Vibrational energy transfer in linear hydrocarbon chains: New quantum results

Dimitri Antoniou and Steven D. Schwartz

Vibrational energy transfer in linear hydrocarbon chains: New quantum results

Dimitri Antoniou and Steven D. Schwartz
Department of Physiology and Biophysics, Albert Einstein College of Medicine,
1300 Morris Park Avenue, Bronx, New York 10461

In this paper we report quantum calculations of the survival probability in linear hydrocarbon chains. We have performed both adiabatic gauge transform calculations and calculations that include corrections beyond the adiabatic approximation. We have managed to perform intermediate steps of the calculations analytically. We require the initial basis set expansion and final summations to be performed numerically. The corrections beyond the adiabatic approximation are shown to be small for this system for multiple time step calculations and large for single time step calculations. We have proved an identity that allows the extension of the calculations for HC_2 to longer chains at little computational cost. In particular, we have proved that the quantum solution for any linear hydrocarbon chain can be obtained from the solution of a problem with 3 degrees of freedom. We have performed multi-step adiabatic calculations for HC_2 and HC_6 that converge at up to 35–40 fs. We have devised a simple diagrammatic scheme that summarizes our method in a very compact form. Finally, we propose an alternative strategy of calculation that might lead to very fast solutions of the quantum dynamics of this system. © *1995 American Institute of Physics.*

I. INTRODUCTION

The understanding of vibrational energy dynamics is crucial for many current problems of chemical physics and biochemistry. For example, problems of practical interest involve scattering with vibrationally excited species, like combustion reactions and photolysis of hemoglobin. The goal in such problems would be the understanding of the effect of vibrational energy on reaction probability. The study of the survival probability for linear hydrocarbon chains we pursue in this paper, is part of an effort to understand this class of problems. The study of vibrational energy transfer is difficult because we deal with a problem with many degrees of freedom. Systems of great practical interest like biomolecules consist of thousands of atoms.

The use of molecular dynamics techniques makes feasible calculations for fairly large molecules. Quantum effects like zero-point motion and quantum tunneling can however become important, for example, when light atoms are involved like H atoms in biomolecules. There have been attempts[1] to enforce zero-point energy conservation with moderate success. To have a satisfactory description we need a fully quantum treatment. As we pass, however, from classical to quantum mechanics, the size of molecules that are tractable is reduced dramatically. Quantum calculations are already difficult for a molecule consisting of seven atoms like HC_6. We were drawn to this problem by Makri and Topaler's work[2] on quantum calculations for this system. After approximating the Hamiltonian by a bi-linear system-bath Hamiltonian, they were able to apply their QUAPI algorithm. In our initial work we use operator and basis set methods which require no such approximate Hamiltonian. The present paper continues this effort to present in a systematic way quantum calculations of vibrational energy transfer in hydrocarbon chains.

In the next section we present the model that will be studied. In Section III we present the adiabatic approximation and use an analogy with gauge transformations to derive a form that can be evaluated partially analytically. We then perform multiple-step calculations that converge up to at least 35 fs. In Section IV we present a systematic way to calculate analytically the corrections beyond the adiabatic approximation, by an expansion of the evolution operator and exponential resummation.[3] We show that for this system the corrections to the adiabatic approximation are very small when multiple time steps are used. In Section V we prove an identity that allows the easy extension of the calculation to HC_6 and present numerical results for multiple-step calculations of the survival probability for HC_6 that converge at up to 35–40 fs. In Section VI we present a simple diagrammatic scheme that summarizes the results of the previous sections in a very compact form. In Section VII we discuss possible extensions of this work and suggest an approach using fast Fourier transforms that might allow very fast evaluations of the quantum dynamics of many-dimensional vibrational systems.

II. THE LINEAR HYDROCARBON MODEL

The simplest Hamiltonian for the study of vibrational energy transfer is that of a linear hydrocarbon chain. The standard model for this molecule is the following. The CC bonds are considered to be harmonic, while the terminal CH bond is described by a Morse oscillator:

$$H = \frac{p_N^2}{2\mu_{CH}} + V_{CH}(r_N)$$
$$+ \sum_{i=1}^{N-1} \left[\frac{p_i^2}{2\mu_{CC}} + \frac{1}{2}\mu_{CC}\omega_{CC}^2 r_i^2 - \frac{p_i p_{i+1}}{m_C} \right], \quad (2.1)$$

where r_i, p_i are the coordinates of the CC bonds and r_N, p_N of the CH bond (μ_{CH}, μ_{CC} are the reduced masses of the CH and CC bonds respectively and m_C is the mass of the carbon atom). In Eq. (2.1) the coordinates refer to displacement from the equilibrium positions. The frequency of the harmonic oscillator that models the CC bond is $\omega_{CC} = 0.008429$ a.u. The Morse potential for the anharmonic oscillator is given by

$$V_{CH}(r_N) = D_{CH}(1 - e^{-\beta_{CH}r_N})^2 \qquad (2.2)$$

with $\beta_{CH} = 1.03\, a_0^{-1}$ and $D_{CH} = 0.134$ a.u. The bond oscillation periods are $T_{CH} = 11$ fs and $T_{CC} = 18$ fs.

In the rest of the paper we shall focus our attention on the following problem. Initially (at time $t = 0$) the CH bond is in its nth excited state while the CC bonds are in their ground state. We shall calculate the survival probability that at a later time t the system will be in its initial state. Earlier works that have examined vibrational energy transfer in linear hydrocarbon chains are Ref. 1, where classical molecular dynamics methods were used, as already mentioned, Ref. 2, where a quantum calculation was performed using influence functional evaluations of the Feynman propagator and Ref. 4, where one of us introduced the formalism that we shall extend in this paper. The model for the linear hydrocarbon chain we have described above actually overestimates the coupling. It is interesting nevertheless, because it allows us to compare with previous theoretical work and test methods for the study of many-dimensional problems. In the next section we shall show how it is possible to obtain partially analytic expressions for the adiabatic results that result from a basis set expansion.

III. THE ADIABATIC APPROXIMATION

For physical clarity of the presentation of the approximations we propose, we first consider the case of the HC_2 molecule. The extension to the HC_6 molecule will be done in Section V. We write the Hamiltonian for HC_2 in the following form:

$$H = H_{CH} + H_{CC} - \frac{p_{CH}p_{CC}}{m_C}, \qquad (3.1)$$

where H_{CH} is the anharmonic Hamiltonian for the Morse oscillator and H_{CC} is the harmonic Hamiltonian for the CC bond. If $\Psi(t=0) = \psi_n(r_{CH})\phi_0(r_{CC})$ is the quantum state of the system at time $t = 0$, where ψ_n, ϕ_0 are eigenfunctions of the Morse potential and harmonic oscillator, respectively (the Morse oscillator is initially in its nth excited state), then the survival probability that the system will be at the same state at time t is

$$P(t) = |\langle \psi_n(r_{CH})\phi_0(r_{CC})|U(t)|\psi_n(r_{CH})\phi_0(r_{CC})\rangle|^2, \qquad (3.2)$$

where $U(t)$ is the evolution operator which is defined by the identity $\Psi(t) = U(t)\Psi(t=0)$ or equivalently $U(t) = e^{-iHt}$, with H defined by Eq. (3.1).

We shall now formulate the adiabatic approximation as an approximate evaluation of the evolution operator. The adiabatic approximation is equivalent to writing

$$U(t) = \exp\left[-i\left(H_{CH} + H_{CC} - \frac{p_{CH}p_{CC}}{m_C}\right)t\right]$$

$$\simeq \exp[-iH_{CH}t]\exp\left[-i\left(H_{CC} - \frac{p_{CH}p_{CC}}{m_{CC}}\right)t\right]. \qquad (3.3)$$

We have chosen to group the coupling term with the CC interaction. In fact, our method allows equally well the evaluation of $U(t)$ in case we group the coupling with the CH interaction, if we had decided that this is physically more reasonable. In order to understand what we leave out by making this approximation we have to recall the Zassenhauss theorem.[5] This states that if A, B are operators, then

$$e^{A+B} = e^A e^B e^{C_1} e^{C_2}..., \qquad (3.4)$$

where C_n contains nth order commutators of A, B. In particular, $C_1 = \frac{1}{2}[A,B]$, $C_2 = -\frac{1}{3}[[A,B],B] - \frac{1}{6}[[A,B],A]$, etc. The adiabatic approximation is equivalent to setting all C_n equal to zero.

The operator $\exp\{-i[H_{CC} - (p_{CH}p_{CC}/m_C)]t\}$ in Eq. (3.3) is related to the propagator of the harmonic oscillator Hamiltonian $\exp(-iH_{CC}t)$. As has been shown in Ref. 4 it can be thought of as a gauge transformation of the harmonic propagator. In particular, if $\mathbf{A}$ is the magnetic potential which is related to the magnetic field by $\mathbf{B} = \nabla \wedge \mathbf{A}$, the potential energy of a particle with momentum p_{CC} is proportional to $\mathbf{A} \cdot \mathbf{p_{CC}}$ and there is no physical difference if we make the gauge transformation $\mathbf{A} \to \mathbf{A} + \nabla\phi$. Setting $\mathbf{A} = 0$ and $\nabla\phi = p_{CH}/m_C$ and requiring gauge invariance leads to[6]

$$\exp\left[-i\left(H_{CC} - \frac{p_{CH}p_{CC}}{m_C}\right)t\right]$$

$$= \exp(ip_{CH}r_{CC}/2)\exp(-iH_{CC}t)$$

$$\times \exp(-ip_{CH}r_{CC}/2). \qquad (3.5)$$

The operators $\exp(\pm ip_{CH}r_{CC}/2)$ are just translational operators in the r_{CH} space (they translate r_{CH} by $\mp r_{CC}/2$). We put Eqs. (3.3,3.5) back into Eq. (3.2) and insert complete sets of states to find the adiabatic result for the survival probability:

$$P_{ad}(t) = |\sum_{jk} e^{-iE_n^{Mo}t}e^{-iE_k^{ho}t}$$

$$\times T_-(n,0;j,k)T_+(j,k;n,0)|^2, \qquad (3.6)$$

where $E_n^{Mo} \simeq (n + \frac{1}{2})\omega_{CH} - (n + \frac{1}{2})^2\omega_{CH}^2/4D_{CH}$, $E_k^{ho} = (k + \frac{1}{2})\omega_{CC}$ are the Morse and harmonic oscillator energies, respectively, and

$$T_\pm(l,m;l',m') \equiv \left\langle \psi_l(r_{CH})\left\langle \phi_m(r_{CC})\right|\right.$$

$$\times \left.\psi_{l'}\left(r_{CH} \pm \frac{r_{CC}}{2}\right)\right\rangle \phi_{m'}(r_{CC})\right\rangle, \qquad (3.7)$$

where ψ_l, ϕ_m are the anharmonic and harmonic eigenfunctions, respectively.

There are two computational advantages in this formulation, of the adiabatic approximation. First, when we extend Eq. (3.6) to multiple-step calculations we shall only need the shifted overlap matrix elements $T_\pm$ of Eq. (3.7), which can

therefore be evaluated once and stored for future use. Second, due to the fact that the coupling is weak there is little mixing of states and the number of the necessary summations in Eq. (3.6) is reduced. We have found numerically that matrix elements T with $|l-l'|>2$ or $|m-m'|>2$ are very small.

The matrix elements $T_\pm$ are two-dimensional integrals and can be evaluated numerically. It is also possible, however, to evaluate them analytically. This leads to the surprising situation where much of the quantum calculation of vibrational energy transfer in hydrocarbon chains has been performed analytically. We again emphasize that an initial basis set expansion and final summations are performed numerically. We shall briefly describe how this analytic evalu-

ation of the matrix elements $T_\pm$ is possible. First, we expand the Morse eigenfunction ψ_n as a series of harmonic oscillator wave functions: $\psi_n = \Sigma_j c_j^{(n)} \phi_j$. The coefficients $c_j^{(n)}$ can be evaluated numerically. For example, for $n=5$ the coefficients $c_j^{(5)}$ for $j=1,...,15$ are: 0.1409, -0.2157, 0.1549, 0.0887, 0.0708, 0.6201, 0.6488, 0.0035, -0.2364, 0.0525, 0.1523, -0.0161, -0.0653, 0.0177, 0.0328. After this expansion we are left with a double integral of Hermite polynomials times Gaussian functions. The Hermite polynomial $H(r_{CH} \pm r_{CC}/2)$ can be expanded and the integration over r_{CH} leads to a sum of associated Laguerre polynomials. These are expanded and the integration over r_{CC} leads to a sum of hypergeometric functions:

$$
\begin{aligned}
T_\pm(l,m;l',m') = \sum_{j,j'} c_j^{(l)} c_{j'}^{(l')} \sum_{s=0}^{\min\{j,n\}} \sum_{n=0}^{j'} \sum_{t=0}^{m+m'} \frac{2^{\max\{j,n\}-3s-2|n-j|+2t-3-\frac{1}{2}(j'-n+|n-j|+2s)}}{\pi(2^{j+j'+m+m'}j!j'!m!m'!)^{1/2}} \\
\times (\pm 1)^{(j'-n)} \binom{j'}{n} \binom{\max\{j,n\}}{|n-j|-s} \frac{\min\{j,n\}!}{s!} \frac{2^{(m+m'-t)/2}m!m'!}{\left(\frac{m+m'-t}{2}-m\right)!\left(\frac{m+m'-t}{2}-m'\right)!\left(\frac{m+m'-t}{2}-t\right)!} \\
\times (-1)^{|n-j|+\left[\frac{t}{2}\right]} 2^{\lambda_t} \left(\frac{32}{17}\right)^{\frac{(j'-n+|n-j|+2s)}{2}+\lambda_t} \Gamma\left(\frac{j'-n+|n-j|+2s}{2}+\lambda_t\right)\Gamma\left(\frac{t}{2}+\lambda_t\right) \\
\times F\left(-\left[\frac{t}{2}\right], \frac{j'-n+|n-j|+2s}{2}+\lambda_t; 2\lambda_t-\frac{1}{2}, \frac{16}{17}\right),
\end{aligned}
\tag{3.8}
$$

where $[t/2]$ is the integer part of $t/2$, while the summation over t and λ_t are defined in the following way. If $j'-n+|n-j|+2s$ is even, we sum over only even values of t and $\lambda_t=\frac{1}{2}$. If $j'-n+|n-j|+2s$ is odd, we sum over only odd values of t and $\lambda_t=1$. It is worth noting that since the first argument of the hypergeometric function F is negative ($-[t/2]$), F can be expressed as a finite series. Equations (3.6,3.8) represent the analytic adiabatic result for the survival probability.

It is easy to extend the above calculation for multiple time steps. In a two-step calculation the survival probability is calculated from

$$
P(t) = \left| \left\langle \psi(t=0) \left| U\left(t, \frac{t}{2}\right) U\left(\frac{t}{2}, 0\right) \right| \psi(t=0) \right\rangle \right|^2,
\tag{3.9}
$$

where $U(t_2, t_1)$ is the evolution operator that evolves the quantum state from time $t=t_1$ to $t=t_2$. If an exact result for $U(t_2, t_1)$ was available, Eq. (3.9) would be equivalent to the one-step result. However, we have at our disposal only approximate expressions for the evolution operator and the two-step calculation will give more accurate results. The reason is that the two-step calculation can capture the dynamics in smaller time scales. Inserting complete sets of states in Eq. (3.9) leads to

$$
\begin{aligned}
P(t) = \Bigg| \sum_{jk} \sum_{j'k'} \sum_{j''k''} \exp[-i(E_n^{Mo}+E_{j'}^{Mo})t/2] \\
\times \exp[-i(E_k^{ho}+E_{k''}^{ho})t/2] \\
\times T_-(n,0;j,k) T_+(j,k;j',k') \\
\times T_-(j',k';j'',k'') T_+(j'',k'';n,0) \Bigg|^2.
\end{aligned}
\tag{3.10}
$$

Note that the energies in the phase factors have indices that appear in the two T_- matrix elements. It is easy to write down analogous expressions for 3 and 4 time steps.

In Fig. 1 we show the results for an adiabatic calculation of the survival probability for HC_2 with the Morse oscillator being initially in its 5th excited state and the harmonic oscillator being initially in its ground state. We have performed calculations with 1–4 time steps. For each value of time t the 4-step calculation required 20 minutes in a RS/6000 workstation. As can be seen in Fig. 1 the results have converged at least up to $t=30$ fs. These results are in complete agreement with those reported by Makri and Topaler in Ref. 2. These authors were the first to perform a quantum calculation for this problem, but in a way quite different than ours, by first performing a canonical transformation and linearizing the coupling term and then using a split-time propagator.[7] We
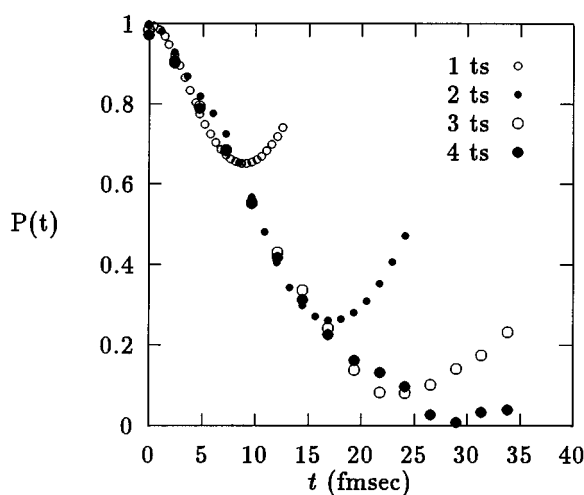
FIG. 1. Adiabatic calculation of the survival probability for HC_2 with 1–4 time steps. The CH bond was initially in its 5th excited state and the CC bonds in their ground state.

have not made any approximation to the coupling term, but on the other hand our adiabatic calculation does not include a correction that is implied by the use of the split-time propagator. In particular, memory effects are inherent in the influence functional calculations. The reason why the gauge transform adiabatic calculation (which is a one time theory) gave results in agreement with Ref. 2 is that this correction is very small in this system as will be explained in the next section. It should be mentioned that the authors of Ref. 2 have also performed an exact calculation of the survival probability of HC_2 in order to test their method and the 4-time-step result in our Fig. 1 is identical to the exact result.

IV. BEYOND THE ADIABATIC APPROXIMATION

As has been demonstrated in Refs. 3,4, it is possible to expand the evolution operator with the help of Zassenhauss theorem Eq. (3.4) and then resume the expansion into an exponential. The result is:

$$\exp(-iHt) = \exp(-iH_{CH}t)\exp\left[-i\left(H_{CC} - \frac{p_{CH}p_{CC}}{m_C}\right)t\right]$$
$$\times \exp(i\sigma_1)\exp(i\sigma_2). \qquad (4.1)$$

The first two terms at the right-hand side represent the adiabatic approximation. σ_1 and σ_2 contain commutators of H_{CH}, H_{CC}, respectively, of first and second order in H_{CC} and of infinite order in H_{CH}. Using operator identities it is possible[4] to find closed expressions for σ_1, σ_2:

$$i\sigma_1 = -\int_0^t dt' \int_0^{t'} dt'' e^{iH_{CH}t''}$$

$$\times \left[H_{CH}, H_{CC} - \frac{p_{CH}p_{CC}}{m_C}\right] e^{-iH_{CH}t''} \qquad (4.2)$$

and

$$i\sigma_2 = -i\int_0^t dt' t'^2 e^{iH_{CH}t'} \left[\left[H_{CH}, H_{CC} - \frac{p_{CH}p_{CC}}{m_C}\right],\right.$$

$$\left. H_{CC} - \frac{p_{CH}p_{CC}}{m_C}\right] e^{-iH_{CH}t'}. \qquad (4.3)$$

It has been numerically established[4] that the effect of σ_2 is much larger than that of σ_1 (because of matrix element selection rules) and that the inclusion of only the correction σ_1 gives results almost identical to those of the adiabatic approximation. For this reason in the following discussion we shall ignore the effect of σ_1.

The split-time evolution propagator formalism[7] (as in Ref. 2), is equivalent to including the correction σ_1 only (which in the short-time limit goes like t^2). That has a very small effect and should give results similar to the adiabatic approximation we discussed in Section III. The effect of σ_2 (which in the short-time limit goes like t^3), however, cannot be described in the split-time propagator formulation.

Before we proceed it is useful to think of these approximations in the spirit of more conventional perturbation theory. We are employing a short-time expansion and as we shall soon see the dimensionless parameter to express it is $(\omega_{CC}t)(\omega_{CH}t)^2$. From Eq. (4.5) below, we can find that an order of magnitude evaluation of the corrections beyond the adiabatic result gives the approximate result $(t^3/3)(\mu_{CC}\mu_{CH}/m_C^2)\omega_{CC}\omega_{CH}^2 \approx 1.6(t/T_{CC})(t/T_{CH})^2$. Since $T_{CH} = 11$ fs and $T_{CC} = 18$ fs, we expect the first-order power expansion of Eq. (4.5) to be valid at least as far as $t \approx 10$ fs for a one-step calculation (or 20 fs for a 2-step calculation). It is not certain that the expansion will fail for longer times, because the corrections σ_1 and σ_2 have resulted from resummations of H_{CH} to infinite order. This was the motivation for resumming the expansion of the evolution operator to infinite order for the *fastest* oscillating mode H_{CH} and not for H_{CC} (we could have also resummed to infinite order with respect to H_{CC} if it was needed).

The exponential resummation that leads to Eq. (4.1) resembles the linked-cluster expansion of many-body theory. The linked-cluster expansion has been most successfully used in the polaron problem. Detailed discussion of polarons and of the linked-cluster expansion can be found in Ref. 8. In brief, the polaron Hamiltonian is written as the sum of an unperturbed part and a coupling term. The evolution operator is expressed in the interaction picture and is expanded in a series (S-matrix expansion). The matrix elements of the expanded terms are found (they are the Green's functions) and finally an exponential resummation is performed. In that method, the polaron propagator is calculated *before* the exponential resummation. The resummation is performed because it leads to a term of the form $e^{\sigma_1 + \sigma_2}$ (in the language of the present paper) and the long-time limit of $\sigma_1 + \sigma_2$ in that problem turns out to be linear in time t. In our method, no matrix elements are calculated after the expansion of the evolution operator, but instead operator identities are used so that the *fast* degree of freedom H_{CH} is resummed to *infinite* order. Matrix elements are calculated (see Eq. (4.5)) after the resummation and after making the expansion $e^{i\sigma_2} = 1 + i\sigma_2$. Our exponential resummation has different physical content than that of the polaron problem: σ_2 contains commutators of H_{CH} of *infinite* order, while the corre-

sponding term in the polaron problem is *second* order with respect to the electron-phonon interaction.

After inserting complete sets of states the survival probability is found to be equal to

$$P(t) = \left| \sum_{jk} \sum_{j'k'} e^{-iE_n^{Mo}t} e^{-iE_k^{ho}t} T_-(n,0;j,k) \right.$$

$$\left. \times T_+(j,k;j',k') \langle \psi_{j'} \langle \phi_{k'} | e^{i\sigma_2} | \psi_n \rangle \phi_0 \rangle \right|^2, \quad (4.4)$$

where $T_\pm$ were defined in Eq. (3.7). In comparison with the adiabatic result, the additional computation we have to do is to calculate the matrix element of $e^{i\sigma_2}$.

The matrix element of $e^{i\sigma_2}$ can be calculated if we make the expansion (it is equivalent to a short-time expansion since as we can see from Eq. (4.3), $\sigma_2 \sim t^3$ in the small t limit) $e^{i\sigma_2} = 1 + i\sigma_2$:

$$\langle \psi_{j'} \langle \phi_{k'} | (1+i\sigma_2) | \psi_n \rangle \phi_0 \rangle$$

$$= \delta_{k',0} \delta_{j',n} + i[f(t)-f(0)] \left\langle \phi_{k'} \left| \left(\frac{p_{CC}}{m_C}\right)^2 \right| \phi_0 \right\rangle$$

$$\times \left\langle \psi_{j'} \left| \frac{d^2V}{dr_{CH}^2} \right| \psi_n \right\rangle, \quad (4.5)$$

where

$$f(t) = \begin{cases} t^3/3 & \text{if} \quad j'=n \\ -ie^{i(E_{j'}^{Mo}-E_n^{Mo})t} \left[\dfrac{t^2}{(E_{j'}^{Mo}-E_n^{Mo})} + \dfrac{2it}{(E_{j'}^{Mo}-E_n^{Mo})^2} \right. \\ \qquad\qquad \left. - \dfrac{2}{(E_{j'}^{Mo}-E_n^{Mo})^3} \right] & \text{if} \quad j' \neq n \, . \end{cases}$$

$$(4.6)$$

Since $p_{CC}^2 \sim \omega_{CC}$ and $d^2V/dr_{CH}^2 \sim \omega_{CH}^2$, the correction to the adiabatic is proportional to $(\omega_{CC}t)(\omega_{CH}t)^2$ as was mentioned earlier in this section. The dominant contribution in Eq. (4.5) comes from the term $j'=n$.

The first term in Eq. (4.5) leads to the adiabatic result. To evaluate the second term we need to calculate two kinds of matrix elements. First, $\langle \phi_{k'} | p_{CC}^2 | \phi_0 \rangle$ which can be calculated trivially since ϕ is just the harmonic oscillator eigenfunction. Second, the matrix element of d^2V/dr_{CH}^2 which can also be evaluated easily since the functional form of the Morse potential V is known (Eq. (2.2)). After some algebra we arrive at the following result for a general matrix element:

$$\langle \psi_j \langle \phi_k | (1+i\sigma_2) | \psi_{j'} \rangle \phi_{k'} \rangle = \delta_{k,k'} \delta_{j,j'} + i[f(t)-f(0)] \frac{\mu_C \omega_{CC}}{2} \{ (2k+1)\delta_{k,k'} - \sqrt{k(k-1)}\delta_{k-2,k'}$$

$$- \sqrt{(k+1)(k+2)}\delta_{k+2,k'} \} \sum_{l,m} c_l^{(j)} c_m^{(j')} 4\sqrt{\pi} D_{CH} \beta_{CH}^2 \frac{2^{\min\{l,m\}}\min\{l,m\}!}{(2^{l+m}l!m!)^{1/2}}$$

$$\times \left\{ \left(\frac{2\beta_{CH}}{\sqrt{\mu_{CH}\omega_{CH}}} \right)^{|l-m|} L_{\min\{l,m\}}^{|l-m|} \left(\frac{-2\beta_{CH}^2}{\mu_{CH}\omega_{CH}} \right) - \frac{1}{2} \left(\frac{\beta_{CH}}{\sqrt{\mu_{CH}\omega_{CH}}} \right)^{|l-m|} L_{\min\{l,m\}}^{|l-m|} \left(\frac{-\beta_{CH}^2}{2\mu_{CH}\omega_{CH}} \right) \right\}. \quad (4.7)$$

In Eq. (4.7) the term proportional to $\mu_C \omega_{CC}$ corresponds to the matrix element of p_{CC}^2 while the term after the sum over l,m corresponds to the matrix element of d^2V/dr_{CH}^2. In the latter result, L_m^n is the associated Laguerre polynomial and $c_l^{(j)}$ are the coefficients of the expansion $\psi_j = \Sigma_l c_l^{(j)} \phi_l$, similar to Section III. Equations (4.4,4.5,4.6,4.7) constitute the result that includes corrections beyond the adiabatic approximation.

Proceeding in a similar way as in Section III we can extend the calculation to 2 time steps:

$$P(t) = | \sum_{jk} \sum_{j'k'} \sum_{j''k''} \sum_{j'''k'''} \sum_{j''''k''''} e^{-i(E_n^{Mo}+E_{j''}^{Mo})t/2} e^{-i(E_k^{ho}+E_{k'''}^{ho})t/2}$$

$$\times T_-(n,0;j,k) T_+(j,k;j',k') T_-(j'',k'';j''',k''') T_+(j''',k''';j'''',k'''')$$

$$\times \left[f(t)-f\left(\frac{t}{2}\right) \right] \left[f\left(\frac{t}{2}\right)-f(0) \right] \langle \psi_{j'} \langle \phi_{k'} | e^{i\sigma_2} | \psi_{j''} \rangle \phi_{k''} \rangle \langle \psi_{j'''} \langle \phi_{k'''} | e^{i\sigma_2} | \psi_n \rangle \phi_0 \rangle |^2. \quad (4.8)$$

In Ref. 4, a significant deviation from the 1-step adiabatic result was found when quantum corrections were included. However, as was shown in Fig. 1, the adiabatic approximation radically improves when multiple time steps are used. In Fig. 2 we compare the results of 2-time-step calculations using the adiabatic approximation with calculations that go beyond the adiabatic, in the regime where the 2-time-

step adiabatic calculation has converged. The Morse oscillator that models the CH bond is assumed to be initially in its fifth excited state and the harmonic CC bonds in their ground state. As can be seen there is no significant difference between the two results. The conclusion is that in this system we can safely ignore corrections beyond the adiabatic result when we perform multiple time steps. It is not hard to prove
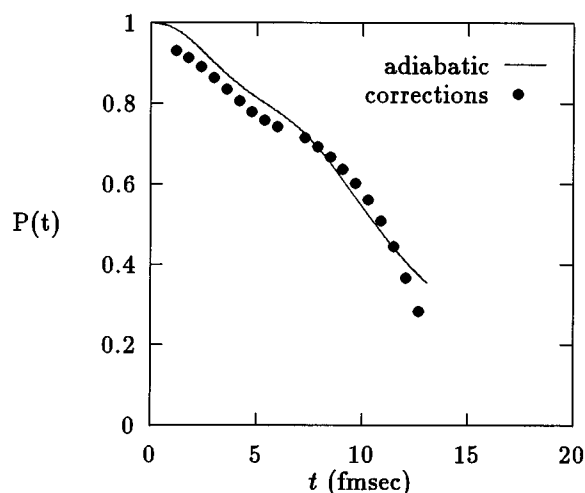
FIG. 2. Comparison of the adiabatic 2-step calculation for HC_2 with a 2-step calculation that includes corrections beyond the adiabatic.

that for a N-time-step calculation, the adiabatic calculation requires $4N-2$ nested summations and the calculation with corrections beyond the adiabatic requires $6N-2$ nested summations. Therefore a 2-time-step calculation with corrections has as many nested summations as a 3-time-step adiabatic, a 3-time-step calculation with corrections 2 more than a 4-time-step adiabatic, etc. In particular a 3-time-step calculation that includes corrections beyond the adiabatic approximation requires two hours of computer time on our RS/6000 workstation. We did not do a 4 step with corrections calculation because for this system the effects are small.

V. EXTENSION OF THE CALCULATION TO HC_6

In this section we shall show how to use the results of the HC_2 calculation to evaluate the survival probability for HC_6. We shall prove an identity that allows easy extension to even longer chains. The particular case of HC_6 allows us to compare with previous theoretical work. First we shall show how to add to HC_2 an additional degree of freedom to get HC_3. Let us denote by the superscript (1) quantities that refer to the CC bond adjacent to the CH bond and by (2) those of the other CC bond. The evolution operator for HC_3 is

$$\exp\left[-i\left(H_{CH}+H_{CC}^{(1)}-\frac{p_{CH}p_{CC}^{(1)}}{m_C}\right)t\right]\exp\left[-i\left(H_{CC}^{(2)}\right.\right.$$
$$\left.\left.-\frac{p_{CC}^{(1)}p_{CC}^{(2)}}{m_C}\right)t\right]\equiv U(t)A(t). \quad (5.1)$$

We have denoted by $U(t)$ the first exponential which is just the evolution operator for HC_2. We have denoted by $A(t)$ the other exponential which is not the evolution operator for the C_3 part of the chain, because it includes only $H_{CC}^{(2)}$ instead of $H_{CC}^{(1)}+H_{CC}^{(2)}$. The survival probability if the Morse wave function is in its nth state and the 2 harmonic CC bonds in their ground state is then written as

$$P(t)=|\langle\psi_n\phi_0^{(1)}\phi_0^{(2)}|U(t)A(t)|\psi_n\phi_0^{(1)}\phi_0^{(2)}\rangle|^2. \quad (5.2)$$

Since the Hamiltonian Eq. (2.1) couples only neighboring bonds, $U(t)$ does not have any effect on $\phi_0^{(2)}$ and $A(t)$ does not have any effect on ψ_n. After inserting a complete set of $\phi_k^{(1)}$ states we find that

$$P(t)=\left|\sum_k \langle\psi_n\phi_0^{(1)}|U(t)|\psi_n\phi_k^{(1)}\rangle\right.$$
$$\left.\times\langle\phi_k^{(1)}\phi_0^{(2)}|A|\phi_0^{(1)}\phi_0^{(2)}\rangle\right|^2$$
$$=\left|\sum_k \langle\psi_n\phi_0^{(1)}|U(t)|\psi_n\phi_k^{(1)}\rangle A_{k0}\right|^2, \quad (5.3)$$

where the matrix A_{lm} is defined by

$$A_{lm}\equiv\langle\phi_l^{(1)}\phi_0^{(2)}|A(t)|\phi_0^{(1)}\phi_m^{(2)}\rangle \quad (5.4)$$

and can be evaluated similarly to the other matrix elements in this work, by using the analogy with the gauge transformation and inserting complete sets of states.

As an example, we shall write down the detailed expressions for the 2-step calculation. In that case, the survival probability for HC_3 is given by replacing in the result for HC_2

$$\langle\psi_n\phi_0\mid U(t)\mid\psi_n\phi_0\rangle\rightarrow\langle\psi_n\phi_0\mid U(t)\mid\psi_n\rangle\sum_k\mid\phi_k\rangle$$

$$\times\sum_{lm}\sum_{l'm'}\sum_{l''m''}e^{-i(E_m^{ho}+iE_{m''}^{ho})t/2}F_-(k''',0;l,m)$$
$$\times F_+(l,m;l',m')F_-(l',m';l'',m'')F_+(l'',m'';0,0), \quad (5.5)$$

where $F_\pm$ are shifted overlap matrix elements analogous to $T_\pm$, but they include only harmonic eigenfunctions (they are related by $F_-=(-1)^{m+m'}F_+$):

$$F_\pm(j,m;j',m')\equiv\left\langle\phi_j(\mathbf{r}_p)\left\langle\phi_m(\mathbf{r}_{p+1})\right|\right.$$
$$\left.\times\phi_{j'}\left(\mathbf{r}_p\pm\frac{\mathbf{r}_{p+1}}{2}\right)\right\rangle\phi_{m'}(\mathbf{r}_{p+1})\right\rangle, \quad (5.6)$$

where $\mathbf{r}_p$ is the coordinate of the pth CC bond. The matrix elements $F_\pm$ can be evaluated analytically. In fact, $F_\pm$ is just equal to Eq. (3.8) without the summation $\Sigma_{j,j'}c_j^{(l)}c_{j'}^{(l')}$. It is not difficult to prove the following selection rule:

$$F_\pm(j,m;j',m')=0 \quad \text{if} \quad j+m+j'+m'=\text{odd.} \quad (5.7)$$

This selection rule is very important because it reduces the computer time needed for the nested summations in Eq. (5.5).

The nested summations of the F's times the phase factor in Eq. (5.5) represent the 2-time-step result for the matrix element A_{k0}. The only difference with the analogous matrix element of the evolution operator is that the indices in the phase factors are associated with the last argument of F_- instead of with both the first and last (compare with Eq. (3.10)).

It is easy to prove that when we extend the calculation from HC_3 to HC_4 we have to multiply by exactly the same matrix A and in particular we have to replace in Eq. (5.3)

$$A_{k0} \to \sum_m A_{km}A_{m0}. \qquad (5.8)$$

However, the summation in Eq. (5.8) is just equal to $(A^2)_{k0}$. Repeating the same steps, we can add 4 CC bonds to HC_2 to get HC_6, by replacing in Eq. (3.2)

$$|\phi_0\rangle \to \sum_k |\phi_k\rangle (A^4)_{k0} \qquad (5.9)$$

to obtain for the survival probability

$$P(t) = \left| \sum_k \langle \psi_n \phi_0 | U(t) | \psi_n \phi_k \rangle (A^4)_{k0} \right|^2. \qquad (5.10)$$

It is implied that if an $N-$time$-$step calculation is used for $U(t)$, A is also calculated in N time steps. Of course, the matrix elements of $U(t)$ (which is the evolution propagator for HC_2) are just the results of Section III, except for the fact that the $|\phi_0\rangle$ has been replaced by $|\phi_k\rangle$. As we mentioned earlier, the 2-time-step result for A is shown in Eq. (5.5). It is easy to derive analogous results for A for more time steps. The difference with the corresponding results of Section III is that the shifted overlap matrix elements T are replaced by the F of Eq. (5.6) and there are no phase factors that correspond to the first argument of F_- (the reason being that A has $H_{CC}^{(p+1)}$ instead of $H_{CC}^{(p)} + H_{CC}^{(p+1)}$ of the evolution operator proper, as discussed after Eq. (5.1)).

Equation (5.10) allows the addition of CC bonds in a very simple and economic manner, since it reduces to 3 the number of degrees of freedom that need to be solved. From the practical point of view the additional burden compared to the HC_2 calculation is just the additional summation over k in Eq. (5.10), since the calculation of the matrix elements of A takes little time because of the constraint Eq. (5.7). As far as we know this simple result has not been noticed before, having been obscured by the overwhelming notational complexity of the equations that have to be solved. It is a consequence of the fact that the Hamiltonian couples only neighboring bonds. Makri reports a similar time savings, but for a different reason. Their accurate but approximate bilinear Hamiltonian allows influence functional integration of bath degrees of freedom. If the couplings were stronger (for example less mass and frequency mismatch), then the bilinear approximation might not be accurate, but the present exact calculation would still grow linearly in complexity. In the next section we shall develop a simple diagrammatic scheme that will make this result quite transparent.

Figure 3 shows our calculation of the survival probability for HC_6. We take the CH bond to be initially in its 5th excited state and the CC bonds in their ground state. For each value of time t, the 4-time-step calculation required about $2\frac{1}{2}$ hours in a RS/6000 workstation. Our results are again in agreement with those reported in Ref. 2. The only difference is that in our calculation the probability stays at very low values for longer time. For example, the 4-step calculation in both this work and Ref. 2 has a minimum
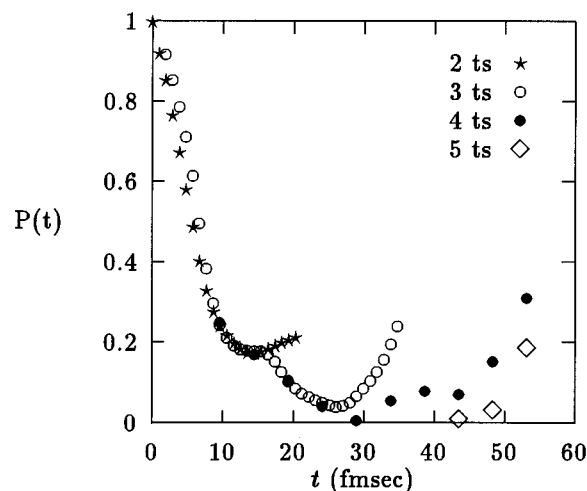

FIG. 3. Adiabatic calculation of the survival probability for HC_6 with 2–5 time steps. The CH bond was initially in its 5th excited state and the CC bonds in their ground state.

around $t = 30$ fs, but whereas in Ref. 2 the probability reaches a minimum equal to 0.1 and rises again, in our result the minimum is practically equal to 0 and the probability stayed at values less than 0.1 for about 25 fs. This small discrepancy is probably due to the fact that the coupling has been linearized in Ref. 2. A quantum calculation that were to converge for long times would most probably show a survival probability that stays at very low values for a long time, since the additional (to HC_2) degrees of freedom have enlarged the available phase space and we do not expect the system to return quickly to its initial state. Classical calculations that support this conjecture have been performed in Ref. 2. In any case, Fig. 3 suggests that the survival probability is effectively equal to zero between 30 and 40 fs.

VI. DIAGRAMMATIC REPRESENTATION

In this section we shall develop a simple diagrammatic scheme that summarizes in a very compact way the results of the previous sections. We begin by defining 3 species of vertices as shown in Fig. 4. The indices on the top side label CH bond eigenstates and the indices on the bottom side label
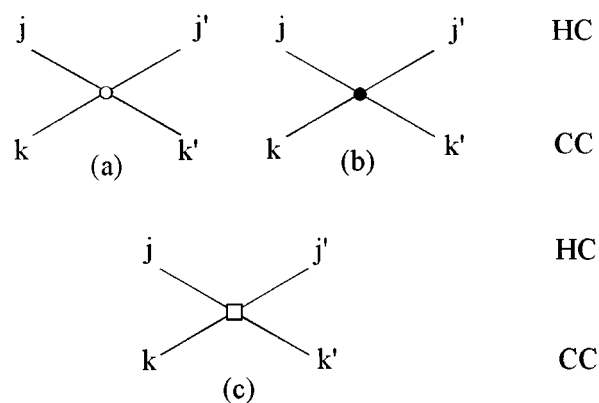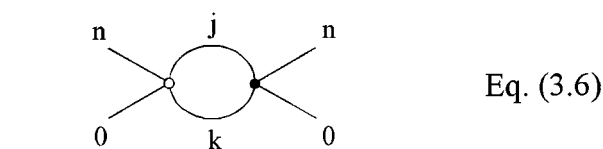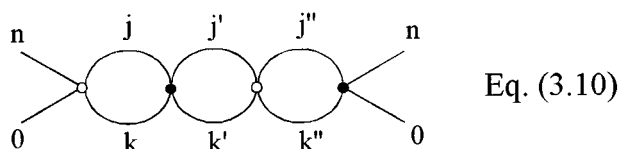

FIG. 4. The three basic vertices, which are defined in Eq. (6.1).

Eq. (3.6)

Eq. (3.10)

FIG. 5. Adiabatic calculation with 1 time step (top) and 2 time steps (bottom). These diagrams reproduce the results of Section III.
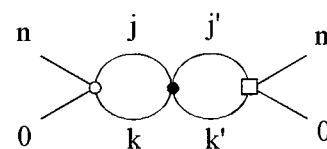

Eq. (4.4)

Eq. (4.8)

FIG. 6. Calculation with corrections beyond the adiabatic approximation with 1 time step (top) and 2 time steps (bottom). These diagrams reproduce the results of Section IV.

CC bond eigenstates. With each vertex we associate the following terms (the system propagates from $t = t_1$ to $t = t_2$):

$$\bigcirc (\text{Fig. } [4a]) \rightarrow e^{-i(E_j^{\text{Mo}} + E_{k'}^{\text{ho}})(t_2 - t_1)} \, T_-(j, k; j', k'),$$

$$\bullet (\text{Fig. } [4b]) \rightarrow T_+(j, k; j', k'),$$

$$\square (\text{Fig. } [4c]) \rightarrow \delta_{k,k'} \delta_{j,j'} + [f(t_2) - f(t_1)] \qquad (6.1)$$

$$\times \langle \psi_j \phi_k | e^{i\sigma_2} | \psi_{j'} \phi_{k'} \rangle.$$

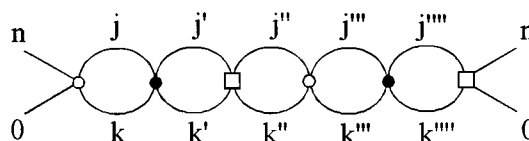We can construct diagrams that reproduce the results of the previous sections if we define the following rules:

(i)   Indices on the top of the diagrams label CH eigenstates, while indices on the bottom label CC eigenstates.

(ii)   The outer legs of the diagrams represent the initial and the final state.

(iii)   For an N-step calculation, the diagram must have N vertices of *each* species. They are arranged from left to right in this order: open circle, closed circle, square, repeated N times. The explanation for this rule becomes clear when we look back at Eqs. (3.5,4.1). For each time step we obtain a product of factors $\exp(ip_{\text{CH}} r_{\text{CC}}/2) \exp(-ip_{\text{CH}} r_{\text{CC}}/2) \exp(i\sigma_2)$ in this order. The first two lead to the overlap matrix elements T_-, T_+ and the third to the matrix element of the nonadiabatic corrections.

(iv)   We sum over all indices except those in the outer legs.

(v)   The times that enter Eq. (6.1) are defined in an obvious way. For a 1-time-step calculation, $(t_1, t_2) = (0, t)$. For a 2-time-step calculation, $(t_1, t_2) = (0, t/2)$ for the right half of the diagram and $(t_1, t_2) = (t/2, t)$ for the left half, etc.

(vi)   We take the square of the absolute value of the summation.

We shall show how these rules work with a couple of examples from Section III. For a 1-step calculation we have to include 1 open-circle and 1 closed-circle vertex. The initial and final state is $\psi_n \phi_0$. According to the rules stated above, we draw the upper diagram of Fig. 5. We have to sum over the indices that label the loop and square the sum. Therefore, the upper diagram in Fig. 5 is equal to

$$\left| \sum_{jk} (\text{open circle}) \times (\text{closed circle vertex}) \right|^2$$

$$= \left| \sum_{jk} [e^{-i(E_n^{\text{Mo}} + E_k^{\text{ho}})t} T_-(n, 0; j, k)] T_+(j, k; n, 0) \right|^2,$$

which is identical to Eq. (3.6).

For a 2-time-step adiabatic calculation we have to include 2 vertices of each species in this order: open, closed, open, closed circle. The initial and final state (at the outer leg of the diagram) is $\psi_n \phi_0$. This results in the lower diagram of Fig. 5. We sum over the indices that label the loops and square the sum:

$$\left| \sum_{jk} \sum_{j'k'} \sum_{j''k''} (\text{product of the 4 vertices}) \right|^2.$$

Using Eq. (6.1) for the factors associated with each vertex we arrive at Eq. (3.10). In a similar fashion we can draw diagrams for the calculation that include corrections beyond the adiabatic. These are shown in Fig. 6. It is easy to verify that they reproduce Eqs. (4.4,4.8).

Now we turn our attention to longer hydrocarbon chains. In order to avoid constructing very large diagrams, we introduce the diagrams shown in Fig. 7. The upper diagram stands for

$$\langle \psi_n \phi_0 | U(t) | \psi_n \phi_k \rangle. \qquad (6.2)$$

If a 1-step calculation is used for $U(t)$, then the diagram in Fig. 7a reduces to the upper diagram of Fig. 5 (after the substitution $0 \rightarrow k$ in the lower leg). If a 2-step calculation is used, then diagram [7a] reduces to the lower diagram of Fig. 5, etc.

The diagram in Fig. 7b stands for

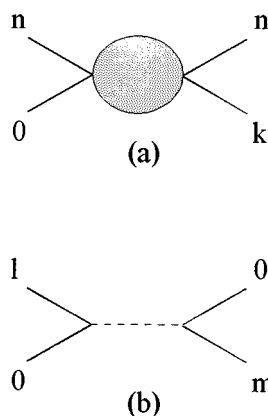$$A_{lm} \equiv \langle \phi_l^{(p)} \phi_0^{(p+1)} | A(t) | \phi_0^{(p)} \phi_m^{(p+1)} \rangle, \qquad (6.3)$$

FIG. 7. Matrix elements of the evolution operator of HC_2 and of the operator A, which are defined in Eqs. (6.2,6.3).

which was defined in Eq. (5.4). We have to slightly modify the rules for this kind of diagram. The vertices of Fig. 4 are associated with the following factors:

$$\bigcirc (\text{Fig. } [4a]) \rightarrow e^{-iE_{k'}^{ho}(t_2-t_1)} F_-(j,k;j',k'),$$
$$\bullet (\text{Fig. } [4b]) \rightarrow F_+(j,k;j',k'). \tag{6.4}$$

The rule (i) at the beginning of this section also has to be modified: the indices at the top of the diagram label the eigenfunctions of the pth bond, while the indices at the bottom are those of the $(p+1)$th bond. For a 1(2)-time step calculation, Fig. 7b reduces to the upper (lower) diagram of Fig. 5.

Figure 8 is the diagrammatic representation of Eq. (5.5). The extension to HC_6 is represented in Fig. 9. The names at the right in these diagrams represent the bonds whose eigenfunctions are labeled by the indices in the corresponding line. From Fig. 9 it is immediately obvious that the extension to longer chains is equivalent to a simple multiplication of the HC_2 result by the power of a matrix.

VII. CONCLUSION

In this paper we have reported quantum calculations of vibrational energy transfer in HC_2 and HC_6. We used an analogy with gauge transformations to bring the adiabatic approximation in a form that can be calculated very easily. We also showed that for this system the corrections beyond the adiabatic are small when multiple time steps are used. We then performed multi-step calculations that converged for times up to 35–40 fs.
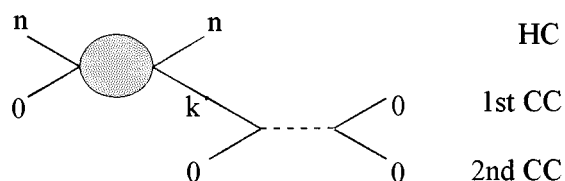

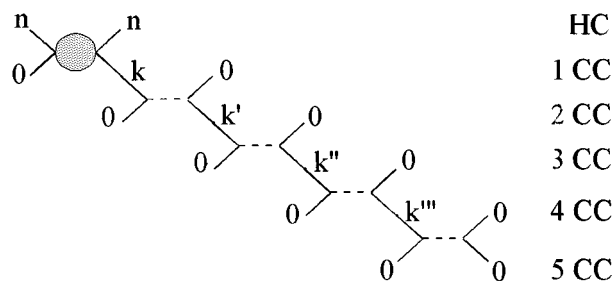FIG. 8. The survival probability for HC_3 as calculated in Eq. (5.3).

FIG. 9. The survival probability for HC_6 as calculated in Eq. (5.10).

To the best of our knowledge the only other quantum calculations for this system are the influence functional calculations reported in Ref. 2 which give results in agreement with ours. We believe that our method has the advantage of conceptual simplicity requiring no transformations to and approximations of the Hamiltonian, and simple extension to longer hydrocarbon chains. In addition, our method allows the calculation of corrections beyond those that are included in the split-time propagator formalism, in systems where this would be relevant. Currently we are trying to apply this method to the problem of proton transfer in proteins, by using a formalism that combines quantum and classical mechanics. In such a problem one has to solve the quantum problem repeatedly for different configurations of the classical degrees of freedom. Since the correlation functions decay very rapidly one needs a method that can quickly solve the quantum dynamics for short times. Single time step calculations with non-adiabatic corrections provide an obvious answer.

Finally, we propose a calculational strategy that might allow very fast multi-step quantum calculations for this system. This strategy is based on the well-known Gaussian nature of the harmonic oscillator (the same mathematical happenstance that allows influence functional calculations) and the highly efficient nature of the fast Fourier transform. It is much like the methods Metiu[9] has used for the evaluation of the flux correlation function for reactive scattering calculations. For notational simplicity we shall illustrate our idea using the 1-step adiabatic calculation as an example. We start by combining Eqs. (3.2,3.5):

$$P(t) = |\langle \psi_n \langle \phi_0 | e^{-iH_{CH}t} e^{ip_{CH}r_{CC}/2}$$
$$\times e^{-iH_{CC}t} e^{-ip_{CH}r_{CC}/2} |\psi_n\rangle \phi_0\rangle|^2. \tag{7.1}$$

By inserting complete sets of position states on either side of $\exp[-iH_{CC}t]$ we arrive at

$$P(t) = \left| \left\langle \psi_n \left| e^{-iH_{CH}t} \int dx_{CC} \int dx'_{CC} \phi_0(x_{CC}) \phi_0(x'_{CC}) \right.\right.\right.$$
$$\left.\left.\left. \times e^{ip_{CH}x_{CC}/2} K_{ho}(x_{CC},x'_{CC},t) e^{-ip_{CH}x'_{CC}/2} \right| \psi_n \right\rangle \right|^2, \tag{7.2}$$

where K_{ho} is the Feynman propagator for the simple harmonic oscillator which turns out to be a Gaussian.[6] Since K_{ho} is a Gaussian, the double integral over x_{CC}, x'_{CC} can be performed analytically and the result is a Gaussian with re-

spect to the operator p_{CH}. Let us denote the result of this double integral by $N(t)\exp[-f(t)p_{CH}^2]$ where $N(t), f(t)$ are functions of time that can be determined by performing the integrals over x_{CC}, x_{CC}' in Eq. (7.2). We have thus arrived at the following result:

$$P(t) = |N(t)e^{-iE_n^{Mo}t}\langle\psi_n|e^{-f(t)p_{CH}^2}|\psi_n\rangle|^2. \quad (7.3)$$

Finally, we insert complete sets of momentum states after $\langle\psi_n|$ and complete sets of momentum states before $|\psi_n\rangle$ to obtain the result we are looking for:

$$P(t) = \left| N(t)e^{-iE_n^{Mo}t}\int dp_{CH}e^{-f(t)p_{CH}^2} \right.$$
$$\left. \times \psi(p_{CH})\psi(-p_{CH}) \right|^2, \quad (7.4)$$

where $\psi(p_{CH})$ is the Fourier transform of $\psi(r_{CH})$. The advantage of using Eq. (7.4) for a numerical calculation is two-fold: first, $\psi(p_{CH})$ can be calculated using fast Fourier transform algorithms which are very fast and second, after $\psi(p_{CH})$ is calculated we are left with a one-dimensional integration over p_{CH} that should also be performed very efficiently. For a two-step calculation we would need 4 fast Fourier transforms and a two-dimensional integral, etc.

Unfortunately, there is a detail that complicates this scheme. The Morse wave function is a sum of harmonic oscillator eigenfunctions ϕ_n. The Fourier transform of $\phi_n(x)$ is (except for a multiplication factor) $\phi_n(p)$. This means that the product $\psi(p_{CH})\psi(-p_{CH})$ is a sum of products of pairs of Hermite polynomials $\Sigma_{i,j}H_i(p)H_j(p)$. Since $H_i(p)H_j(p)$ has $i+j$ nodes, the product $\psi(p_{CH})\psi(-p_{CH})$ and the integrand of Eq. (7.4) is very oscillatory. Therefore, the one-dimensional integral that appears in Eq. (7.4) is not easy to evaluate numerically. On the other hand, there are special methods (polynomial quadratures) to handle oscillatory integrands. We are currently working on this problem. If it is smoothed out, it will most probably allow very fast multi-step calculations.

[1] W. H. Miller, W. L. Hase, and C. L. Darling, J. Chem. Phys. **91**, 2863 (1989); D. H. Lu and W. L. Hase, *ibid.* **89**, 6723 (1988); **91**, 7490 (1989); J. S. Hutchinson, W. P. Reinhardt, and J. T. Hynes, *ibid.* **79**, 4247 (1983).

[2] M. Topaler and N. Makri, J. Chem. Phys. **97**, 9001 (1992).

[3] S. D. Schwartz, J. Chem. Phys. **91**, 7621 (1989); **96**, 5952 (1992); **97**, 7377 (1992); **100**, 8795 (1994).

[4] S. D. Schwartz, J. Chem. Phys. **101**, 10 436 (1994).

[5] W. Magnus, Comm. Pure Appl. Math. **VII**, 649 (1954).

[6] L. S. Schulmann, *Techniques and Applications of Path Integration* (Wiley, New York, 1981).

[7] M. D. Feit and J. A. Fleck, Jr., J. Chem. Phys. **78**, 301 (1983).

[8] G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1981).

[9] G. Wahnstrom and H. Metiu, Chem. Phys. Lett. **134**, 531 (1987).