(\xi)$ is the integrand in Eq. (23), and $G(\xi)$ is the corresponding integrand for Q . These functions depend on the value of ϵ , as does $P_{10}(t)$. We choose the unnormalized sampling function in most calculations to be

$$P(\xi) = \max\{|F(\xi)|, |G(\xi)|\} c. \quad (29)$$

By appropriately choosing the constant c , a Metropolis Monte Carlo calculation, employing P as the sampling function, should give roughly equal weight to those regions of the integration domain which make significant contributions to the numerator integral and those regions which are important for the denominator integral. In practice a series of short preliminary calculations are performed with different values of c , and a value of c is chosen which provides good statistics for both the numerator and denominator integrals.

The sampling procedure just outlined is effective as long as there is significant overlap between the regions important for the numerator and those important for the denominator. However, if they are separated by a wide region across which the sampling function is small, the procedure crosses very infrequently between numerator regions and the denominator regions. In this case, very long simulation runs are required in order to obtain statistically accurate results.

If instead of F and G as the integrands, suppose we had $F_0 = F$ and $F_1 = F^{(1-\gamma_1)} G^{\gamma_1}$ as the integrands of the numerator and the denominator, respectively, where $0 < \gamma_1 < 1$. If γ_1 is small enough, then the numerator regions and denominator regions should overlap significantly in a simulation employing the procedure just described. The same is true if

TABLE I. Probabilities, $P_{10}(t)$ for $t=0.1$ ps.

ϵ	n	$N=3$		$N=6$		$N=9$	
		$P_{10}(t) \times 10^4$	n	$P_{10}(t) \times 10^4$	n	$P_{10}(t) \times 10^4$	n
200.0	1	1.416 \pm 0.02	1	1.856 \pm 0.19	1	1.923 \pm 0.07	
100.0	1	1.090 \pm 0.02	1	1.409 \pm 0.12	1	1.304 \pm 0.05	
50.0	1	0.889 \pm 0.04	1	1.023 \pm 0.15	1	1.099 \pm 0.01	
25.0	1	0.847 \pm 0.05	1	0.862 \pm 0.02	1	0.970 \pm 0.15	
12.5	1	0.796 \pm 0.03	1	0.929 \pm 0.09	2	1.143 \pm 0.09	
6.25	1	0.887 \pm 0.03	2	0.902 \pm 0.21	2	0.848 \pm 0.12	
0.0		0.779 ^a		0.810 ^a		0.931 ^a	
$P_{10}(t)^b \times 10^4$		1.037 \pm 0.125		0.923 \pm 0.113		1.250 \pm 0.129	

^aObtained by linear least squares extrapolation of ϵ to zero.

^bProbabilities obtained from our previous work (Ref. 9).

$F_1 = F^{(1-\gamma_1)} G^{\gamma_1}$ is the numerator integrand and $F_2 = F^{(1-\gamma_2)} G^{\gamma_2}$ is the denominator integrand, if γ_2 is not too different from γ_1 . Thus the statistical difficulties due to the lack of crossings between the numerator and denominator regions can be avoided by performing a number of simulations, which employing the (unnormalized) sampling functions

$$P_j(\xi) = \max\{|F_j(\xi)|, |F_{j+1}(\xi)| c_j\}, \quad (30)$$

where $F_j = F^{(1-\gamma_j)} G^{\gamma_j}$, and $0 = \gamma_0 < \gamma_1 < \gamma_2 \dots < \gamma_{n-1} < \gamma_n = 1$. The ratio $\langle F_j/P_j \rangle_{\rho_j} / \langle F_{j+1}/P_j \rangle_{\rho_j}$ is obtained from the j th calculation, and ρ_j is the normalized weighing function proportional to P_j . The transition probability is given by

$$P_{10}(t) = \frac{\langle F_0/P_0 \rangle_{\rho_0}}{\langle F_1/P_0 \rangle_{\rho_0}} \frac{\langle F_1/P_1 \rangle_{\rho_1}}{\langle F_2/P_1 \rangle_{\rho_1}} \dots \frac{\langle F_{n-1}/P_{n-1} \rangle_{\rho_{n-1}}}{\langle F_n/P_{n-1} \rangle_{\rho_{n-1}}} \quad (31)$$

since $F_0 = F$ and $F_n = G$.

III. RESULTS

In order to compare our results to the results obtained previously,⁹ in which no assumptions regarding closeness of the two paths were made, we apply the procedure described in the preceding sections to the same prototype system consisting of a diatomic Br_2 in two Ar atoms. The specific potentials are the same as employed in Ref. 9.

The simulations are carried out for two different times, 0.1 and 0.2 ps. As it was shown in our previous paper⁹ (Table III), for times shorter than 0.1 ps regions where the two paths are extremely close dominate, since the simulations with $N=1$ give converged results. For each time considered the vibrational transition probability, $P_{10}(t)$, is calculated for a number of different N 's, the number of discretized points in a given solvent coordinate path, and a set of different ϵ 's. For the times considered, relatively small values of N accurately approximate the solvent path. These results are summarized in Tables I and II. In the last row of each table the value of the probability, $P_{10}(t)$, from our previous work is given for comparison. Also given in the tables are values for n , the number of simulations employed in the calculation [see Eq. (31)]. For moderately large values of ϵ , there are enough crossings between the

TABLE II. Probabilities, $P_{10}(t)$ for $t = 0.2$ ps.

ϵ	n	$N=6$		$N=9$		$N=12$	
		$P_{10}(t) \times 10^4$	n	$P_{10}(t) \times 10^4$	n	$P_{10}(t) \times 10^4$	n
200.0	1	5.951 ± 1.05	1	4.410 ± 0.02	1	6.332 ± 0.60	
100.0	1	2.738 ± 0.52	1	2.859 ± 0.28	1	3.183 ± 0.06	
50.0	1	2.117 ± 0.43	1	2.935 ± 0.49	1	2.608 ± 0.42	
25.0	2	2.188 ± 0.32	2	2.309 ± 0.41	2	1.816 ± 0.17	
12.5	2	1.699 ± 0.23	2	1.412 ± 0.21	2	1.778 ± 0.04	
0.0		1.707^a		1.732^a		1.549^a	
$P_{10}(t)^b \times 10^4$		1.711 ± 0.326		1.672 ± 0.172		1.650 ± 0.226	

^aObtained by linear least squares extrapolation of ϵ to zero.

^bProbabilities obtained from our previous work (Ref. 9).

numerator and denominator to ensure statistically accurate results when $n=1$. However, for smaller values of the ϵ_K 's a value of $n=2$ is required to obtain good statistics.

The probabilities given are the averaged result of three independent runs with deviations shown. The total number of moves per runs 3×10^6 for $N=3$, 3.6×10^6 for $N=6$, 4.2×10^6 for $N=9$, and 4.8×10^6 for $N=12$. Since the deviations are calculated on the basis of only three runs, they should be viewed only as crude estimates. Since the result for $N=3$, $\epsilon=6.25$, and $t=0.10$ ps seemed to deviate from the expected linear behavior in ϵ , an extra ten runs were performed. The result based on this ten run set is $P_{10}(t) = 0.804 \times 10^{-4} \pm 0.04 \times 10^{-4}$. This agrees with the expected behavior to within statistical error. This result also indicates that the uncertainty in the three run set for this case should be a factor of 2 or more higher than the value given in Table I.

IV. CONCLUSION

In this paper, we have introduced a new technique for calculation of solvent induced vibrational transition probability. The system considered is Br_2 in Ar at room temperature. It is assumed that the diatomic is in its first vibrational state at $t=0$. The probability of finding the diatomic in its ground vibrational state at time t is computed. By expanding the solvent diatomic potential around the equilibrium bond length, r_e , through first order, we are able to employ the Feynman forced oscillator propagator¹³ to analytically obtain the vibrational coordinates contribution to the transition amplitude. Furthermore, we have introduced a new technique for nearly classical real time path integral simulations. For such simulations it is assumed that the integrals are dominated by regions of the integration domain for which the two solvent paths are very close. If this is valid, then one may expand the potential around the average path through first order. This transforms the integrands into real functions, and as a result no local averaging is needed. While the final result is real, it should be noted that this method does account for phase interference between the paths through the integration over the variables $\delta_1, \delta_2, \dots, \delta_{N-1}$, which describe the difference between paths a and b . The assumption in the method is that a low order approximation of the phase in these variables is valid. This results in the integrations being analytical. The quadratic terms in the expression of the

exponent in $\delta_1, \delta_2, \dots, \delta_{N-1}$ are ignored. These terms are real. If these were included there would be corrections to the numerator and denominator which are linear in the second derivatives of the exponent with respect to these variables. This follows from the same argument which yields the ϵ dependence in Eq. (26). The approximation used in this work, which avoids the evaluation of the second derivatives, neglects these terms, assuming they are negligible. Comparison of our results with the results of our previous work⁹ show an excellent agreement, as is evident in Tables I and II. The linear least squares extrapolated probability ($\epsilon=0$) differs from our previous work by 0% to 25% for both times considered.

By multiplying the integrands by Gaussian factors $\exp(-\epsilon \delta_K^2)$ in the variables describing the difference between the two solvent paths, the function of the mean path which results from the integrations over the difference variables is broadened from a delta function to a weighing function peaked at the point (in the mean path space) satisfying the delta function condition obtained in the $\epsilon \rightarrow 0$ case. The mean squared width of the weighing functions is proportional to the ϵ . We have shown that the leading correction to the $\epsilon \rightarrow 0$ result is linear in ϵ . For very large ϵ , the correction terms become large, and the introduction of the $\exp(-\epsilon \delta_K^2)$ factors significantly alters the result. For small ϵ , the important regions of the integration domains become sharply peaked. In this case sampling problems arise due to the lack of overlap of the regions important for the numerator and the denominator. We are able to overcome these difficulties by a combination of two additional features in the calculations, a multistage sampling procedure and the use of a least squares extrapolation to $\epsilon \rightarrow 0$. For relatively small ϵ , we express the transition probability as a product of ratios of integrals. These ratios are chosen so that the denominator in one cancels the numerator in the next. After these cancellations are accounted for all that remains is the ratio of the first numerator and the last denominator, which is the same expression for $P_{10}(t)$ as is present in the simpler calculation procedure. Each individual ratio in this method is the quotient of two integrals. The two integrands are chosen to be similar, to avoid the sampling problem which arises in the simpler single ratio procedure. Each ratio can be readily evaluated by a separate Monte Carlo calculation.

With this procedure it is feasible to evaluate $P_{10}(t)$ for sufficiently small ϵ that a linear least squares extrapolation to the $\epsilon \rightarrow 0$ result is quite accurate. Some care must be taken in the choice of the range of ϵ employed in the least squares extrapolation. If too large a range is chosen, higher order correction terms in ϵ can cause errors.

For larger t , the method becomes somewhat more difficult to implement. The sampling difficulties arise at larger values of ϵ . In the 0.1 ps calculation $n=1$ calculations are feasible down to $\epsilon=6.25$. For $t=0.2$ ps, $n=1$ calculations become difficult below $\epsilon=50$. Even with $n=2$, $\epsilon=12.5$ is about the limit that can be readily obtained. Furthermore, the slope of $P_{10}(t)$ as a function of ϵ is higher for $t=0.2$ ps than for $t=0.1$ ps, indicating that the correction terms become important more rapidly at large t .

ACKNOWLEDGMENT

This work is supported by NSF Grant No. CHE-9108500.

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