

MULTICONFIGURATION TIME-DEPENDENT SELF-CONSISTENT FIELD APPROXIMATION FOR CURVE CROSSING IN PRESENCE OF A BATH. A FAST FOURIER TRANSFORM STUDY

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The applicability of the multiconfiguration time-dependent self-consistent field approximation (MCTDSCF) for the dynamics of curve crossing processes under the influence of "external" degrees of freedom is tested on a simple model. The fast Fourier transform (FFT) algorithm for solving the time-dependent Schrödinger equation is used to solve the exact equations of motion and the corresponding approximate ones. Good agreement is obtained in adiabatic as well as in non-adiabatic situations.

1. Introduction

There have recently been several studies of the effect of coupling to a heat bath on curve crossing and other non-adiabatic processes [1-3]. Viewed generally, the description of such processes is a multidimensional extension of familiar one-dimensional studies such as the Landau-Zener model and its generalizations. In many situations it is advantageous to keep the simple one-dimensional picture of a (non-adiabatic) reaction coordinate coupled to a heat bath.

In this paper we explore the applicability of a numerical approach based on the fast Fourier transform (FFT) algorithm to solve the Schrödinger equation associated with the multiconfiguration time-dependent self-consistent field (MCTDSCF) approximation to this problem. The FFT algorithm [4] is a very efficient way to solve the time-dependent Schrödinger equation; however, it is limited to low-dimensional systems. For larger systems the size of the numerical problem can be effectively reduced by applying the time-dependent self-consistent field (TDSCF) approximation^{#1}. Combination of the FFT algorithm and TDSCF approximation for solving the multidimensional time-dependent Schrödinger equation has been successfully applied to several systems [6,7].

The TDSCF approximation, written schematically for two subsystems 1 and 2 of the overall system characterized by the Hamiltonian $H(A, B) = H_A + H_B + V_{AB}$, relies on the approximate representation of $\Psi(A, B, t)$ as a product $\Psi(A, B, t) = \chi(A, t) \phi(B, t)$ leading to the TDSCF equations of motion:

$$\dot{\chi} = -i\hbar(H_A + \langle V_{AB} \rangle_B)\chi, \quad (1a)$$

^{#1} For molecular dynamics applications, see e.g. ref. [5].

$$\dot{\phi} = -i\hbar(H_B + \langle V_{AB} \rangle_A)\phi, \quad (1b)$$

where e.g. $\langle V_{AB} \rangle_A = \langle \chi(A, t) | V_{AB}(A, B) | \chi(A, t) \rangle$ is the partial average of V_{AB} over the instantaneous distribution of subsystem A.

When the process of interest involves non-adiabatic transitions between different channels (e.g. electronic states) of subsystem A (say), the time evolution of this system is described by a set of close coupled equations for the components of the vector wavefunction which are associated with the motion on the different potential surfaces. The diagonal elements of the matrix Hamiltonian H_A , correspond to these surfaces while the non-diagonal elements are associated with non-adiabatic transitions. In the presence of coupling to the system B an equation analogous to (1) may still be derived from the general Hamiltonian by seeking a solution of the form

$$\psi(A, B; t) = \chi(A, t) \phi(B, t) = \begin{pmatrix} \chi_1(A, t) \\ \chi_2(A, t) \\ \vdots \end{pmatrix} \phi(B, t). \quad (2)$$

This leads to eq. (1) with (1a) now describing a set of close coupled equations for the motion of system A ($\chi \rightarrow \chi$, $H_A \rightarrow H_A$ and, in principle, $V_{AB} \rightarrow V_{AB}$ are vector and matrix operators in the space of the electronic states of system A) and where the motion of the "external" system B is described by (1b) with

$$\langle V_{AB} \rangle_A = \sum_i \sum_j \langle \chi_i(A, t) | V_{AB}^{ij} | \chi_j(A, t) \rangle \quad (3)$$

(the sums over i and j are over the different electronic states or more generally the channels of system A).

This approximation works reasonably well only if the equilibrium configuration of system B (the "bath") is not very sensitive to transitions between states of system A. This may be the case when eqs. (1)–(3) are used to describe vibrational relaxation within a manifold of vibrational states of system A due to interaction with the bath B. In many cases involving electronic transitions this is not the case. In particular, when the non-adiabatic transitions within the molecular system involve charge transfer, the force on the bath B is strongly state dependent. In this case eqs. (1)–(3) will fail to yield the correction time evolution.

A similar situation occurs also when the dynamics of system A involves tunneling across an adiabatic potential surface. Makri and Miller [8] have shown that a simple (single-configuration) TDSCF fails when the bath responds differently to the system being on the different side of the barrier. On the other hand, Wahnström, Carmeli, and Metiu [9] have calculated the tunneling rate in a model for H diffusion on Cu(001) surface and using essentially a single-configuration TDSCF method have reported good agreement with an exact calculation. These authors note, however, that the applicability of single-configuration TDSCF in their calculation is due to the large Cu mass, which made the substrate only weakly sensitive to the position of the H. Also, the flux-flux correlation function used in this work to calculate the hopping rate decays fast and is already small at the time when the wavepacket splitting becomes important.

It has recently been proposed by Kosloff, Hammerlich and Ratner [7], and more recently by Makri and Miller [8], that in situations characterized by a well-defined system configuration and strong coupling to the bath (or other "irrelevant" coordinates) the use of a multiconfiguration TDSCF procedure can considerably improve the results without substantially increasing the size of the calculation. Makri and Miller [8] have demonstrated the usefulness of this scheme for the problem of tunneling across an adiabatic barrier in the presence of coupling to "external" degrees of freedom. In this paper we apply a similar method to study the effect of such external coordinates on the dynamics of curve crossing processes.

2. MCTDSCF for a simple curve crossing model

Our system consists of a two-level system (referred to as "electronic states") and an oscillator S which represents the molecular nuclear motion. It is coupled to a bath, schematically represented below by the coordinate Q . The Hamiltonian is assumed to be of the form (see fig. 1)

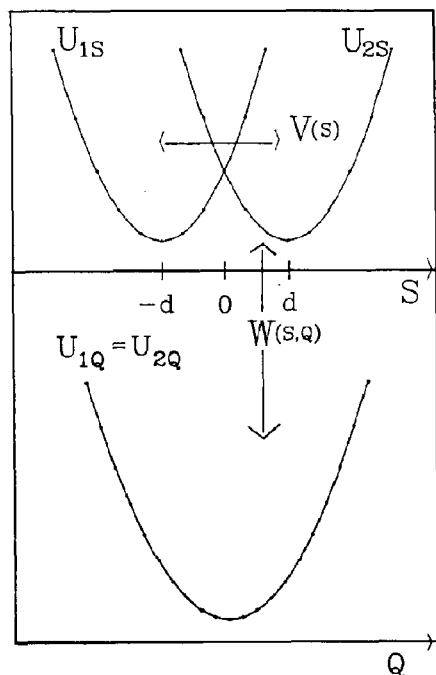


Fig. 1. The model system used in the calculation described in sections 2 and 3. U_{1S} and U_{2S} are the potential surfaces associated with the two channels ("electronic states") of the system. $U_{1Q}=U_{2Q}$ is the potential surface of the "bath" oscillator taken to be the same in the two channels. $V(s)$ is the intra-system non-adiabatic coupling and $W(s, Q)$ is the system-bath coupling.

$$\frac{\partial \Psi(S, Q, t)}{\partial t} = -\frac{i}{\hbar} \begin{pmatrix} H_1(S, Q) & H_{12}(S, Q) \\ H_{21}(S, Q) & H_2(S, Q) \end{pmatrix} \begin{pmatrix} \psi_1(S, Q, t) \\ \psi_2(S, Q, t) \end{pmatrix} = -\frac{i}{\hbar} \mathbf{H}(S, Q) \Psi(S, Q, t), \quad (4)$$

where

$$H_i(S, Q) = H_{iS}(S) + H_{iQ}(Q) + W_i(S, Q), \quad i = 1, 2, \quad (5a)$$

$$H_{iA}(A) = T_A + U_{iA}(A), \quad i = 1, 2; A = S, Q, \quad (5b)$$

$$H_{12}(S, Q) = H_{21}^*(S, Q) \equiv V(S, Q). \quad (5c)$$

Here T and U are kinetic and single particle potentials respectively, V is the coupling between the two electronic states and W is the "system"-"bath" coupling.

The MCTDSCF approximation consists of assuming separability in the components ψ_i of Ψ :

$$\Psi(S, Q, t) = \begin{pmatrix} \chi_1(S, t) \phi_1(Q, t) \\ \chi_2(S, t) \phi_2(Q, t) \end{pmatrix}, \quad (6)$$

which when used with eq. (4) yields

$$\dot{\chi}_1 \phi_1 + \chi_1 \dot{\phi}_1 = -(i/\hbar) (\phi_1 H_{1S} \chi_1 + \chi_1 H_{1Q} \phi_1 + W_1 \chi_1 \phi_1 + V \chi_2 \phi_2), \quad (7a)$$

$$\dot{\chi}_2 \phi_2 + \chi_2 \dot{\phi}_2 = -(i/\hbar) (\phi_2 H_{2S} \chi_2 + \chi_2 H_{2Q} \phi_2 + W_2 \chi_2 \phi_2 + V \chi_1 \phi_1). \quad (7b)$$

In eqs. (4)–(7) there is no formal distinction between the system coordinates S and the bath coordinates Q . We make this distinction by choosing the molecular diabatic potential surfaces $U_{1S}(S)$ and $U_{2S}(S)$ to be bound surfaces with their minimum positions displaced (see fig. 1). In the calculation reported below, the bath potential surface $U_{iQ}(Q)$ is assumed to be independent of the electronic state i , and is taken to be quadratic in Q (i.e. a bath of harmonic oscillators). These assumptions are not used in the formal derivation of the

MCTDSCF below. We also impose normalization conditions which correspond to the designation of ϕ_i and χ_i as bath and system wavefunctions, respectively. We require that at all times

$$\langle \phi_1 | \phi_1 \rangle_Q = \langle \phi_2 | \phi_2 \rangle_Q = 1, \quad (8)$$

which implies (since $\langle \phi | \phi \rangle = 1$) that

$$\langle \chi_1 | \chi_1 \rangle_S + \langle \chi_2 | \chi_2 \rangle_S = 1. \quad (9)$$

Here $\langle \rangle_Q$ and $\langle \rangle_S$ denote integrations over the Q and S coordinates, respectively. Multiplying eq. (7a) by $\phi_1^*(Q)$ or $\chi_1^*(S)$ and integrating over Q or S , respectively, and doing the same with eq. (7b) and the functions $\phi_2(Q)$, $\chi_2(S)$ lead to

$$\dot{\chi}_1 + \langle \phi_1 | \dot{\phi}_1 \rangle_Q \chi_1 = -(i/\hbar) (H_{1S} + \langle \phi_1 | H_{1Q} | \phi_1 \rangle_Q + \langle \phi_1 | W_1 | \phi_1 \rangle_Q) \chi_1 - (i/\hbar) \langle \phi_2 | V | \phi_2 \rangle_Q \chi_2, \quad (10a)$$

$$\dot{\chi}_2 + \langle \phi_2 | \dot{\phi}_2 \rangle_Q \chi_2 = -(i/\hbar) (H_{2S} + \langle \phi_2 | H_{2Q} | \phi_2 \rangle_Q + \langle \phi_2 | W_2 | \phi_2 \rangle_Q) \chi_2 - (i/\hbar) \langle \phi_2 | V^* | \phi_1 \rangle_Q \chi_1, \quad (10b)$$

$$\begin{aligned} \langle \chi_1 | \dot{\chi}_1 \rangle_S \dot{\phi}_1 = & -\langle \chi_1 | \dot{\chi}_1 \rangle_S \phi_1 - (i/\hbar) (\langle \chi_1 | H_{1S} | \chi_1 \rangle + \langle \chi_1 | \chi_1 \rangle H_{1Q} + \langle \chi_1 | W_1 | \chi_1 \rangle_S) \phi_1 \\ & - (i/\hbar) \langle \chi_1 | V | \chi_2 \rangle_S \phi_2, \end{aligned} \quad (10c)$$

$$\begin{aligned} \langle \chi_2 | \dot{\chi}_2 \rangle_S \dot{\phi}_2 = & -\langle \chi_2 | \dot{\chi}_2 \rangle_S \phi_2 - (i/\hbar) (\langle \chi_2 | H_{2S} | \chi_2 \rangle + \langle \chi_2 | \chi_2 \rangle H_{2Q} + \langle \chi_2 | W_2 | \chi_2 \rangle_S) \phi_2 \\ & - (i/\hbar) \langle \chi_2 | V^* | \chi_1 \rangle_S \phi_1. \end{aligned} \quad (10d)$$

The terms containing $\langle \phi_1 | \dot{\phi}_1 \rangle$ and $\langle \phi_2 | \dot{\phi}_2 \rangle$ in eqs. (10a) and (10b) may be disregarded without loss of generality; this may be seen by making the phase transformations

$$\chi_i \rightarrow \chi_i \exp\left(-\int dt' \alpha_i(t')\right) \quad \text{and} \quad \phi_i \rightarrow \phi_i \exp\left(\int dt' \alpha_i(t')\right),$$

where $\alpha_i(t)$ ($i=1, 2$) are the purely imaginary numbers $\langle \phi_i | \dot{\phi}_i \rangle$. The fact that we eliminated terms containing $\dot{\phi}_1$ from the equations for $\dot{\chi}_1$ has numerical advantages as discussed by Makri and Miller [8].

Another technical problem arises from the structure of eqs. (10c) and (10d): If at time $t=0$ the system starts in electronic state 1, we have $\langle \chi_2(t=0) | \chi_2(t=0) \rangle_S = 0$ and $\phi_2(t=0)$ is not well defined in eq. (10d). A way out of this problem is to use in eqs. (10c) and (10d) not χ_1 , and χ_2 at $t=0$ but $\chi_1(\Delta t)$ and $\chi_2(\Delta t)$ obtained from the first time step integration of eqs. (10a) and (10b), i.e. replacing $\chi_{10} \equiv \chi_1(S, t=0)$ by $\chi_{10} + \dot{\chi}_{10} \Delta t$ ($\dot{\chi}_{10}$ is given by the rhs of eq. (10a)) and taking $\chi_{20} \equiv \chi_2(S, t=0) = -(i/\hbar) \langle \phi_{20} | V^* | \phi_{10} \rangle_Q \chi_{10} \Delta t$ (with $\phi_{10} \equiv \phi_1(Q, t=0)$). In the calculation reported below we have used this prescription for the initial χ_1 and χ_2 functions, where the initial ϕ_1 and ϕ_2 functions were both taken to be the ground state of the bath oscillator. A similar method has been used by Sawada and Metiu [10].

It should be noted that a more consistent choice of initial wavefunctions is possible. Using in eq. (10d), for $\Delta t \rightarrow 0$,

$$\dot{\chi}_2 = -(i/\hbar) \langle \phi_{20} | V^* | \phi_{10} \rangle_Q \chi_{10} + \mathcal{O}(\Delta t), \quad \chi_2 = -(i/\hbar) \langle \phi_{20} | V^* | \phi_{10} \rangle_Q \chi_{10} \Delta t + \mathcal{O}(\Delta t^2) \quad (11)$$

and keeping terms of order Δt we get

$$\langle \chi_{10} | \bar{V}(S) |^2 | \chi_{10} \rangle_S \phi_{20}(Q) = \langle \chi_{10} | \bar{V}(S) V^*(S, Q) | \chi_{10} \rangle_S \phi_{10}(Q), \quad (12)$$

where $\bar{V}(S) = \langle \phi_{10} | V(S, Q) | \phi_{20} \rangle_Q$. Eq. (12) is a self-consistent equation for $\phi_2(Q, t=0)$ given the initial χ_{10} and ϕ_{10} wavefunctions. If ϕ_{20} is chosen according to eq. (12), eq. (10d) becomes (for $\Delta t=0$, and taking $V(S, Q) \equiv V(S)$)

$$\dot{\phi}_2 = -(i/\hbar) [H_{2Q} - \langle \phi_{20} | H_{2Q} + \bar{W}_2(Q) | \phi_{20} \rangle + \bar{W}_2(Q)] \phi_{20}, \quad (13)$$

where

$$\bar{W}_2(Q) = \langle \chi_{10} \| V |^2 W_2 | \chi_{10} \rangle_S / \langle \chi_{10} \| V |^2 | \chi_{10} \rangle_S, \quad (14)$$

We have tested the MCTDSCF equations of motion, eqs. (10), for the following simple example involving a single bath oscillator: U_{1S} and U_{2S} were taken to be two identical horizontally shifted harmonic potentials (fig. 1),

$$U_{1S} = \frac{1}{2} m_S \omega_S^2 (S+d)^2, \quad U_{2S} = \frac{1}{2} m_S \omega_S^2 (S-d)^2. \quad (15)$$

The bath oscillator was taken harmonic with the same potential surface in the two electronic states

$$U_{1Q}(Q) = U_{2Q}(Q) \equiv U_Q(Q) = \frac{1}{2} m_Q \omega_Q^2 Q^2. \quad (16)$$

The coupling $V(S, Q)$ between the two electronic states was taken independent of Q and of the form

$$V(S, Q) = V(S) = V_0 \exp[-(S/R_0)^2]. \quad (17)$$

The coupling between the two systems was taken to be the same in the two electronic states, $W_1(S, Q) = W_2(S, Q) \equiv W(S, Q)$. We have examined two forms,

$$W_a(S, Q) = A Q \exp(-B S^2) \quad (18)$$

and

$$W_b(S, Q) = C S Q. \quad (19)$$

Note that the form a is symmetric in S and (for a fixed Q) will not remove the degeneracy between the states in the right and left wells, while the asymmetric form b will remove this degeneracy.

The initial nuclear wavefunction $\chi_{10}(S)$ was taken to be the normalized ground state in the harmonic potential $U_{1S}(S)$ multiplied by $\exp(iP_0 S)$, so P_0 is the initial momentum. The initial wavefunction $\phi_{10}(Q)$ and $\phi_{20}(Q)$ were both taken to be the ground states of the potential $U_{1Q}(Q+\lambda)$, where the shift due to the coupling to the system oscillator is given by

$$\lambda = \langle \chi_{10} | \partial W(S, Q) / \partial Q | \chi_{10} \rangle_S / m_Q \omega_Q^2. \quad (20)$$

A better choice of $\phi_{20}(Q)$ is obtained in principle from eq. (12), however for the case $V(S, Q) = V(S)$ one gets again the choice $\phi_{20} = \phi_{10}$ used above.

3. Results and discussion

Our results are summarized in figs. 2–4. In all cases we have taken $m_S = m_Q = 1$, $\omega_S = 0.5$, $\omega_Q = 0.8$, $d = 5$ and $R_0 = 3$. In fig. 2 we have used the S -symmetric form W_a of the system – “bath” interaction potential with $A = 1.0$, $B = 0.05$. The non-adiabatic coupling was taken to be $V_0 = 0.5$ and the initial momentum $P_0 = 2.0$. In fig. 3 we have used the S -asymmetric form W_b of the system – “bath” coupling with $C = -0.1$ and again $V_0 = 0.5$, $P_0 = 2.0$. In fig. 4 we used W_a ($A = 0.5$, $B = 0.5$) with $V_0 = 2.0$ and $P_0 = 1.0$. All three figures show the time evolution of the population P_2 in the right well ($P_2 = \langle \chi_2 | \chi_2 \rangle_S$) obtained from an exact calculation (using two-dimensional FFT algorithm on each potential surface) and from the TDSCF equations (10). Also shown in the time evolution of P_2 for the case where the system and “bath” oscillator are uncoupled ($W = 0$). Figs. 2 and 3 also show the results of a single-configuration SCF calculation based on eqs. (1)–(3).

The time evolutions displayed in figs. 2 and 3 correspond to a non-adiabatic situation where bursts of probability transfer occur in every transition across the potential intersection region. Fig. 4 shows the time evolution in the adiabatic limit due essentially to tunneling across the adiabatic potential surface. In both cases the agreement between the evolutions based on the MCTDSCF approximation and on the exact equations of motion is very good. Interestingly, the single-configuration TDSCF results shown in figs. 2 and 3 remain close to the

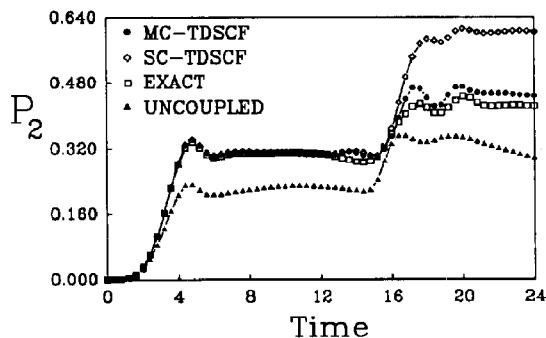


Fig. 2. The time evolution of the transition probability $P_2(t) = \langle \chi_2(S, t) | \chi_2(S, t) \rangle_S$ obtained with and without coupling to the "bath" coordinate. For the coupled case both the solution of the exact equations of motion of the MCTDSCF equations (10) and eqs. (1)–(3) are shown. The system "bath" coupling is the function W_a (eq. (18)). Parameters (given in the text) correspond to the non-adiabatic limit.

exact solution during the first non-adiabatic transition event, and deviate strongly from it only after the second transition event. The (double-configuration) MCTDSCF result remains close to the exact solution for the duration of our calculation which shows two such non-adiabatic transitions.

It should be noted that both the single- and the double-configuration SCF schemes work better than expected (see figs. 2 and 3): The SCTDSCF approximation describes well the first non-adiabatic transition probably due to the fact that in the transition region near the potential crossing point the two "systems" configurations are close to each other. The success of the MCTDSCF approximation in describing the second crossing shown in figs. 2 and 3 is remarkable because at the time of this second crossing the wavefunction has already split once due to the first crossing of the non-adiabatic interaction region. This multiple splitting of the initial wavepacket is expected to lead to deterioration of the approximate calculation at longer times.

Another interesting point associated with eqs. (2) and (3) is the fact that the symmetric coupling W_a to the bath oscillator causes an increase in the transition probability while the asymmetric coupling W_b has the opposite effect. This behavior is associated with the two-dimensional potential surface in the S - Q plane: A close examination of this potential surface reveals that in the presence of the asymmetric coupling the two-dimensional barrier is broader, and for the symmetrical coupling it is lower than in the uncoupled case.

In conclusion, we have demonstrated that the MCTDSCF approximation is a reliable tool for evaluating rates associated with simple curve crossing processes. In conjunction with the FFT algorithm for solving time-dependent Schrödinger equations it is expected to be a very valuable computational tool of chemical dynamics.

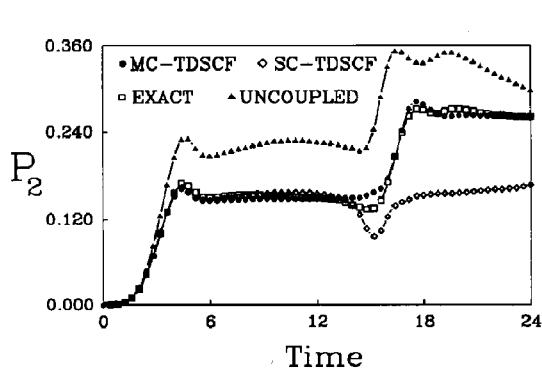


Fig. 3. Same as fig. 2 with the system "bath" coupling given by W_b (eq. (19)). Parameters are given in the text, and except for those describing W_b are identical to those of fig. 1.

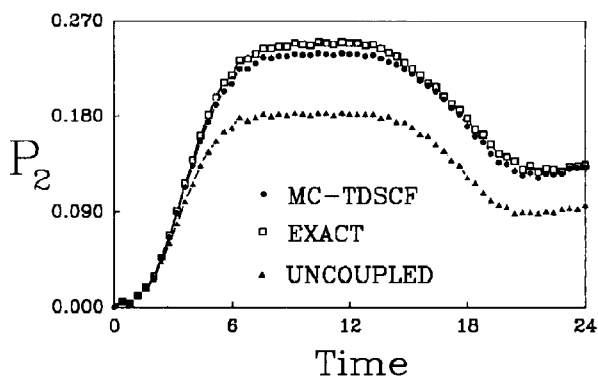


Fig. 4. Same as fig. 2 with parameters (given in the text) corresponding to the adiabatic limit.

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References

- [1] A. Garg, J.N. Onuchic and V. Ambegaokar, *J. Chem. Phys.* 83 (1985) 4491.
- [2] H. Frauenfelder and P.G. Wolynes, *Science* 229 (1985) 337;
P.G. Wolynes, *J. Chem. Phys.* 86 (1987) 1957.
- [3] I. Rips and J. Jortner, *J. Chem. Phys.* 87 (1987) 2090.
- [4] M.E. Feit, J.A. Fleck Jr. and A. Steiger, *J. Comput. Phys.* 47 (1982) 412;
D. Kosloff and R. Kosloff, *J. Comput. Phys.* 52 (1983) 35;
R. Kosloff and D. Kosloff, *J. Chem. Phys.* 79 (1983) 1823.
- [5] R.B. Gerber, V. Buch and M.A. Ratner, *J. Chem. Phys.* 77 (1982) 3022;
R.B. Gerber and M.A. Ratner, *Advan. Chem. Phys.* 70 (1988) 97, and references therein.
- [6] R.H. Bisseling, R. Kosloff, R.B. Gerber, M.A. Ratner, L. Gibson and C. Cerjan, *J. Chem. Phys.* 87 (1987) 2760.
- [7] R. Kosloff, A. Hammerlich and M.A. Ratner, in: *Large Finite Systems*, 20th Jerusalem Symposium, eds. A. Pullman and J. Jortner (Reidel, Dordrecht, 1987).
- [8] N. Makri and N.H. Miller, *J. Chem. Phys.* 87 (1987) 5781.
- [9] G. Wahnström, B. Carmeli and H. Metiu, *J. Chem. Phys.* 88 (1988) 2478.
- [10] S. Sawada and H. Metiu, *J. Chem. Phys.* 84 (1986) 227, 6293.