Time-dependent self-consistent-field dynamics based on a reaction path Hamiltonian. II. Numerical tests

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Numerical tests are presented for a method that combines the time-dependent self-consistent-field (TDSCF) method with the reaction path Hamiltonian (RPH) derived by Miller, Handy, and Adams [J. Chem. Phys. 72, 99 (1980)]. The theoretical basis for this TDSCF-RPH method was presented in a previous paper. The equations of motion were derived for three different cases: (1) zero coupling matrix (i.e., zero reaction path curvature and zero coupling between the normal modes); (2) zero reaction path curvature and nonzero coupling between the normal modes; and (3) zero coupling between the normal modes and nonzero but small reaction path curvature. For these three cases the dynamics can always be reduced to a one-dimensional numerical time propagation of the reaction coordinate. In this paper the TDSCF-RPH methodology for all three cases is tested by comparing the TDSCF-RPH dynamics to exact quantum dynamics based on the exact Hamiltonian for simple model systems. The remarkable agreement indicates that the TDSCF-RPH method could be useful for the calculation of the real-time quantum dynamics of a wide range of chemical reactions involving polyatomic molecules. © 1998 American Institute of Physics. [S0021-9606(98)01041-1]

I. INTRODUCTION

In a previous paper\textsuperscript{1} we developed the theory and numerical methodology for real-time quantum dynamical wave packet calculations of polyatomic systems based on a reaction path Hamiltonian. In particular, we developed the TDSCF-RPH method, which combines the time-dependent self-consistent-field (TDSCF) method\textsuperscript{2–6} with the reaction path Hamiltonian (RPH) of Miller, Handy, and Adams.\textsuperscript{7} The reaction path Hamiltonian derived by Miller, Handy, and Adams\textsuperscript{7} characterizes the reaction dynamics of a polyatomic system in terms of motion along the minimum energy path (MEP) and vibrational motion orthogonal to this path, where the MEP is defined\textsuperscript{8} as the path of steepest descent in mass-weighted Cartesian coordinates starting from a saddle point on the potential surface down to various minima. This reaction path Hamiltonian has been discussed extensively in the literature and has been used successfully to describe a variety of chemical processes.\textsuperscript{9–30} Reference 1 applies the TDSCF methodology to this MEP reaction path Hamiltonian\textsuperscript{9,31} and presents an approach for solving the normal mode equations of motion that allows efficient numerical quantum dynamical calculations.

The TDSCF-RPH equations of motion have been derived\textsuperscript{1,32} for three special cases of the MEP reaction path Hamiltonian: (1) zero coupling matrix (i.e., zero reaction path curvature and zero coupling between the normal modes); (2) zero curvature and nonzero coupling between the normal modes; and (3) zero coupling between the normal modes and nonzero but small curvature. For the first and third cases the TDSCF-RPH dynamics always reduces to a one-dimensional numerical time propagation of the reaction coordinate. For the second case with the adiabatic representation of the reaction path Hamiltonian, the TDSCF-RPH dynamics reduces to a one-dimensional problem for a specific choice of initial wave packet (which can have an arbitrary component for the reaction coordinate) but not for a general initial wave packet. Reference 32 shows that with the diabatic representation of the RPH,\textsuperscript{9} which involves a transformation of variables that shifts the coupling between the vibrational modes from the kinetic energy to the potential energy, the TDSCF-RPH dynamics always reduces to a one-dimensional numerical time propagation even for the second case described above (i.e., zero curvature and nonzero coupling between the normal modes). Thus for all cases with zero or small curvature, the TDSCF-RPH dynamics can be reduced to a one-dimensional time propagation.

This paper presents numerical tests of the TDSCF-RPH methodology presented in Refs. 1 and 32 by comparing the TDSCF-RPH dynamics to exact quantum dynamics for simple model systems. (In this paper “exact quantum dynamics” refers to use of the Chebyshev expansion\textsuperscript{33} to integrate the equations of motion for the exact Hamiltonian.) These comparisons test the two basic approximations of TDSCF-RPH dynamics: (1) the RPH approximation for the Hamiltonian and (2) the TDSCF approximation for the wave function. The paper is organized as follows. Section II describes the relevant background, including the reaction path Hamiltonian and the TDSCF method. Sections III through VI present the numerical tests of the equations of motion: Sec. III addresses the case of zero coupling matrix, Secs. IV and V address the case of zero curvature but nonzero coupling between the normal modes for the adiabatic and diabatic representations of the RPH, and Sec. VI addresses the case.
modes. Section VII summarizes the results and discusses future directions.

II. BACKGROUND AND BASIC METHODS

This paper concerns $F$-dimensional systems without the complications of overall rotations and translations. The potential energy surface is given by $V(r)$, where $r$ denotes the mass-weighted Cartesian coordinates. As described in the introduction, the minimum energy path (MEP) is defined as the path of steepest descent in mass-weighted Cartesian coordinates starting from a transition state on the potential surface down to products and back to reactants. In this paper $s$ denotes the internal reaction coordinate, which is the arc length along the MEP, $a(s)$ denotes the mass-weighted Cartesian coordinates of points on the MEP, and $v(s)$ denotes the normalized gradient vector that points along this MEP:

\[ v(s) = -c[\nabla_r V(r)]_{r=a(s)}, \]

where $c$ is a normalization constant. The potential energy and Hessian matrix along the MEP are denoted $V_p(s)$ and $\bar{K}(s)$, respectively. The reaction coordinate $s$ is defined to be the $F$th degree of freedom, and the coordinates of the $F-1$ vibrational modes orthogonal to the MEP are denoted $Q_k$, where $k = 1, \ldots, F-1$. The frequencies $\{\omega_k^2(s)\}$ and directions $\{L_k(s)\}$ (where $k = 1, \ldots, F-1$) corresponding to the $F-1$ vibrational modes orthogonal to the MEP can be obtained by diagonalizing the projected Hessian matrix

\[ \bar{K}^p = (\mathbf{I} - \bar{P}) \cdot \bar{K} \cdot (\mathbf{I} - \bar{P}), \]

where $\mathbf{I}$ denotes the identity matrix and $\bar{P}$ denotes a projection matrix that projects out the gradient vector $v$. The frequencies $\{\omega_k^2(s)\}$ are related to the eigenvalues $\lambda_k$ of $\bar{K}^p$ by

\[ \omega_k^2(s) = \lambda_k \]

and the $\{L_k(s)\}$ are the eigenvectors of $\bar{K}^p$, where $L_p(s) = v(s)$ (corresponding to a zero eigenvalue of $\bar{K}^p$). Note that a general component of the projection matrix is

\[ P_{ij} = v_i v_j, \]

where $v_i$ and $v_j$ are components of $v$. Moreover, the normal mode coordinates $\{Q_k\}$ are defined by

\[ Q_k = (r - a) \cdot L_k, \]

where the displacement $(r - a)$ is orthogonal to the reaction path, leading to

\[ (r - a) \cdot v = 0. \]

Finally, from the definition of arc length

\[ ds^2 = \sum_{j=1}^{F} (dr_j)^2. \]

For zero total angular momentum the reaction path Hamiltonian derived by Miller, Handy, and Adams' is

\[ H(p, s, \{p_k, Q_k\}) = \frac{1}{2} \frac{p^2}{1 + \sum_{k=1}^{F-1} Q_k^2} + \frac{1}{2} \sum_{k=1}^{F-1} \frac{p_k^2}{2} + V_o(s) + \frac{1}{2} \sum_{k,k'=1}^{F-1} Q_k A_{k,k'} Q_{k'}, \]

where $p$ and $\{p_k\}$ are the conjugate momenta of the reaction coordinate $s$ and the normal mode coordinates $\{Q_k\}$, respectively, and the coupling matrix $\bar{B}$ is defined to have elements

\[ B_{k,l}(s) = \mathbf{L}_k' (s) \cdot \mathbf{L}_l(s) = \sum_{l=1}^{F} L_k' (s) L_{l,l}(s), \]

where $L_{i,l}(s)$ is the $i$th component of the eigenvector $\mathbf{L}_l(s)$, and $L_k' (s) = d\mathbf{L}_k(s)/ds$. Note that $B_{k,l}(s)(k,l=1, \ldots, F-1)$ are the coupling elements between normal modes $Q_k$ and $Q_l$, and $B_{k,l}(s)(k, l = 1, \ldots, F-1)$ are the coupling elements between the normal mode $Q_k$ and the reaction coordinate $s$. As described in Ref. 7, the coupling elements in the numerator of the first term of Eq. (8) are Coriolis-like interactions, and the coupling elements in the denominator of this term describe the effects of reaction path curvature, where the curvature $\kappa(s)$ is defined as

\[ \kappa(s) = \left[ \sum_{k=1}^{F-1} B_{k,k}(s)^2 \right]^{1/2}. \]

As shown in Refs. 9 and 14, the Coriolis coupling terms can be eliminated from this reaction path Hamiltonian by a straightforward transformation of the variables in which the coupling between the vibrational modes is shifted from the kinetic energy to the potential energy. The variables $(p_s, s, \{p_k, Q_k\})$ are transformed to new variables $(\tilde{p}_s, s, \{\tilde{p}_k, \tilde{Q}_k\})$ as follows:

\[ \tilde{Q}_k = \sum_{l=1}^{F} U_{l,k}(s) Q_l, \quad \tilde{P}_k = \sum_{l=1}^{F} U_{l,k}(s) P_l, \]

\[ \tilde{s} = s, \quad \tilde{p}_s = p_s - \sum_{k,l=1}^{F-1} Q_k P_l B_{k,l}(s), \]

where $\mathbf{U}(s)$ is an orthogonal $(F-1) \times (F-1)$ matrix chosen to satisfy the equation

\[ U_{k,k'}(s) = dU_{k,k'}(s)/ds = \sum_{l=1}^{F-1} B_{k,l}(s) U_{l,k'}(s). \]

Applying this transformation to the reaction path Hamiltonian and dropping the overbars leads to the “diabatic” reaction path Hamiltonian

\[ H_d(p, s, \{p_k, Q_k\}) = \frac{1}{2} \frac{p^2}{1 + \sum_{k=1}^{F-1} \tilde{Q}_k^2} + \frac{1}{2} \sum_{k=1}^{F-1} \frac{p_k^2}{2} + V_o(s) + \frac{1}{2} \sum_{k,k'=1}^{F-1} \tilde{Q}_k A_{k,k'} \tilde{Q}_{k'}, \]

where
\[
\phi_i(s) = \sum_{l=1}^{F-1} U_{i,l}(s) B_{l,p}(s) 
\]
(13)
and
\[
\Lambda_{i,k} = \sum_{l=1}^{F-1} U_{i,l}(s) \omega_l(s)^2 U_{i,k}(s). 
\]
(14)
As shown in Ref. 32, the diabatic representation is useful for cases in which the coupling between the normal modes does not vanish.

This paper concerns the combination of the reaction path Hamiltonians in Eqs. (8) and (12) with the TDSCF method to study the real-time quantum dynamics of a polyatomic system. Reference 1 proves that for zero curvature the transformation of the classical reaction path Hamiltonians to the corresponding quantum mechanical Hamiltonian operators involves the standard replacements \( \rho \rightarrow \frac{i}{\hbar} \partial / \partial s \), \( p_k \rightarrow \frac{i}{\hbar} \partial / \partial Q_k \).

For nonzero curvature this straightforward transformation is not valid, but for the case of small curvature we will use this standard transformation to approximate the quantum mechanical Hamiltonian.

For a system with \( F \) degrees of freedom the TDSCF-RPH method approximates the total wave packet as a simple product of single mode functions
\[
\Psi(s, Q_k; t) = \phi_i(s, t) \prod_{k=1}^{F-1} \phi_k(Q_k, t) 
\]
with the normalization conditions
\[
\langle \phi_i | \phi_i \rangle = \langle \phi_k | \phi_k \rangle = 1, \quad k = 1, 2, \ldots, F - 1. 
\]
(17)
In this paper we compare the TDSCF-RPH dynamics to exact quantum dynamics (based on the exact Hamiltonian) for simple two- and three-dimensional model systems. For these simple model systems we can calculate analytical expressions for all of the quantities required for the reaction path Hamiltonian [i.e., \( V_o(s) \), \( \mathbf{K}^p(s) \), \( \mathbf{L}_i(s) \), \( \omega_l(s) \), and \( \mathbf{B}(s) \)]. For example, consider a general two-dimensional model with mass-weighted Cartesian coordinates \( \mathbf{r} = (x, y) \), potential energy \( V(x, y) \), and normalized gradient vector \( \mathbf{v} = (v_x, v_y) \) along the MEP. Equations (2) and (4) can be used to show that the projected force constant matrix is
\[
\mathbf{K}^p = \begin{pmatrix} a & c \\ c & b \end{pmatrix}, 
\]
where
\[
a = V_{xx} v_x^2 + 2V_{xy} v_x v_y + V_{yy} v_y^2, \\
b = V_{yy} v_y^2 + 2V_{xy} v_x v_y + V_{xx} v_x^2, \\
c = -V_{xx} v_x^2 - V_{yy} v_y^2 + 2V_{xy} v_x v_y. 
\]
Here \( V_{\alpha\beta} = (\partial^2 V)/(\partial \alpha \partial \beta) \) [e.g., \( V_{xx} = (\partial^2 V)/(\partial x^2) \)]. The eigenvalues of \( \mathbf{K}^p \) are
\[
\lambda_1 = a + b, \quad \lambda_2 = 0 
\]
and the corresponding eigenvectors are
\[
\mathbf{L}_1 = \begin{pmatrix} v_y \\ -v_x \end{pmatrix}, \quad \mathbf{L}_2 = \begin{pmatrix} v_x \\ v_y \end{pmatrix}. 
\]
(20)
Note that the frequencies \( \{ \omega_l(s) \} \) are obtained from the eigenvalues using Eq. (3), and the coupling matrix \( \mathbf{B}(s) \) is obtained from the eigenvectors using Eq. (9). Equations (5), (6), and (7) can be used to transform between the mass-weighted Cartesian coordinates and the reaction path coordinates. Similar expressions can be obtained for a general three-dimensional system.

For the numerical tests reported in this paper, the equations of motion were integrated using the Chebyshev expansion \(^{33} \) for the exact dynamics and the third order predictor-corrector algorithm \(^{33} \) for the TDSCF-RPH dynamics.

III. ZERO COUPLING MATRIX

For zero coupling matrix the \( F \)-dimensional TDSCF-RPH dynamics reduces to a one-dimensional time propagation of the reaction coordinate. First consider a special initial wave packet in which the initial normal mode wave functions \( \phi_j(Q_j, t=0) \) are pure eigenstates \( G_{nj} \) with eigenvalues \( E_{nj} \) for a harmonic oscillator Hamiltonian with quantum number \( n_j \), unit mass, center at zero, and frequency \( \omega_{oj} \), where
\[
\omega_{oj} = (\langle \phi_j | \omega_j(s) | \phi_j \rangle)^{1/2}. 
\]
(21)
In this case the normal mode wave functions are of the form
\[
\phi_j(Q_j, t) = G_{nj} \exp \left( -\frac{i}{\hbar} E_{nj} t \right). 
\]
(22)
where \( G_{nj} \) and \( E_{nj} \) are evaluated at time \( t \), and the equation of motion for the reaction coordinate \( s \) is
\[
i \hbar \dot{\phi}_s = \left[ \frac{1}{2} p_s^2 + V_o(s) + \hbar \sum_{j=1}^{F-1} \frac{1}{2} n_j \frac{\omega_j(s)^2}{2 \omega_{oj}} \right] \phi_s. 
\]
(23)
Next consider a general initial wave packet in which the initial normal mode wave functions are of the form \( \phi_j(Q_j, t=0) = \sum_{n=0}^{\infty} a_n G_n \), where \( G_n \) are eigenfunctions of a harmonic oscillator with unit mass and frequency \( \omega_{oj} \). In this case the normal mode wave functions are of the form
\[
\phi_j = \sum_{n=0}^{\infty} a_n G_n \exp \left( -\frac{i}{\hbar} E_n t \right), 
\]
(24)
where \( G_n \) and \( E_n \) are evaluated at time \( t \) and \( a_n \) are time-independent expansion coefficients (all corresponding to the \( j \)th normal mode). The equation of motion for the reaction coordinate \( s \) is
\[
i \hbar \dot{\phi}_s = \left[ \frac{1}{2} p_s^2 + V_o(s) + \sum_{j=1}^{F-1} \frac{1}{2} n_j \frac{\omega_j(s)^2}{2 \omega_{oj}} \right] \phi_s, 
\]
(25)
where
Each time step the effective frequencies \( \tilde{v} \) about the result for the situation in which function at each time step can be calculated from Eq. (21), and \( \phi_j \) is propagated for this time step using Eq. (23) or Eq. (25). The total wave function at each time step can be calculated from Eq. (16), in which the normal mode wave functions \( \phi_k \) are of the form given in either Eq. (22) or Eq. (24), where \( G_{nk} \) are harmonic oscillator eigenfunctions with unit mass, center at zero, frequency \( \omega_{nk} \), and quantum number \( n_k \).

Note that Eq. (24) is the solution for \( \phi_j(t) \) only if \( G_n \) and \( E_n \) are constant over the time interval \( t \). In the TDSCF-RPH method, however, \( G_n \) and \( E_n \) vary with time since the frequency \( \omega_{nj} \) varies with time through Eq. (21). Thus, in this numerical scheme with a time step of \( \delta t \), the phase factor \( e^{-iE_j(t)\delta t/\hbar} \) is accumulated in the expansion coefficients \( a_n \) (i.e., the coefficients \( a_n \) are multiplied by this phase factor at each time step), and the time \( t \) in the exponential in Eq. (26) is replaced with \( \delta t \). Note that this scheme leads to the correct result for the situation in which \( \omega_{nj} \) and thus \( E_n \) are constant.

### A. Model system

The model system used to test the TDSCF-RPH methodology for the case of zero coupling matrix is the two-dimensional system with Hamiltonian

\[
H = -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} \right) + V(x,y)
\]  

(27)

and potential energy

\[
V(x,y) = \frac{1}{27.212} \left[ e^{-\alpha(x+y)} - \frac{\beta xy}{1 + e^{\gamma(x+y)}} \right]
\]  

(28)

where \( \alpha = 6.0 \times 10^{-3} \), \( \beta = 3.78 \times 10^{-4} \), and \( \gamma = 3.9 \times 10^{-3} \), all in atomic units. (Note that \( x \) and \( y \) are mass-weighted Cartesian coordinates.)

This two-dimensional potential energy surface is shown in Fig. 1. The saddle point is located at \( x = y = -42.45 \) with \( V = 0.04659 \), and the two minima are at \( x = y = 212.0 \) with \( V = -0.05621 \) and \( x = y = 288.5 \) with \( V = -0.1091 \), all in atomic units. The potential energy surface is symmetric about the \( x=y \) plane, and the MEP is the straight line \( x = y \), so

\[
a_x(s) = a_y(s),
\]  

(29)

where \( a(s) \) represents the mass-weighted Cartesian coordinates of points on the MEP.

For this simple model the normalized gradient vector [Eq. (1)] is

\[
\mathbf{v} = (v_x, v_y) = \left( \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right)
\]  

(30)

(Here the coefficients \( a_n \) are understood to correspond to the \( i \)th normal mode.) The numerical procedure presented in Ref. 1 is as follows: starting with a specified initial \( \phi_j(s,t=0) \), at each time step the effective frequencies \( \omega_{nk} \) for the normal modes \( Q_k \) are calculated from Eq. (21), and \( \phi_j \) is propagated for this time step using Eq. (23) or Eq. (25). The total wave function at each time step can be calculated from Eq. (16), in which the normal mode wave functions \( \phi_k \) are of the form given in either Eq. (22) or Eq. (24), where \( G_{nk} \) are harmonic oscillator eigenfunctions with unit mass, center at zero, frequency \( \omega_{nk} \), and quantum number \( n_k \).

FIG. 1. The two-dimensional potential energy surface used to study the dynamics for zero coupling matrix. The saddle point and two minima all lie on the line \( x=y \). The saddle point is at \( x=y=-42.45 \) a.u. with energy 1.2678 eV, and the two minima are at \( x=y=-212.0 \) a.u. and \( x=y=288.5 \) a.u. with energies -1.5295 and -2.9677 eV, respectively.

and the projected force matrix in Eq. (18) is

\[
\mathbf{K}^p = \begin{pmatrix}
  a & -a \\
  -a & a
\end{pmatrix}
\]  

(31)

with

\[
a = \frac{1}{4} \begin{pmatrix}
  \frac{\partial^2 V}{\partial x^2} - 2 \frac{\partial^2 V}{\partial x \partial y} + \frac{\partial^2 V}{\partial y^2}
\end{pmatrix}
\]  

(32)

The eigenvalues of the matrix \( \mathbf{K}^p \) are obtained from Eq. (19) as

\[
\lambda_1 = \omega_1^2 = 2a, \quad \lambda_2 = 0
\]  

(33)

with normalized eigenvectors obtained from Eq. (20) as

\[
\mathbf{L}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix}
  1 \\
  -1
\end{pmatrix}, \quad \mathbf{L}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix}
  1 \\
  1
\end{pmatrix}
\]  

(34)

Since these eigenvectors are constant, the coupling matrix \( \mathbf{\tilde{B}} \) is zero. Equations (5) and (29) lead to the following relation between the normal mode coordinate \( Q \) and the Cartesian coordinates \( (x,y) \):

\[
Q = \frac{1}{\sqrt{2}}(x-y).
\]  

(35)

Equations (6), (7), and (29) lead to the following relation between the reaction coordinate \( s \) and the Cartesian coordinates \( (x,y) \):

\[
s = \frac{1}{\sqrt{2}}(x+y).
\]  

(36)

Equations (35) and (36) can be used to transform between the Cartesian coordinates \( (x,y) \) and the reaction path coordinates \( (s,Q) \), which allows the comparison between wave packets from TDSCF-RPH and exact dynamics.

### B. Special initial wave packet

The special initial wave packet is chosen as
The two-dimensional wave packets at times \( t = 0, 1000, 1500, \) and 4000 a.u. for the potential energy surface given in Fig. 1 using (a) exact quantum dynamics; (b) TDSCF-RPH dynamics.

\[
\psi_0(s, \mathbf{Q} ; t = 0) = \phi_s(s; t = 0) \phi_Q(Q; t = 0) \\
= A \exp \left[ -\frac{1}{2\hbar} \omega_s (s - s_o)^2 \right] \\
\times \exp \left[ -\frac{1}{2\hbar} \omega_Q (Q - Q_o)^2 \right]. \tag{37}
\]

where \( A \) is the normalization constant, \( \omega_s = 2.09 \times 10^{-3} \) a.u., and \( s_o = 141.4 \) a.u. Although the \( s \) component can be any arbitrary function, without loss of generality we choose it to be a simple Gaussian function. The \( Q \) component, however, is determined by the \( s \) component and corresponds to the pure ground state of a harmonic oscillator with unit mass, center at zero (i.e., \( Q_o = 0.0 \)), and frequency \( \omega_Q \) defined in Eq. (21) (leading to \( \omega_Q = 2.09 \times 10^{-3} \) a.u.).

Figure 2 presents the contours of the two-dimensional wave packets at the four different times \( t = 0, 1000, 1500, \) and 4000 a.u. Figure 2(a) depicts the exact results, while Fig. 2(b) depicts the RPH-TDSCF results. The system starts near the transition state and then moves toward the minimum at \( x = y = 288.5 \) a.u. The wave packet reaches this minimum at \( t \sim 1100 \) a.u. and continues to move in the same direction until \( t \sim 4000 \) a.u., when it collides with the potential wall and moves back toward the minimum. During this process the shape of the wave packet changes continuously. Note that in the TDSCF approximation the frequency of the normal mode coordinate is independent of \( s \) at a given time [since the frequency is defined by Eq. (21)]. As a result, the width of the TDSCF wave packet along \( Q \) is constant at a given time, while the width of the exact wave packet along \( Q \) is a function of the reaction coordinate \( s \) at a given time. This difference is shown clearly in Fig. 2 for the final time of 4000 a.u. Other than these minor discrepancies, however, throughout the process the TDSCF-RPH wave packet closely follows the exact wave packet. The solid curve in Fig. 3 depicts the overlap (modulus) between the exact and the TDSCF-RPH wave packets for the special initial wave packet. The overlap is greater than 91% throughout the dynamics, representing nearly quantitative agreement. Typically the TDSCF method is capable of reproducing averaged quantities, but the overlap of a TDSCF wave packet with an exact wave packet is expected to be poor. The remarkable agreement for the model systems studied in this paper is due to the nearly separable form of the reaction path Hamiltonian. In particular, for this model with zero coupling matrix, the kinetic energy operator is separable, and the coupling in the potential energy is not problematic for this type of trajectory.

### C. General initial wave packet

The general initial wave packet is chosen as

\[
\psi_0(s, \mathbf{Q} ; t = 0) = \phi_s(s; t = 0) \phi_Q(Q; t = 0) \\
= A \exp \left[ -\frac{1}{2\hbar} \omega_s (s - s_o)^2 \right] \\
\times \sum_{n=0}^{2} a_n G_n(Q; t = 0), \tag{38}
\]

where \( G_n \) are eigenfunctions of a harmonic oscillator with unit mass, center at zero, frequency \( \omega_Q \) [defined in Eq. (21)], and quantum number \( n \). For this model \( \omega_s \), \( s_o \), and thus \( \omega_Q \) are the same as in the previous subsection, and \( a_0 = 0.95 \), \( a_1 = 0.3 \), and \( a_2 = 0.0866 \). Although the normal mode component can be any arbitrary function that is expanded in the basis set of the eigenfunctions \( G_n \), without loss of generality we assume that only the first three eigenfunctions have non-zero expansion coefficients.
The dashed curve in Fig. 3 depicts the overlap between the exact and the TDSCF-RPH wave packets for the general initial wave packet. Again the agreement is very impressive, but the TDSCF-RPH dynamics is not as quantitatively accurate as for the special initial wave packet (given by the solid line). This poorer agreement is due to the existence of the excited components (the \(a_1\) and \(a_2\) terms) in the initial wave packet. These excited components access regions further from the MEP, and since the RPH is based on a harmonic approximation about the MEP its accuracy deteriorates rapidly for regions far from the MEP. Thus, as wave packets access regions further from the MEP, the RPH is no longer a good approximation to the exact Hamiltonian. In addition, the excited components lead to greater difficulties with the TDSCF approximation since in this case the shape of the wave packet becomes more complex as the wave packet evolves in time, so the wave packet is no longer separable.

### IV. ZERO REACTION PATH CURVATURE: ADIABATIC REPRESENTATION

For the adiabatic representation of the reaction path Hamiltonian with zero curvature and nonzero coupling between the normal modes, the \(F\)-dimensional TDSCF-RPH dynamics reduces to a one-dimensional time propagation for a special initial wave packet, but \(F\) coupled equations of motion must be solved for an arbitrary initial wave packet. First consider a special initial wave packet in which the initial normal mode wave functions \(\phi_j(Q_j,t=0)\) are pure eigenstates \(G_{n_k}\) of a harmonic oscillator with quantum number \(n_j\), center at zero, effective mass \(m_j'\), and effective frequency \(\omega_j'\), where

\[
\frac{1}{m_j'} = 1 + \hbar \sum_{i \neq j}^{F-1} \langle \phi_j | B_{k,j}(s)^2 | \phi_i \rangle \left( \frac{1}{2} + n_k \right) \frac{1}{m_k' \omega_k'},
\]

\[
m_j' \omega_j'^2 = \omega_j^2 + \hbar \sum_{i \neq j}^{F-1} \langle \phi_j | B_{k,j}(s)^2 | \phi_i \rangle \left( \frac{1}{2} + n_k \right) m_k' \omega_k',
\]

where \(\omega_j^2 = \langle \phi_j | \omega(s)^2 | \phi_j \rangle\). In this case the normal mode wave functions are of the form given in Eq. (22) and the equation of motion for the reaction coordinate \(s\) is

\[
\hbar \dot{\phi}_s = \frac{1}{2} p_s^2 + V_o(s) + \hbar \sum_{i=1}^{F-1} \left( \frac{1}{2} + n_i \right) \omega_i(s)^2 \frac{m_i' \omega_i'}{m_j' \omega_j'} \phi_i \\
+ \left( \frac{\hbar}{2} \sum_{k=1}^{F-1} \left( \frac{1}{2} + n_k \right) \frac{m_k' \omega_k'}{m_j' \omega_j'} - \frac{4}{3} \right) \times B_{k,j}(s)^2 \phi_j.
\]

For a general wave packet in which the normal mode wave functions are of the form \(\phi_j(Q_j,t=0) = \sum_n \phi_n G_n\), where \(G_n\) are eigenfunctions of a harmonic oscillator Hamiltonian, the reduction to a one-dimensional time propagation is not possible in the adiabatic representation. In this case the \(F-1\) normal mode equations of motion

\[
\hbar \dot{\phi}_j = \left[ \frac{1}{2} (1 + A_j) p_j^2 + \frac{1}{2} (\omega_j' + B_j) q_j^2 + \frac{1}{2} (C_j P_j Q_j + D_j Q_j P_j + E_j P_j + F_j Q_j + G_j) \right] \phi_j
\]

must be solved along with the reaction coordinate equation of motion

\[
\hbar \dot{\phi}_s = \left[ \frac{1}{2} p_s^2 + V_o(s) + H(s) + I(s) \right]
\]

\[
+ \sum_{i=1}^{F-1} \frac{1}{2} \omega_i(s)^2 \langle \phi_i | Q_i^2 | \phi_j \rangle \phi_s,
\]

where the quantities \(A_j\) through \(G_j\) and \(H(s)\) and \(I(s)\) are defined in the Appendix.

The numerical procedure for the special initial wave packet is analogous to that described in the previous section: starting with a specified initial \(\phi_j(s,t=0)\), at each time step the effective masses \(m_j'\) and the effective frequencies \(\omega_j'\) for the normal modes \(Q_k\) are calculated using Eqs. (39) and (40), and \(\phi_j\) is propagated for this time step using Eq. (41). In this numerical scheme, \(m_k'\) and \(\omega_k'\) on the right-hand sides of Eqs. (39)–(41) are their values at the beginning of the current time step. The total wave function at each time step can be calculated from Eq. (16), in which the normal mode wave functions \(\phi_k\) are of the form given in Eq. (22), where \(G_{n_k}\) are harmonic oscillator eigenfunctions with mass \(m_k'\), frequency \(\omega_k'\), center at zero, and quantum number \(n_k\). For arbitrary initial wave packets the \(F\) one-dimensional equations of motion must be propagated numerically.

### A. Three-dimensional model system

The model system used to test the TDSCF-RPH methodology for the case of zero curvature and nonzero coupling between the normal modes is the three-dimensional system with Hamiltonian

\[
H = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2} \frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2} \frac{\partial^2}{\partial z^2} + V(x,y,z)
\]

and potential energy

\[
V(x,y,z) = \alpha x^2 + \beta y^2 + \gamma xy [u + \delta] + f(z),
\]

where \(\alpha, \beta, \gamma,\) and \(\delta\) are adjustable parameters, and \(u = df(z)/dz\). Here \(f(z)\) is the double well function

\[
f(z) = \frac{12 \Delta E}{(q_2 - q_1)^3 (2q_3 - q_1 - q_2)} \left( \frac{z^4}{4} - (q_1 + q_2 + q_3) \frac{z^3}{8} \right)
\]

\[
+ (q_1 q_2 + q_1 q_3 + q_2 q_3) \frac{z^2}{2} - (q_1 q_2 q_3) z
\]

\[
+ q_3^2 \left( \frac{z^2}{2} - 2 q_2 (q_1 + q_3) + 6 q_1 q_3 \right) / 12.
\]

where \(\Delta E\) is the energy difference between the first minimum and the maximum, and if \(q_3 > q_2 > q_1\) then \(q_1\) and \(q_3\) correspond to the positions of the two minima and \(q_2\) to the position of the maximum. The constant (last) term in Eq. (46) shifts the function so the maximum is zero [i.e., \(f(q_2)\)
In this paper $\Delta E = 0.0441$, $q_1 = -100.0$, $q_2 = 300.0$, $q_3 = 800.0$, $\alpha = 5.2 \times 10^{-7}$, $\beta = 5.0 \times 10^{-7}$, $\gamma = 5.3 \times 10^{-6}$, and $\delta = 2.1 \times 10^{-2}$, all in atomic units.

The saddle point of this three-dimensional potential energy surface is at $(0,0,300.0)$ with $V = 0.0$, and the minima are at $(0,0,800.0)$ with $V = 0 - 0.07998$ and $(0,0,100.0)$ with $V = 0 - 0.04410$, all in atomic units. For this model system the MEP is along the $z$ axis, so

$$a_x = a_y = 0.$$  

(47)

The normalized gradient vector [Eq. (1)] along the MEP is

$$\mathbf{v} = (v_x, v_y, v_z) = (0,0,1)$$  

(48)

and the projected force matrix $\mathbf{K}^p$ [Eq. (2)] is symmetric with components

$$K_{11}^p = \frac{\partial^2 V}{\partial x^2} = 2\alpha, \quad K_{22}^p = \frac{\partial^2 V}{\partial y^2} = 2\beta,$$

$$K_{12}^p = K_{21}^p = \frac{\partial^2 V}{\partial x \partial y} = \gamma(u + \delta),$$

$$K_{13}^p = K_{23}^p = 0, \quad i = 1,2,3.$$  

(49)

The eigenvalues of the matrix $\mathbf{K}^p$ are

$$\lambda_1 = (\alpha + \beta) + \Delta, \quad \lambda_2 = (\alpha + \beta) - \Delta, \quad \lambda_3 = 0,$$

where

$$\Delta = \sqrt{(\alpha - \beta)^2 + \gamma^2(u + \delta)^2}.$$  

(50)

The corresponding normalized eigenvectors are

$$L_1 = A_1 \begin{pmatrix} \gamma(u + \delta) \\ \beta - \alpha + \Delta \\ 0 \end{pmatrix}, \quad L_2 = A_2 \begin{pmatrix} \gamma(u + \delta) \\ \beta - \alpha - \Delta \\ 0 \end{pmatrix},$$

$$L_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$  

(51)

where

$$A_1 = \frac{1}{\sqrt{2[(\alpha - \beta)^2 + \gamma^2(u + \delta)^2 - (\alpha - \beta)\Delta]}},$$

$$A_2 = \frac{1}{\sqrt{2[(\alpha - \beta)^2 + \gamma^2(u + \delta)^2 + (\alpha - \beta)\Delta]}}.$$  

(52)

The coupling matrix is

$$B = \begin{pmatrix} 0 & -B_{21} & 0 \\ B_{21} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$  

(53)

where

$$B_{21} = A_1 \gamma(u + \delta)[A_2 \gamma(u + \delta) + A_2 \gamma u']$$

$$+ A_1 (\beta - \alpha + \Delta)[A_2 (\beta - \alpha - \Delta) - A_2 \Delta'],$$  

(54)

Here the primes indicate the derivative with respect to the reaction coordinate $s$. Equations (6) and (47) lead to $a_z = z$, and Eq. (7) [together with the identity $a = (0,0,1)$] leads to $s = z$.

Furthermore, Eqs. (5) and (47) lead to

$$Q_1 = A_1 \gamma(u + \delta)x + A_1 (\beta - \alpha + \Delta)y,$$

$$Q_2 = A_2 \gamma(u + \delta)x + A_2 (\beta - \alpha - \Delta)y.$$  

(55)

Equations (58)–(60) allow the transformation between the mass-weighted Cartesian coordinates $(x,y,z)$ and the reaction path coordinates $(Q_1, Q_2, s)$.

### B. Special initial wave packet

The special initial wave packet is chosen as

$$\psi_o(s,Q_1,Q_2; t=0)$$

$$= A \exp \left[ -\frac{1}{2\hbar} \omega(s-s_o)^2 \right] \exp \left[ -\frac{1}{2\hbar} (\omega_1 (Q_1 - Q_{o1})^2 + \omega_2 (Q_2 - Q_{o2})^2) \right],$$  

(56)

where $A$ is the normalization factor, $s_o = 450.0$ a.u., and $\omega_s = 4.0 \times 10^{-3}$ a.u. The normal mode components are determined by the reaction coordinate component and correspond to pure ground states of harmonic oscillators with effective masses $m'_i = 1$, centers at zero (i.e., $Q_{o1} = Q_{o2} = 0$), and effective frequencies $\omega'_i = \omega_{s_i}$ given by Eq. (21) (leading to $\omega_1 = 1.044 \times 10^{-3}$ a.u. and $\omega_2 = 1.015 \times 10^{-3}$ a.u.). Since $\langle \phi, \phi | B_{12}(s)^2 | \phi, \phi \rangle \sim 0$ for this initial wave packet, these initial effective masses and frequencies satisfy Eqs. (39) and (40).

The solid curve in Fig. 4 depicts the overlap between the exact three-dimensional wave packets and the corresponding TDSCF-RPH wave packets for the special initial wave packet. The overlap is nearly 100% throughout the dynamics, indicating highly quantitative agreement.
C. General initial wave packet

The general initial wave packet is of the form given in Eq. (61) with the parameters \( \omega_s = 4.0 \times 10^{-3} \) a.u. and \( s_o = 450.0 \) a.u., \( Q_{o1} = Q_{o2} = 0 \), \( \omega_1 = 1.0 \times 10^{-3} \), and \( \omega_2 = 3.0 \times 10^{-3} \), all in atomic units. Note that in order to obtain a general initial wave packet, the frequencies \( \omega_1 \) and \( \omega_2 \) are chosen so that the effective masses and frequencies do not satisfy Eqs. (39) and (40) [i.e., the frequencies do not satisfy Eq. (21)]. The dashed curve in Fig. 4 depicts the overlap between the exact three-dimensional wave packet and the corresponding TDSCF-RPH wave packet for the general initial wave packet. The overlap is better than 94% throughout the dynamics, again indicating highly quantitative agreement. The slight decrease in accuracy compared to the special initial wave packet is due to the same reasons as discussed in Sec. III (i.e., the wave packet is accessing regions further from the MEP, so the reaction path Hamiltonian is not as good an approximation to the exact Hamiltonian, and the wave packet becomes less separable as it evolves in time, so the TDSCF approximation is not as valid).

V. ZERO REACTION PATH CURVATURE: DIABATIC REPRESENTATION

For the diabatic representation of the reaction path Hamiltonian with zero curvature and nonzero coupling between the normal modes, the \( F \)-dimensional TDSCF-RPH dynamics always reduces to a one-dimensional time propagation. First consider a special initial wave packet in which the initial normal mode wave functions \( \phi_j(Q_j, t = 0) \) are pure eigenstates \( G_{n_j} \) with eigenvalues \( E_{n_j} \) for a harmonic oscillator Hamiltonian with quantum number \( n_j \), unit mass, frequency \( \omega_{o_{n_j}} \), and center \( Q_{o_{n_j}} \), where

\[
\omega_{o_{n_j}} = (\Lambda_{n_{j_1}})^{1/2},
\]

\[
Q_{o_{n_j}} = -\sum_{k=1}^{F-1} \frac{Q_k \Lambda_{n_{j_k}}}{\Lambda_{n_{j_1}}},
\]

where \( \Lambda_{n_{j_1}} = |\phi_j|\Lambda_{n_{j_1}}(|\phi_j) \) and \( Q_{o_{n_j}} = |\phi_k|Q_k|\phi_k) \). In this case the normal mode wave functions are of the form given in Eq. (22) and the equation of motion for the reaction coordinate \( s \) is

\[
i\hbar \dot{\phi}_j = \left[ \frac{1}{2} \frac{p_s^2 + V_o(s)}{\omega_{o_{n_j}}} + \sum_{k=1}^{F-1} \left( \frac{1}{2} \frac{h \Lambda_{n_{j_k}}(s)}{2 \omega_{o_{n_k}}} \right) + \frac{1}{2} \sum_{k=1}^{F-1} \Lambda_{n_{j_k}}(s) Q_{o_{n_k}} Q_{o_{n_k^*}} \right] \phi_j.
\]

For a general initial wave packet in which the initial normal mode wave functions are of the form \( \phi_j(Q_j, t = 0) = \sum_{n=-\delta}^{\infty} G_n \) where \( G_n \) are eigenfunctions of a harmonic oscillator with unit mass, frequency \( \omega_{o_{n_j}} \), and center \( Q_{o_{n_j}} \), the normal mode wave functions are of the form given in Eq. (24) and the equation of motion for the reaction coordinate \( s \) is

\[
i\hbar \dot{\phi}_j = \left[ \frac{1}{2} \frac{p_s^2 + V_o(s)}{\omega_{o_{n_j}}} + \sum_{k=1}^{F-1} \left( \frac{1}{2} \frac{h \Lambda_{n_{j_k}}(s)}{2 \omega_{o_{n_k}}} \right) + \frac{1}{2} \sum_{k=1}^{F-1} \Lambda_{n_{j_k}}(s) Q_{o_{n_k}} Q_{o_{n_k^*}} \right] \phi_j.
\]

(Here the coefficients \( a_n \) correspond to the \( k \)th normal mode.)

The numerical procedure for this case is analogous to that described in Sec. III: starting with a specified initial \( \phi_j(s, t = 0) \), at each time step the effective frequencies \( \omega_{o_{n_j}} \) and centers \( Q_{o_{n_j}} \) for the normal modes \( Q_k \) are calculated from Eqs. (62) and (63), respectively, and \( \phi_j \) is propagated for this time step using Eq. (64) or Eq. (65). In this numerical scheme the right-hand sides of Eqs. (62)–(67) are evaluated for the wave function calculated at the beginning of the current time step. The total wave function at each time step can be evaluated from Eq. (16), in which the normal mode wave functions \( \phi_k \) are of the form given in either Eq. (22) or Eq. (24), where \( G_{n_k} \) are harmonic oscillator eigenfunctions with unit mass, frequency \( \omega_{o_{n_k}} \), center \( Q_{o_{n_k}} \), and quantum number \( n_k \). Note that as discussed in Sec. III, in this numerical scheme the time \( t \) in the exponentials of Eqs. (66) and (67) is replaced with the time step \( \delta t \), and the phase factors are properly accumulated in the expansion coefficients \( a_n \).

A. Model system

In order to test the TDSCF-RPH methodology for the case of zero curvature but nonzero coupling between the normal modes in the diabatic representation, we used the same three-dimensional model system as in Sec. IV.

B. Special initial wave packet

The special initial wave packet is of the form given in Eq. (61) with the parameters \( \omega_s = 4.0 \times 10^{-3} \) a.u. and \( s_o = 450.0 \) a.u. The normal mode components are determined by the reaction coordinate component and correspond to pure ground states of harmonic oscillators with unit masses, centers at zero, and frequencies defined in Eq. (62) (leading to \( \omega_1 = 1.021 \times 10^{-3} \) a.u. and \( \omega_2 = 9.993 \times 10^{-4} \) a.u.). The solid
curve in Fig. 5 depicts the overlap between the exact and the TDSCF-RPH wave packets for the special initial wave packet. The agreement is nearly 100% throughout the dynamics.

C. General initial wave packet

The general initial wave packet is chosen as

$$
\psi_o(s, Q_1, Q_2; t=0) = \phi_s(s; t=0) \phi_{Q_1}(Q_1; t=0) \phi_{Q_2}(Q_2; t=0) = A \exp \left[ -\frac{1}{2\hbar} \sum_{n=0}^{2} a_n G_n(Q_1; t=0) \times \sum_{m=0}^{2} b_m G_m(Q_2; t=0) \right],
$$

(68)

where $G_n$ and $G_m$ are eigenfunctions of harmonic oscillators with unit masses, frequencies defined in Eq. (62), centers defined in Eq. (63) [with centers at zero for the evaluation of $Q_i$ on the right-hand side of Eq. (63)], and quantum numbers $n$ and $m$. We used the same values for $\omega_n$ and $s_n$ as for the special initial wave packet with this model. The $Q$ components can be any arbitrary function that is expanded in the basis set of the eigenfunctions $G_n$ or $G_m$, but without loss of generality we are assuming that only the first three eigenfunctions have nonzero expansion coefficients. These coefficients are chosen to be $a_0=0.95$, $a_1=0.3$, $a_2=0.8066$, $b_0=0.92$, $b_1=0.35$, and $b_2=0.17635$. The dashed curve in Fig. 5 depicts the overlap between the exact and TDSCF-RPH wave packets for the general initial wave packet. The agreement is very good but not as good as for the special initial wave packet (given by the solid curve) for the same reasons as discussed in Sec. III.

VI. SMALL CURVATURE AND ZERO COUPLING BETWEEN NORMAL MODES

For small reaction path curvature and zero coupling between the normal modes we retain only terms linear in the coupling $B_{ij}(s)$ and approximate the quantum mechanical Hamiltonian using the standard transformations in Eq. (15). In this case the $F$-dimensional TDSCF-RPH dynamics always reduces to a one-dimensional time propagation of the reaction coordinate. First consider a special initial wave packet in which the initial normal mode wave functions $\phi_j(Q_j, t=0)$ are pure eigenstates $G_{nj}$ with eigenvalues $E_{nj}$ for a harmonic oscillator Hamiltonian with quantum number $n_j$, unit mass, frequency $\omega_{nj}$ [defined in Eq. (21)], and center

$$
Q_{oj} = \sum_{i=0}^{2} \left[ \frac{p_i^2}{2} B_{ij}(s) \right]_+ + \frac{1}{2} \omega_{nj} \left[ \frac{1}{2} + n_j \right] \frac{1}{2\omega_{nj}} + \frac{1}{2} \sum_{i=0}^{2} \frac{Q_{oi}^2}{2\omega_{oi}^2} + \frac{1}{2} \sum_{i=0}^{2} \frac{Q_{oi}^2}{2\omega_{oi}^2},
$$

(69)

where $\left[ p_i^2 B_{ij}(s) \right]_+ = p_i^2 B_{ij}(s) + B_{ij}(s) p_i^2$ and $\left[ p_i^2 B_{ij}(s) \right]_+ = \{ \phi_j [\left[ p_i^2 B_{ij}(s) \right]_+] \} \phi_j$. In this case the normal mode wave functions are of the form given in Eq. (22), and the equation of motion for the reaction coordinate $s$ is

$$
i\hbar \phi_s = \left\{ -\frac{1}{2} p_i^2 - \frac{1}{2} \sum_{i=1}^{F-1} Q_{oi}^2 \frac{p_i^2}{2} B_{ij}(s) \right\}_+ + V_o(s) + \sum_{i=1}^{F-1} \left[ \frac{1}{2} \frac{\hbar \omega_i(s)}{2\omega_i} + \frac{1}{2} \omega_i^2 \right] \phi_i.
$$

(70)

For a general initial wave packet in which the initial normal mode wave functions are of the form $\phi_j(Q_j, t=0) = \sum_{n=0}^{\infty} a_n G_n$, where $G_n$ are eigenfunctions of a harmonic oscillator with unit mass, frequency $\omega_{nj}$, and center $Q_{oj}$, the normal mode wave functions are of the form given in Eq. (24) and the equation of motion for the reaction coordinate $s$ is

$$
i\hbar \phi_s = \left\{ -\frac{1}{2} p_i^2 + V_o(s) + \sum_{i=1}^{F-1} \frac{1}{\omega_i^2} \left[ \frac{p_i^2}{2} B_{ij}(s) \right]_+ + \frac{1}{2} \omega_i(s) \right\}_+ \phi_i + \sum_{i=1}^{F-1} \left[ \frac{1}{2} \frac{\hbar \omega_i(s)}{2\omega_i} + \frac{1}{2} \omega_i^2 \right] \phi_i.
$$

(71)

where
\[ Q = \frac{[p_r^2, B_i,F(s)]_+}{2\omega_i(s)^2} = \left( \frac{\phi_i}{Q_i} \right)^2 \left( \frac{[p_r^2, B_i,F(s)]_+}{2\omega_i(s)^2} \right)^2 \phi_i \]
\[ = \frac{\hbar}{\omega_i} \sum_{n=0}^{\infty} \left( \left( \frac{1}{2} + n \right) |a_n|^2 + \sqrt{(n+1)(n+2)} \Re(a_n a_n^* \exp(i2\omega_i t)) \right) - 2 \left( \frac{[p_r^2, B_i,F(s)]_+}{2\omega_i(s)^2} \right)^2 Q_i \]
\[ \times \left[ Q_i + \frac{\hbar}{2\omega_i} \right] \left( \frac{1}{2} + n \right) \Re(a_n a_n^* \exp(i2\omega_i t)) \right) + \left( \frac{[p_r^2, B_i,F(s)]_+}{2\omega_i(s)^2} \right)^2 Q_i. \]

(Here the coefficients \( a_n \) correspond to the \( i \)th normal mode.)

The numerical procedure for this case is analogous to that described in Sec. III: starting with a specified initial \( \phi_i(s,t=0) \), at each step the effective frequencies \( \omega_{i\alpha} \) and centers \( Q_{i\alpha} \) for the normal modes \( Q_i \) are calculated from Eqs. (21) and (69), respectively, and \( \phi_i \) is propagated for this time step using Eq. (70) or Eq. (71). The total wave function at each time step can be calculated from Eq. (16), in which the normal mode wave functions \( \phi_i \) are the Fourier transforms of the functions given in either Eq. (22) or in Eq. (24), where \( G_{n\alpha} \) are harmonic oscillator eigenfunctions with unit mass, frequency \( \omega_{i\alpha} \), center \( Q_{i\alpha} \), and quantum number \( n_i \) . Note that as discussed in Sec. III, in this numerical scheme the time \( t \) in the exponentials of Eq. (72) is replaced with the time step \( \delta t \), and the phase factors are properly accumulated in the expansion coefficients \( a_n \).

A. Model system

The model system used to test the TDSCF-RPH methodology for the case of small curvature and zero coupling between the normal modes is the two-dimensional system with Hamiltonian given by Eq. (27) and potential energy

\[ V(x,y) = \frac{1}{27.212} \left[ e^{-a(x+\delta x^2+y)} - \frac{\beta(x+\delta x^2+y)}{1 + e^{a(x+\delta x^2+y)}} \right]. \]

(73)

This model is similar to the two-dimensional model in Sec. III except that here an extra term \( \delta x^2 \) is added. Based on this similarity, we postulate that the MEP is the curve \( y=x+\delta x^2 \), so

\[ a_x = a_x + \delta a_x^2. \]

(74)

To ensure a small reaction path curvature, we choose a small value for \( \delta \). For the calculations in this paper, we use \( a = 6.0 \times 10^{-3} \) a.u., \( \beta = 3.78 \times 10^{-4} \) a.u., \( \gamma = 3.9 \times 10^{-3} \) a.u., and several different values of \( \delta \) that are given below.

The two-dimensional potential energy surfaces closely resemble the surface described in Sec. III. For \( \delta = 2.0 \times 10^{-4} \) a.u., the saddle point is located at \((-42.82, -42.45)\) with \( V = 0.04659 \), and the two minima are at \((-221.4, -211.6)\) with \( V = -0.05621 \) and \( (274.3, 289.4) \) with \( V = -0.1091 \), all in atomic units. For smaller \( \delta \), the locations of the saddle point and the minima converge to the \( \delta = 0 \) case described in Sec. III.

Using this equation as the MEP, we can show that the normalized gradient vector \( \{ Eq. (1) \} \) along the MEP is

\[ \mathbf{v} = (v_x, v_y) = \frac{1}{\sqrt{1 + (1 + 2\delta a_x)^2}} (1 + 2\delta a_x, 1). \]

(75)

The relation between the reaction coordinate \( s \) and \( a_x \) can be obtained using Eqs. (7) and (74):

\[ s = \frac{1}{4\delta} \left( (1 + 2\delta a_x) \sqrt{1 + (1 + 2\delta a_x)^2} \right) + \ln[1 + 2\delta a_x + \sqrt{1 + (1 + 2\delta a_x)^2}]. \]

(76)

This relation can be used to transform \( v \) [given in Eq. (75)] into a function of the reaction coordinate \( s \). The eigenvalues \( \lambda_1(s) \) and \( \lambda_2(s) \) and eigenvectors \( L_1(s) \) and \( L_2(s) \) are given by Eqs. (19) and (20). The normal mode \( Q \) in terms of \( a_x, x, \) and \( y \) can be obtained using Eqs. (5) and (74)

\[ Q = \frac{1}{\sqrt{1 + (1 + 2\delta a_x)^2}} [2\delta^2 a_x^2 + 3\delta a_x^2 - 2\delta y a_x + x - y]. \]

(77)

The relation between \( a_x \) and a general point \((x,y)\) can be obtained using Eqs. (6) and (74):

\[-3\delta a_x^2 + (2\delta x - 2)a_x + y + x = 0. \]

(78)

Equations (76) and (78) can be used to obtain the relation between \( s \) and a general point \((x,y)\), and Eqs. (77) and (78) can be used to obtain the relation between \( Q \) and a general point \((x,y)\). In this manner, the equations for the transformation between the mass-weighted Cartesian coordinates \((x,y)\) and the reaction path coordinates \((Q,s)\) can be obtained.

B. Special initial wave packet

The special initial wave packet is chosen to be the same form as Eq. (37) with \( \omega_o = 2.0 \times 10^{-3} \) a.u. The value of \( s_o \) varies for different values of \( \delta \) to ensure that the initial wave packet is located near the transition state. We studied three different cases with \( \delta = 2.0 \times 10^{-4}, 1.0 \times 10^{-4}, \) and \( 2.0 \times 10^{-5} \) with \( s_o = 3013.0, 5880.0, \) and \( 28850.0, \) respectively, all in atomic units. The \( Q \) component of the initial wave packet is determined by the \( s \) component with \( Q_o \) defined by Eq. (69) and \( \omega_o \) defined by Eq. (21) (leading to \( \omega_o = 2.099 \times 10^{-3}, 2.101 \times 10^{-3}, \) and \( 2.038 \times 10^{-3} \) a.u., respectively, for the values of \( \delta \) given above). Figure 6(a) depicts the overlap between the exact and the TDSCF-RPH wave packets for the special initial wave packet with three different values of \( \delta \). Note that a smaller value of \( \delta \), which
corresponds to a smaller reaction path curvature, leads to better agreement between the two methods. This phenomenon arises because the approximations used to derive the equations of motion are more accurate for smaller reaction path curvature [i.e., we retain only terms linear in the coupling $B_{k,F}(s)$ in the RPH and use the standard transformations in Eqs. (15) to transform to quantum mechanical operators]. In addition, the RPH is a better approximation to the exact Hamiltonian and the TDSCF approximation is more accurate for small reaction path curvature. Further test calculations have shown that smaller values of $\delta$ ($<2.0 \times 10^{-5}$ a.u.) lead to virtually the same results as those for $\delta=2.0 \times 10^{-5}$, indicating convergence with respect to the reaction path curvature.

C. General initial wave packet

The general initial wave packet is chosen to be the same form as in Eq. (38) with the same values for $\omega_0$ and $s_0$, used for the three values of $\delta$ given above for the special initial wave packet. In this case $G_n$ are eigenfunctions of a harmonic oscillator with unit mass, center $Q_n$ defined by Eq. (69), frequency $\omega_n$ defined in Eq. (21), and quantum number $n$. For this model $a_0=0.95$, $a_1=0.3$, and $a_2=0.0866$. Figure 6(b) depicts the overlap between the exact and the TDSCF-RPH wave packets for the general initial wave packet with three different values of $\delta$. Again the agreement is better for smaller values of $\delta$, which correspond to smaller reaction path curvature. Further test calculations confirm that the convergence with respect to the reaction path curvature is reached at $\delta=2.0 \times 10^{-5}$ a.u. Note that the total simulation time is shorter than that shown in Fig. 3 (for $\delta=0$) due to the more rapid divergence for the larger values of $\delta$.

VII. SUMMARY

This paper presents numerical tests comparing TDSCF-RPH dynamics to exact quantum dynamics for model systems. We investigated three different cases: (1) zero coupling matrix; (2) zero reaction path curvature and nonzero coupling between the normal modes; and (3) zero coupling between the normal modes and nonzero but small reaction path curvature. The equations of motion were derived for these three cases in Refs. 1 and 32. For the first and third cases, the dynamics always reduces to a one-dimensional numerical time propagation. For the second case the equations of motion were derived for both the adiabatic and the diabatic representation of the RPH. In the adiabatic representation the dynamics reduces to a one-dimensional numerical time propagation for a special initial wave packet but not for general initial wave packets. In the diabatic representation, however, the dynamics always reduces to a one-dimensional numerical time propagation. In this paper we performed TDSCF-RPH and exact quantum dynamical calculations for all of these cases and calculated the time evolution of the overlap between the TDSCF-RPH and the exact wave packets. In all of these cases the TDSCF-RPH method was shown to be highly accurate.

These calculations test the two basic approximations of TDSCF-RPH dynamics. The first basic approximation of TDSCF-RPH dynamics is the RPH approximation for the Hamiltonian. Since the RPH is based on a harmonic approximation about the MEP, its accuracy is expected to deteriorate for regions far from the MEP. A wave packet will access regions far from the MEP when the process involves a large reaction path curvature or when the initial wave packet includes significant excited components. Our results indicate that the accuracy of the TDSCF-RPH dynamics diminishes in these cases. For example, we found that the TDSCF-RPH dynamics is more accurate for special initial wave packets that include only ground state normal mode components than for general initial wave packets that include excited normal mode components. In addition, for the case of nonzero but small reaction path curvature (the third case), we studied a range of different magnitudes of the reaction path curvature and found that the accuracy of the TDSCF-RPH dynamics deteriorates as the reaction path curvature increases. The study of processes involving large reaction path curvature will require a different reaction path Hamiltonian, such as a diabatic straight-line reaction path Hamiltonian\textsuperscript{14} or a reaction path surface Hamiltonian.\textsuperscript{17–20} The second basic approximation of TDSCF-RPH dynamics is the TDSCF approximation for the wave function. Since the TDSCF approximation assumes that each component moves in an averaged potential, its accuracy is expected to deteriorate...
when the wave packet branches into two or more pieces or, in general, when the shape of the wave packet becomes complex. In the tests presented in this paper, the wave packet started near the transition state and moved down into one minimum, so branching processes were not involved. Moreover, these tests involved only zero or small reaction path curvature, so the shapes of the wave packets remained relatively compact and uniform. Therefore, the TDSCF approximation was adequate for the tests presented in this paper. As shown by Makri and Miller, the multiconfigurational method is useful for processes in which the TDSCF approximation is not adequate. Thus, our results indicate that the TDSCF-RPH methodology is accurate for reactions involving small reaction path curvature and a single reaction pathway (i.e., no branching processes). For these types of reactions the application of TDSCF-RPH to study the real-time quantum dynamics is straightforward. First the potential energy, gradient vector, and Hessian matrix along the MEP are obtained from standard quantum chemistry calculations. Then these quantities are used as input for the TDSCF-RPH dynamics, which involves integration of only a single equation of motion for the reaction coordinate. This methodology can be extended to a broader range of reactions by combining the MC-TDSCF method with various reaction path and surface Hamiltonians.

\[ E_j = \sum_{k=1}^{F-1} \bar{Q}_k \langle p_j, B_{k,j}(s) \rangle_+ \]

\[ + \sum_{k,l,k' \neq l} B_{k,j}(s) B_{k',l}(s) \langle Q_k Q_l P_t \rangle \]

\[ + \bar{Q}_k P_t Q_k \], \quad (A5) \]

\[ F_j = \sum_{k=1}^{F-1} \bar{P}_k \langle p_j, B_{k,j}(s) \rangle_+ \]

\[ + \sum_{k,l,j' \neq l} B_{k,j}(s) B_{k',l}(s) \langle P_l Q_k P_l \rangle \]

\[ + Q_k P_l P_t, \]

\[ G_j = \sum_{k,l=1}^{F-1} \bar{Q}_k P_l [p_j, B_{k,l}(s)]_+ \]

\[ + \sum_{k,l,k',l' \neq l} Q_k P_l Q_l P_l B_{k,l}(s) B_{k',l'}(s). \]

Here the notation is such that

\[ B_{k,l}(s) B_{k',l'}(s) = \langle \phi_{l' k'} B_{k,l}(s) B_{k',l'}(s) | \phi_{l k} \rangle \]

and

\[ Q_k P_l Q_l P_l = \langle \phi_{l' k'} \phi_{l' k} | Q_k P_l | Q_l P_l | \phi_{l' k'} | \phi_{l' k} \rangle \]

\[ = \langle \phi_{l' k'} | \bar{Q}_k \bar{P}_l | \phi_{l' k} \rangle \langle \phi_{l' k'} | \bar{P}_l | \phi_{l' k} \rangle \langle \phi_{l' k} | P_l | \phi_{l' k} \rangle \]

\[ \times \langle \phi_{l' k} | P_l | \phi_{l' k} \rangle \]

when all indices are different, but if any of the indices are the same the normal mode wave function appears only once (e.g.,

\[ \bar{Q}_k P_l Q_l P_l = \langle \phi_{l' k'} \phi_{l' k} | Q_k P_l Q_l P_l | \phi_{l' k'} | \phi_{l' k} \rangle \]

\[ = \langle \phi_{l' k'} | Q_k^2 | \phi_{l' k'} \rangle \langle \phi_{l' k'} | P_l | \phi_{l' k'} \rangle \langle \phi_{l' k'} | P_l | \phi_{l' k'} \rangle \]

\[ \times \langle \phi_{l' k'} | P_l | \phi_{l' k'} \rangle \]

Moreover, the square brackets \([\alpha, \beta]_+\) indicate the anticommutator of the operators \(\alpha\) and \(\beta\) (e.g.,

\[ [\bar{p}_j, B_{j,k}(s)]_+ = \langle \phi_{l' k'} | p_j B_{j,k}(s) + B_{j,k}(s) | p_j \phi_{l' k'} \rangle. \]

The quantities in Eq. (43) are defined as

\[ H(s) = -\frac{1}{2} \sum_{k,j=1}^{F-1} \bar{Q}_k P_l [p_j B_{k,j}(s) + B_{k,j}(s) | p_j \phi_{l k} \rangle. \]

\[ I(s) = \frac{1}{2} \sum_{k,j,k',l',l=1}^{F-1} \bar{Q}_k P_l Q_l P_l B_{k,j}(s) B_{k',l}(s). \]

\[ (A9) \]

\[ (A7) \]

\[ (A6) \]

\[ (A5) \]

\[ (A4) \]

\[ (A3) \]

\[ (A2) \]

\[ (A1) \]

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\[ \text{APPENDIX} \]

This appendix presents the definitions of the quantities in the equations of motion for the case of zero reaction path curvature and nonzero coupling between the normal modes in the adiabatic representation with a general initial wave packet. The quantities in Eq. (42) are defined as

\[ A_j = \sum_{k,l=1}^{F-1} \bar{Q}_k Q_k B_{k,j}(s) B_{k',j}(s), \]

\[ B_j = \sum_{l,j' \neq j} \bar{P}_j P_{l'} B_{j,j'}(s) B_{j',l}(s), \]

\[ C_j = \sum_{k,l' \neq l} \bar{Q}_k Q_{l'} B_{k,j}(s) B_{j,l'}(s), \]

\[ D_j = \sum_{l' \neq l} \bar{P}_l Q_{l'} B_{j,l'}(s) B_{j,l}(s), \]

\[ (42) \]

\[ (41) \]

\[ (40) \]

\[ (39) \]

\[ (38) \]

\[ (37) \]

\[ (36) \]

\[ (35) \]

\[ (34) \]

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\[ (10) \]

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\[ (8) \]

\[ (7) \]

\[ (6) \]

\[ (5) \]

\[ (4) \]

\[ (3) \]

\[ (2) \]

\[ (1) \]