Quantum mechanical and semiclassical dynamics at a conical intersection

A. Ferretti  
*Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R., Italy*

G. Granucci  
*Dipartimento di Chimica e Chimica Industriale Università di Pisa, via Risorgimento 35, I-56126 Pisa, Italy*

A. Lami  
*Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R., Italy*

M. Persico  
*Dipartimento di Chimica e Chimica Industriale Università di Pisa, via Risorgimento 35, I-56126 Pisa, Italy*

G. Villani  
*Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R., Italy*

(Received 13 November 1995; accepted 4 January 1996)

We present simulations of wave-packet dynamics for a model of a conical intersection in two dimensions. The potential energy surfaces and couplings are functions of a total symmetrical coordinate and of a symmetry breaking one. The wave packet crosses the coupling region once, moving essentially in the direction of the symmetrical coordinate. The dynamics are determined by two methods, one quantum mechanical and the other semiclassical, based on trajectories and surface hopping. The semiclassical approximation is quite adequate for low coupling strengths in the diabatic representation, less so for larger couplings. Approximate analytic solutions for the two-dimensional problem and for one-dimensional analogs are provided, in order to generalize the numerical results and to analyze the reasons of the discrepancies between semiclassical and quantum mechanical results. © 1996 American Institute of Physics. [S0021-9606(96)00714-5]

I. INTRODUCTION

An accessible conical intersection provides a way for very fast radiationless decay, therefore it may be the key feature in a variety of photochemical, photophysical and scattering processes. The importance of conical intersections was first recognized on theoretical grounds;1–3 in the last two decades, theory and experiment concurred in showing that a conical intersection plays a role in an increasing number of specific examples.4,5 These include photodissociations,6 photoisomerizations,7–14 energy transfers,15–17 and ion fragmentations.18,19 Ultrafast internal conversion has recently been discussed in the context of electron-transfer processes.29–31 The models investigated till now, based on the popular spin–boson Hamiltonian, involve an avoided crossing instead of a conical intersection: Despite this important difference, we expect many analogies between the two cases.

In spite of such important advances in quantum dynamics, it is clear that the study of polyatomics (more than three dimensions) in the next years will be within the scope of semiclassical rather than purely quantum mechanical methods. By semiclassical dynamics we mean Newtonian mechanics for the nuclear motions, and any treatment of the time-dependent Schrödinger equation for the electrons, such as surface hopping or related methods.32–35 In particular, Meyer36 and Lorquet and co-workers37,38 have brought out important aspects of the semiclassical dynamics in the proximity of a conical intersection. For recent examples, see Stock39,40 and Smith et al.41

In this paper we present the quantum and semiclassical dynamics of a wave packet traveling through or near a conical intersection in two or three dimensions have been presented: Some refer to model systems13,14 and some to real molecules.12,25–27 The most systematic study is that of Manthe and Köppel.28 They concentrated mainly on the long-time behavior of a wave packet which undergoes fast oscillations in two intersecting bound potentials, and showed what changes are brought about by variations in the coupling strength.

Quantum mechanical computations become rapidly prohibitive as the number of nuclear degrees of freedom increases. In some cases, however, a large number of weakly coupled modes can be treated as a thermal bath and one may resort to the methods of quantum statistical mechanics for computing the dynamics in the presence of dissipation. Some important effects due to dephasing and/or relaxation have been discussed in the context of electron-transfer processes.29–31 The models investigated till now, based on the popular spin–boson Hamiltonian, involve an avoided crossing instead of a conical intersection: Despite this important difference, we expect many analogies between the two cases.
semiperiod of the oscillating wave packet, i.e., to a single passage through the strong interaction region around the conical intersection: no recurrences are therefore observed, as in dissociative or strongly dissipative processes. Transition probabilities and other dynamical features are studied as a function of the coupling strength. The quantum and semiclassical results are compared and analyzed in the light of simplified one-dimensional models leading to useful analytic formulas for the transition probability.

II. MODEL AND METHODS

The Hamiltonian here discussed can be an appropriate model for a linear triatomic \( ABA \). We consider only the two stretching coordinates \( R_1 \) and \( R_2 \) and two diabatic electronic states \( |\eta_1\rangle \) and \( |\eta_2\rangle \), such that the dynamical vibronic couplings in this basis are vanishing or negligible: \( \langle \eta_1|\partial/\partial R_1|\eta_2\rangle=0 \), \( \langle \eta_1|\partial^2/\partial R_1^2|\eta_2\rangle=0 \). The electronic Hamiltonian \( \hat{H}_e \), i.e., the total Hamiltonian \( \hat{H} \) without the nuclear kinetic energy term, is represented in the diabatic basis by the matrix \( \hat{H} \). The diabatic potentials (diagonal elements of \( \hat{H} \)) are quadratic forms in \( R_1 \) and \( R_2 \), and there is an electronic coupling \( H_{12} \), which vanishes only for symmetrical geometries \((R_1=R_2)\):

\[
H_{11}(R_1,R_2)=\frac{K}{2}(R_1-X_1)^2+\frac{K}{2}(R_2-X_1)^2+K_{12}(R_1-X_1)
\times(R_2-X_1)
\]

\[
H_{22}(R_1,R_2)=\frac{K}{2}(R_1-X_2)^2+\frac{K}{2}(R_2-X_2)^2+K_{12}(R_1-X_2)
\times(R_2-X_2)+\Delta
\]

\[
H_{12}(R_1,R_2)=\gamma \frac{R_1-R_2}{2}e^{-\alpha(R_1+R_2-2X_3)^2/4}e^{-\beta(R_1-R_2)^2/4}.
\]

Here \( X_1 \) and \( X_2 \) are the equilibrium bond lengths in the diabatic states \( |\eta_1\rangle \) and \( |\eta_2\rangle \), respectively. The Gaussian damping factors in \( H_{12} \) prevent divergence for large \( R \)’s.

We define a symmetric stretch coordinate \( X \) and an antisymmetric one, \( Y \), as

\[
X=\frac{R_1+R_2}{2}, \quad Y=\frac{R_1-R_2}{2}.
\]

As a function of the symmetry coordinates \( X \) and \( Y \), the Hamiltonian matrix \( \hat{H} \) takes the form

\[
H_{11}(X,Y)=\frac{1}{2}K_y(X-X_1)^2+\frac{1}{2}K_xY^2,
\]

\[
H_{22}(X,Y)=\frac{1}{2}K_y(X-X_2)^2+\frac{1}{2}K_xY^2+\Delta,
\]

\[
H_{12}(X,Y)=\gamma Ye^{-\alpha(X-X_3)^2}e^{-\beta Y^2},
\]

where \( K_y=2K+K_{12} \) and \( K_x=2K-K_{12} \). The following values of the parameters have been chosen (atomic units are used throughout this paper):

\[
K_y=0.02, \quad K_x=0.10, \quad \Delta=0.01,
\]

\[
X_1=4, \quad X_2=X_3=3,
\]

\[
M_x=2M_A=20000, \quad M_y=2M_AM_B=6667,
\]

\[
\alpha=3, \quad \beta=1.5,
\]

where \( M_x \) and \( M_y \) are the reduced masses for the \( X \) and \( Y \) coordinates. The parameter \( \gamma \) determines the coupling strength and its value will range from 0.005 to 0.08. The two diabatic surfaces are therefore identical, except that \( H_{22} \) is displaced at smaller \( X \) and higher energy with respect to \( H_{11} \). Both surfaces are paraboloids, with frequencies \( \omega_x=0.001 \) a.u.\( \approx 219 \) cm\(^{-1}\) and \( \omega_y=0.00387 \) a.u.\( \approx 850 \) cm\(^{-1}\). The intersection point coincides with the minimum in the upper potential, at \( X=3 \) and \( Y=0 \): In the classification proposed by Atchity, Xantheas and Ruedenberg,\(^{46}\) it is an intermediate case between the peaked and the sloped crossing.

Although the diabatic basis is a natural choice for the definition of a model Hamiltonian, and is very convenient for the quantum mechanical calculations, it is physically more relevant to express the results of the wave-packet dynamics in the adiabatic basis.\(^{25,28}\) The adiabatic states are given by

\[
|\psi_K\rangle=(|\eta_1\rangle,|\eta_2\rangle)|C_K\rangle.
\]

where the \( C_K \) are the eigenvectors of \( \hat{H} \), with eigenvalues \( E_K \). Some energy profiles as functions of \( X \) are shown in Fig. 1. For small coupling strengths, the lower adiabatic potential has a single minimum at \( X=4 \), \( Y=0 \), \( E_1=0 \). For larger \( \gamma \), two minima appear, at shorter \( X \), with opposite values of \( Y \).

A time-dependent wave function can be expanded in either the diabatic or the adiabatic basis:

\[
|\Psi(t)\rangle=|\eta_1\rangle|\xi_1(X,Y,t)\rangle+|\eta_2\rangle|\xi_2(X,Y,t)\rangle
\]

or

\[
|\Psi(t)\rangle=|\psi_1\rangle|\chi_1(X,Y,t)\rangle+|\psi_2\rangle|\chi_2(X,Y,t)\rangle,
\]

with the \( \chi_k \) wave packets connected to the \( \xi_k \) by the inverse of transformation (5). We shall define the quantum probability density in the adiabatic state \( |\psi_k\rangle \) as

\[
\rho_k^{(g)}(X,Y,t)=|\chi_k(X,Y,t)|^2
\]

and the \( X \) or \( Y \) projected densities as

\[
\rho_k^{(g)}(Y,t)=\int_{-\infty}^{+\infty}|\chi_k(X,Y,t)|^2 dX,
\]

\[
\rho_k^{(g)}(X,t)=\int_{-\infty}^{+\infty}|\chi_k(X,Y,t)|^2 dY.
\]

Reduced densities have been already defined in this way, for instance by Schneider et al.\(^{47}\) Finally, the total probability in state \( |\psi_K\rangle \) is

\[
P_k^{(g)}(t)=\int_{-\infty}^{+\infty}|\chi_k(X,Y,t)|^2 dX \, dY.
\]

Analogous quantities can be defined for the diabatic states.

Given our choice of the parameters, a wave packet with a reasonable spread can probe three well-characterized regions: (A) weak coupling region at small \( X(H_{11} > H_{22}) \); (B)
strong coupling region around $X = 3$; and (C) weak coupling region at large $X(H_{11} < H_{22})$. In the two weak coupling regions the adiabatic states correspond approximately to the diabatic ones: in A, $|\phi_1\rangle = |\eta_1\rangle$, while in C $|\phi_1\rangle = |\eta_1\rangle$ (see Fig. 1). Therefore, electronic transitions are not likely to occur in regions A and C.

To complete the description of the model, we set the initial conditions for the time evolution. We simulate a Franck–Condon excitation to $|\phi_2\rangle$ from a ground state represented by the potential:

$$
H_{00}(X,Y) = \frac{1}{2}K_x(X - X_0)^2 + \frac{1}{2}K_yY^2.
$$

The ground state is not coupled with $|\phi_1\rangle$ and $|\phi_2\rangle$, except through an infinitely short radiation pulse. At $t = 0$ we have

$$
\xi_2(X,Y;0) = \chi_1(X,Y;0) = 0,
$$

$$
\xi_1(X,Y;0) = \chi_2(X,Y;0)
$$

$$
= (\pi \Delta X \Delta Y)^{-1/2}e^{-(X - X_0)^2/2\Delta X^2}e^{-Y^2/2\Delta Y^2},
$$

where the widths (twice a standard deviation) are $\Delta X = 0.150$ and $\Delta Y = 0.197$ bohr. The center of the initial wavepacket is at $X = X_0 = 2$ bohr, $Y = 0$, in the weak coupling region A.

For reasons of computational convenience, in the quantum mechanical calculations the initial state is a pure diabatic state, $|\eta_1\rangle$, rather than an adiabatic one. However, as already observed, the two choices are nearly coincident: In fact, the initial adiabatic probability is $P_{11}^{\eta_0}(0) = 0.9997$ for a coupling strength $\gamma = 0.01$, and $P_{11}^{\phi_0}(0) = 0.9984$ for $\gamma = 0.08$.

In the quantum dynamics approach, the moving wave packet is expanded on a basis of harmonic oscillator eigenfunctions and the time-dependent Schrödinger equation is solved by the Lanczos algorithm. The basis set is built as a tensorial product of the diabatic electronic states and of harmonic vibrational eigenstates, centered at $X = X_2$ and $Y = 0$. The generic basis state is written as $|\eta_1, v_x, v_y\rangle$, where $v_x$ and $v_y$ are the harmonic oscillator quantum numbers, associated with coordinates $X$ and $Y$, respectively. Since the harmonic oscillator basis set is infinite, it is necessary, in practice, to truncate it, taking care that truncation does not affect the results. For the present case we have considered 250 vibrational states for the $X$ oscillator and 30 for the $Y$ oscillator, for a total dimension of the vibronic problem $N = 15\,000$.

The usual approach for solving the time-dependent Schrödinger equation, based on the diagonalization of the matrix representation of the Hamiltonian in a suitable basis set, is unpractical for problems involving a very large number of states. Several numerical methods have been tested for this purpose. The computational method we have developed and applied to a variety of time-dependent and time-independent problems is eigenstate-free, being grounded on the Lanczos algorithm with Householder reorthogonalization. In the past, the Lanczos method, whose application to the wave-packet propagation has been originally proposed by Park and Light, has been extensively applied to the vibronic coupling problem (see for instance Manthe et al. and references therein). Briefly, the Lanczos approach consists in performing a tridiagonalization of the Hamiltonian matrix and involves the iteration scheme $|L_j\rangle$ represents the $j$th Lanczos state:

$$
|L_{j+1}\rangle = \frac{1}{\beta_j}(\hat{H} - \alpha_j\hat{E})|L_j\rangle,
$$

$$
\alpha_j = \langle L_j |(\hat{H} - \alpha_j\hat{E})^2|L_j\rangle^{1/2}.
$$

Here $\hat{E}$ is the identity operator. The $\alpha$'s and $\beta$'s generated in Eq. (14) are the diagonal and off-diagonal matrix elements of the Hamiltonian $\hat{H}$ in the Lanczos basis set. The Lanczos iteration is truncated after a given number of steps $n$, thus generating $n$ Lanczos states, which are only a small fraction of the total number of states: $n \ll N$. In this way the original problem is transformed into a new one, involving only sequentially coupled states. The first state of the Lanczos sequence is the doorway state, i.e., the state we want to propagate: In the present case, it is the wave packet at the beginning of each time interval. Due to their sequentiality, a small number of Lanczos states is needed to reproduce the exact dynamics for a fixed time interval; about 30–40 states are sufficient for a 5 fs time interval in our calculations. Convergence can be verified by the amplitude of the last Lanczos state $|L_n\rangle$, which has to be negligible, or by comparing the wave function obtained with $n$ and $n + 2n$ steps. The great advantage of this approach is due to the analytical representation of any time dependent observable in terms of pseudo-eigenstates and eigenvalues (i.e., eigenvectors and eigenvalues of the truncated tridiagonal Hamiltonian matrix).

In our procedure the matrix elements of the coupling $H_{12}(X,Y)$ are computed separately, while the term, linear in the coordinate and due to the change of equilibrium position
of the $X$ oscillator in the electronic state $|\eta\rangle$ with respect to that on $|\eta_2\rangle$, is computed directly while performing the Lanczos steps for the dynamics, by expressing $H_{11}$ and $H_{22}$ in second quantization form.

We now turn to the semiclassical treatment of the wave-packet dynamics. The nuclear motion is represented by trajectories, computed by integrating the Hamilton equations. In the present calculations, the potential is one of the two adiabatic surfaces $E_K(Q)$, where $Q$ is the vector of the Cartesian coordinates of the nuclei. We modified the Monte Carlo classical trajectory program VENUS \textsuperscript{58} by W. Hase and coworkers, to introduce the surface hopping feature, as briefly reviewed in the following. The time-dependent electronic state is written as

\begin{equation}
|\psi(t)\rangle = \sum_K A_K(t) e^{-i\gamma_K(t)}|\psi_K(Q)\rangle
\end{equation}

and it obeys the Schrödinger equation:

\[ i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H}|\psi(t)\rangle. \]

The phase $\gamma_K$ is

\[ \gamma_K(t) = \frac{1}{\hbar} \int_0^t E_K(Q(t'))dt'. \]

By substituting Eq. (15) into (16) one obtains a set of coupled differential equations for the probability amplitudes $A_K$:

\begin{equation}
\dot{A}_K(t) = -\sum_{L\neq K} A_L(t)e^{i\gamma_{KL}}\sum_a \dot{Q}_a G_{KL}^{(a)}
\end{equation}

with $\gamma_{KL}=\gamma_K-\gamma_L$. $\dot{Q}_a$ is a Cartesian velocity component for one of the nuclei, and $G_{KL}^{(a)}$ is a component of the nonadiabatic coupling vector $G_{KL}$:

\begin{equation}
G_{KL}^{(a)} = \left( |\psi_K\rangle \frac{\partial}{\partial Q_a} |\psi_L\rangle \right) (E_K-E_L)^{-1} C_k^l \frac{\partial H}{\partial Q_a} C_L.
\end{equation}

In this equation for $G_{KL}^{(a)}$ we have exploited the adiabatic nature of the $|\eta\rangle$, i.e., the fact that $\langle \eta|\partial/\partial Q_a|\eta_2\rangle=0$. The coupled equations (18) are integrated by a finite differences scheme, with the same time step $\Delta t$ which is used in the determination of the trajectory:

\begin{equation}
A_K(t+\Delta t) = A_K(t) + \left[ -\frac{\dot{A}_K(t-\Delta t)}{12} + \frac{2\dot{A}_K(t)}{3} \right] \Delta t
+ \frac{5\dot{A}_K(t+\Delta t)}{12} \Delta t
\end{equation}

\begin{equation}
\gamma_{KL}(t+\Delta t) = \gamma_{KL}(t) + \left[ -\frac{\dot{\gamma}_{KL}(t-\Delta t)}{12} + \frac{2\dot{\gamma}_{KL}(t)}{3} \right] \Delta t
+ \frac{5\dot{\gamma}_{KL}(t+\Delta t)}{12} \Delta t,
\end{equation}

where $\dot{A}_K$ is given by Eq. (18) and $\dot{\gamma}_{KL}=(E_K-E_L)/\hbar$. The algorithm is exact up to third order in $\Delta t$, and its accuracy is tested at every step by checking the normalization of the wavefunction.

The semiclassical adiabatic probabilities $P_{KL}^{(a)}(t)=|A_K(t)|^2$ are the analogues of the quantum mechanical ones, $P_L^{(a)}$. The diabatic probabilities can also be computed from the $A_K$ coefficients, by means of transformation (5). In the surface hopping methods, the trajectory can jump from a potential surface to another, according to the variation of the $P_{KL}^{(a)}(t)$ probabilities. We have adopted the “fewest switches” algorithm proposed by Tully. \textsuperscript{32,33} Let us consider a trajectory which is running on the $K$th surface. In a two state problem, at every time step, the probability to jump from $|\psi_K\rangle$ to $|\psi_L\rangle$ is

\[ W_{KL} = \frac{P_{KL}^{(c)}}{P_{KL}^{(c)}} \Delta t, \text{ if } P_{KL}^{(c)}>0, \]

\[ W_{KL} = 0, \text{ if } P_{KL}^{(c)}=0. \]

A random choice whether to jump or not is performed, according to the value of $W_{KL}$. Let us call $D_K(t)$ the fraction of trajectories which are in state $|\psi_K\rangle$ at time $t$. It is important that, given a very large number of trajectories, the distributions $D_K(t)$ approach the $P_{KL}^{(c)}(t)$ probabilities. This is ensured by the “fewest switches” algorithm just described, under the restrictive hypothesis that $P_{KL}^{(c)}(t)$ is the same function of time irrespective of what jumps are actually made. A few tests on models of different nonadiabatic processes have confirmed this appealing feature. \textsuperscript{32} However, one can imagine situations where a switch of potential surface implies an important change in the following course of the trajectory, therefore in the $P_{KL}^{(c)}(t)$ functions: then, the “fewest switches” algorithm cannot guarantee that $D_K(t)=P_{KL}^{(c)}(t)$, even for very many trajectories.

After a jump from surface $E_K$ to $E_L$, the nuclear kinetic energy must be changed from $T$ to $T'=T+E_K-E_L$, so that the total energy is conserved. This is accomplished preferably \textsuperscript{35,39} by varying the nuclear momenta $P_a$ by quantities proportional to the nonadiabatic couplings $G_{KL}^{(a)}$:

\[ P' = P + \sigma G_{KL}, \]

with $\sigma$ determined by

\begin{equation}
\left( \sum_a \frac{G_{KL}^{(a)^2}}{m_a} \right) \sigma^2 + 2 \left( \sum_a \frac{P_a G_{KL}^{(a)}}{m_a} \right) \sigma + 2(E_L-E_K) = 0.
\end{equation}

Here, $M_a$ is the nuclear mass associated with the coordinate $Q_a$. The root of Eq. (24) with the smallest module is chosen. When $T'=0$ but Eq. (24) has no real roots, the constraint (23) is released, and the momenta are simply rescaled: $P'=\sigma P$, with $\sigma' = \sqrt{T'/T}$. Finally, if $T'<0$ the energy matching is impossible, then the surface hop is inhibited. The fact that some surface hops are not done, because they are incompatible with the energy conservation, is another source...
of disagreement between the probabilities $P^c_k(t)$ and the distributions $D_k(t)$: This is a purely classical feature, at variance with quantum dynamics.

Some basic features of the quantum wave packet are reproduced in the semiclassical calculations, by running a large number of trajectories ($N_T=1000$ to 10 000, in our case) with a random choice of initial conditions. The coordinates and momenta at $t=0$ have independent distributions, with the same Gaussian shape as in the quantum mechanical treatment. The total energy is not the same for all trajectories, but its average coincides with the quantum mechanical expectation value.

The $P^c_k(t)$ quantities we discuss in the following are averages of $P^c_k(t)$ over all trajectories. We can also define the semiclassical densities of trajectories; for instance, the reduced density as a function of $Y$ is

$$\rho^c_k(Y,t) = \frac{N_k(Y,t)}{N_T\Delta Y}.$$  

Here $N_k(Y,t)$ is the number of trajectories in state $K$ at time $t$, which are found between $Y$ and $Y+\Delta Y$, with any value of $X$. Notice that $\rho^c_k(Y,t)$ integrates to $D_k(t)$, not to $P^c_k(t)$. [The $\rho^c_k(Y,t)$ functions shown in Figs. 2, 3, 5, and 6 have been numerically smoothed, in order to eliminate the erratic behavior which is obtained for small $\Delta X$ or $\Delta Y$; moreover, $\rho^c_k(Y,t)$ has been symmetrized with respect to inversion of the $Y$ coordinate.]

III. QUANTUM AND SEMICLASSICAL RESULTS

The quantum mechanical and the semiclassical treatments agree in describing the basic qualitative features of the dynamics. The wave packet moves in the positive $X$ direction, and crosses the conical intersection around $t=25$ fs. The crossing takes place in about 15 fs and, after excitation, and crosses the conical intersection around $t$, which are found between $g$, not spread appreciably, until it reaches the intersection region. The component in state 1 retains the initial shape with the exception of the oscillatory behavior at large $t$; it is attracted toward the two minima which exist at $Y=0$; in the latter case, the distribution along the $Y$ axis is considerably widened, and the quantum wave packet shows several nodes. All these features, with the exception of the oscillatory behavior at large $\gamma$, are well reproduced by the semiclassical treatment.

The wave-packet component which remains in state 2, when entering region C presents a node for $Y=0$, as shown in Figs. 2, 3 and 4; the latter contains contour plots of $\rho^q_k(X,Y,t)$, for $\gamma=0.01$, at different times. The presence of the node is a manifestation of Berry’s geometrical phase,60,61 recently brought out by Schön and Köppel27 in their study of the wave-packet dynamics of Na$_3$. It is clear that the classical trajectories cannot reproduce this feature; however, with small $\gamma$, the density $\rho^q_k(Y,t)$ has a minimum around $Y=0$, for $t=40–60$ fs, because the transition probability from state 2 to 1 is larger for trajectories going very close to the conical intersection point.

Figures 5 and 6 show the density profiles as functions of $X$, $\rho^q_k(X,t)$ and $\rho^c_k(X,t)$, at different times. The shape of the wave packets, according to both the quantum and the

![FIG. 2. Reduced density as a function of $Y$, at different times (in fs). Small coupling strength, $\gamma=0.01$. Full lines, quantum results, $\rho^q_k(Y,t)$; dashed lines, semiclassical results, $\rho^c_k(Y,t)$.](image)

![FIG. 3. Reduced density as a function of $Y$, at different times (in fs). Large coupling strength, $\gamma=0.08$. Full lines, quantum results, $\rho^q_k(Y,t)$; dashed lines, semiclassical results, $\rho^c_k(Y,t)$.](image)
semiclassical treatments, is much the same: only the total
probabilities are somewhat different for large $g$, with $P_1^{(c)}$
smaller than $P_1^{(q)}$.

The total probabilities as functions of time, as well as the
trajectory distributions $D_K$, are shown in Figs. 7 and 8. The
population of state $|q_0\rangle$ decreases sharply around $t=25$ fs,
remains stable for about 60 fs, then it decreases again when
the wave packet, having almost completed an oscillation in
the upper potential, goes back to the strong interaction region
B. The agreement between semiclassical and quantum results
is good for small coupling strength $g$ (Fig. 7) and only quali-
tative for large $g$ (Fig. 8). In the latter case, the semiclassical
trajectory distributions $D_K$ differ significantly from the cor-
responding probabilities, $P_K^{(c)}$. Notice that there is no ground
to prefer a priori the $P_K^{(c)}$ or the $D_K$ results, none of which is
independent of the other: The choice of the electronic state
and surface is governed by the $P_K^{(c)}$, for each trajectory,
through the “fewest switches” algorithm; on the other hand,
the surface hops influence the course of the trajectory and the
$P_K^{(c)}$ themselves.

Figure 9 shows how the transition probability for a single passage through the conical intersection depends on
the coupling strength. $P_1^{(q)}$, $P_1^{(c)}$, and $D_1$ at time 50 fs are plotted against $\gamma$. The quantum and the classical treatments
yield the same qualitative trend: The transition probability is
a decreasing function of $\gamma$, for small coupling strengths; it
reaches a minimum, for $\gamma=0.015-0.020$, then it goes up

FIG. 4. Contour plots of $\rho_\gamma^{(q)}(X,Y,t)$ at different times (in fs). Small coupling strength, $\gamma=0.01$.

FIG. 5. Reduced density as a function of $X$, at different times (in fs). Small coupling strength, $\gamma=0.01$. Full lines, quantum results, $\rho_\gamma^{(q)}(X,t)$; dashed lines, semiclassical results, $\rho_\gamma^{(c)}(X,t)$.

FIG. 6. Reduced density as a function of $X$, at different times (in fs). Large coupling strength, $\gamma=0.08$. Full lines, quantum results, $\rho_\gamma^{(q)}(X,t)$; dashed lines, semiclassical results, $\rho_\gamma^{(c)}(X,t)$.
again. It is confirmed that the agreement between quantum and semiclassical results, and between probabilities \( P_{\bar{K}}(c) \) and distributions \( D_K \), is good for small couplings but is partially lost for larger \( g \). The quantum transition probability is never smaller than 80%: In this sense, a single crossing of a conical intersection is always a diabatic process.

IV. SIMPLIFIED MODELS AND DISCUSSION

The main features of the dynamics illustrated in the preceding section can be analyzed in the light of a simple model, which will be referred to as the vibronic model of the conical intersection (VM). To this end we define the Hamiltonian operator \( \hat{H}_{\text{vib}} \), which contains all the electronic terms plus the kinetic energy for the \( Y \) coordinate, \( \hat{T}_Y \):

\[
\hat{H}_{\text{vib}} = \hat{H}_{\text{el}} + \hat{T}_Y.
\]

In other words, \( \hat{H}_{\text{vib}} \) is the total Hamiltonian without the kinetic energy for the \( X \) coordinate. We shall consider a basis of functions of the electronic coordinates and of the nuclear coordinate \( Y \); the basis state \( |I,v\rangle \) is a product of the diabatic electronic state \( |\eta_I\rangle \) and of the \( v \)th eigenstate of the \( Y \) harmonic oscillator. This basis is diabatic with respect to the \( X \) coordinate, in the sense that \( \langle I,v|\partial/\partial X|I,v'\rangle = 0 \). The diagonal matrix elements of \( \hat{H}_{\text{vib}} \) in this basis are:

\[
\langle 1,v|\hat{H}_{\text{el}}|1,v\rangle = \frac{1}{2}K_4(X-X_1)^2 + (v + \frac{1}{2})\hbar\omega_y,
\]

\[
\langle 2,v|\hat{H}_{\text{el}}|2,v\rangle = \frac{1}{2}K_4(X-X_2)^2 + \Delta + (v + \frac{1}{2})\hbar\omega_y.
\]

For the off-diagonal matrix elements we shall adopt a linear approximation of the electronic coupling [see Eqs. (3)], without damping factors: \( H_{12} = \gamma Y \). The only nonvanishing matrix elements are then

\[
\langle 1,v|\hat{H}_{\text{el}}|2,v-1\rangle = \gamma \sqrt{v/2M_y \omega_y},
\]

\[
\langle 1,v|\hat{H}_{\text{el}}|2,v+1\rangle = \gamma \sqrt{(v+1)/2M_y \omega_y}.
\]

The diagonal matrix elements of \( \hat{H}_{\text{vib}} \) can be called the diabatic energies for the vibronic problem and exhibit a char-
characteristic pattern of crossings, which is shown in Fig. 10. The eigenvalues of \( \hat{H}_{\text{vib}} \), i.e., the adiabatic energies, are also drawn.

The motion along the \( X \) coordinate will be treated semiclassically. When the system is prepared in state \( |1,0\rangle \) at \( X = 2 \) bohr, it moves downhill, toward larger \( X \), and crosses many other curves belonging to states \( |2,\nu\rangle \): however, there is a nonvanishing transition probability only to state \( |2,1\rangle \), through the crossing labeled \( A \) in Fig. 10, because the other states are not coupled to \( |1,0\rangle \). If the system switches to \( |2,1\rangle \), it reaches another branching point, \( B \), where a transition can occur to state \( |1,2\rangle \). We apply the Landau–Zener rule, taking into account the couplings (28), to obtain the probabilities of the three states \( |1,0\rangle, |1,2\rangle \) and \( |2,1\rangle \), after a single crossing of the interaction region:

\[
P_{1,0} = e^{-\lambda}, \\
P_{1,2} = 1 - e^{-\lambda} - e^{-2\lambda} + e^{-3\lambda}, \\
P_{2,1} = e^{-2\lambda} - e^{-3\lambda},
\]

with

\[
\lambda = \frac{\pi \gamma^2}{X \Delta F M_\gamma \omega_\gamma}.
\]

Here \( \dot{X} \) is the velocity in the \( X \) direction at the time of the crossing, which is assumed for simplicity to be the same at points \( A \) and \( B \); we compute it by neglecting the vibrational energy of the \( Y \) coordinate: \( \dot{X} = \sqrt{2(H_{11}(X_0,0) - H_{11}(X_2,0))/M_\gamma} \). \( \Delta F \) is the slope difference between the diabatic curves, which is a constant in our model: \( \Delta F = K_s(X_1 - X_2) \).

The VM probabilities (29) depend on a single parameter, \( \gamma \), which includes the coupling strength \( \gamma \); the characteristics of the wave packet as a function of \( Y \), and the dynamical variables of the motion along \( X \), that is \( \dot{X} \) and \( \Delta F \). The essential assumptions made in setting up the VM model are: (1) only two coordinates are relevant; (2) the motion is mainly directed along \( X \), with a sufficiently well-defined average velocity \( \dot{X} \), while the wave packet is almost stationary in the \( Y \) coordinate during the time required to cross the interaction region. Within the validity of this model, Eqs. (29)–(30) allow one to generalize the results of simulations to other choices of the parameters: The adimensional parameter \( \lambda \) takes the place of \( \gamma \) as a measure of the coupling strength.

The total probability of the electronic state \( |\eta\rangle \), i.e.,

\[
P_{1}^{\text{VM}} = P_{1,0} + P_{1,2} = 1 - e^{-2\lambda} + e^{-3\lambda}
\]

is compared in Fig. 9 with the results of quantum and semiclassical calculations. In spite of the approximations made in deriving the Eqs. (29), the general trend of the quantum results is correctly reproduced by the VM curve. The presence of a minimum in the probability of state \( |\eta\rangle \) as a function of \( \gamma \) is easily interpreted. In order to be in state \( |2,1\rangle \) after going through both branching points, \( A \) and \( B \), the system should cross \( A \) adiabatically and \( B \) diabatically (that is, without changing the adiabatic state in the former case, and the diabatic one in the latter). The best compromise between these two contrasting requirements is obtained for \( \gamma = 0.405 \), i.e., with our choice of the other parameters, \( \gamma = 0.0107 \); the maximum of \( P_{2,1} \) is 0.15. For smaller coupling strengths the dynamics at the crossing \( A \) is substantially diabatic, therefore the system remains in state \( |1,0\rangle \); for larger \( \lambda \) and \( \gamma \), both crossings are traversed adiabatically, so that the final electronic state is the same, \( |\eta\rangle \), but with two quanta of vibrational excitation in the \( Y \) direction. This is confirmed by the simulation results: In fact, the population of the excited vibrational states in \( |\eta\rangle \), and particularly that of \( |1,2\rangle \), increases with \( \gamma \). Notice, however, that the vibronic model does not take into account the effect of the anharmonicity of the potentials, which is important for large \( \gamma \); other approximations here done, namely the linear form of \( H_{12} \), may also play a role. The symmetry properties of the wave packets, which have been already discussed in connection with Berry’s phase, are very simply explained in the VM framework. In fact, a vibrational wave function in state \( |\eta\rangle \), symmetric in the \( Y \) coordinate, only interacts with other symmetric wave functions in the same state, and with antisymmetric ones in \( |\eta\rangle \); this remains true for any functional dependence of \( H_{12}(X,Y) \), not only the linear form, provided it is antisymmetric in \( Y \). Therefore, after crossing the interaction region, we have an antisymmetric wave packet in the upper state, and a symmetric one in the lower, as shown in Figs. 2–4.
For large coupling strengths $\lambda$, the final probabilities depend on $v$ changing transitions, i.e., on the coupling between the electronic and the $Y$ motions. The importance of considering the $Y$-electronic coupling can be demonstrated by setting up another model, which takes into account only the motion along the $X$ coordinate. This model is adequate for small $\lambda$, but fails utterly for large $\lambda$. It will be called the avoided crossing model (ACM) of the conical intersection. We consider a trajectory with constant $Y$, such that the conical intersection is seen as an avoided crossing with a minimum energy gap depending on $Y$. Applying again the Landau–Zener rule and the linear approximation for $H_{12}$, the probability of state $|\eta_i\rangle$ after the crossing is $e^{-2\pi^2 \gamma^2 Y^2 / X \Delta E}$. Taking the average over the Gaussian distribution of the $Y$ coordinate, one obtains:

$$P_1^{(ACM)} = (1 + 2\lambda)^{-1/2}. \quad (32)$$

The $P^{(ACM)}$ curve is shown in Fig. 9 as a function of $\gamma$. For small $\gamma$, or $\lambda$, it approximates very well the $P^{(VM)}$ probability. When expanding the two functions in powers of $\lambda$, the lowest order difference is $P^{(VM)} - P^{(ACM)} \approx \lambda^2$. Therefore, one can treat a conical intersection as a sort of avoided crossing, only when the coupling strength $\lambda$ is lower than 0.1: with our choice of the other parameters, this means $\gamma < 0.01$.

The $Y$ motion becomes important in determining the transition probabilities at the same coupling strengths where the semiclassical and the quantum results are somewhat at variance. Moreover, Figs. 2, 3, 5, and 6 show that the semiclassical simulation of the wave packet motion is better for the $X$ than for the $Y$ coordinate. These considerations suggest that the difference between semiclassical and quantum probabilities is due to some inability of the semiclassical method to treat the $Y$-electronic coupling. We have confirmed this idea by setting up a third model, in which the $X$ motion is suppressed. The $X$-frozen model (XFM) does not yield an approximate evaluation of the transition probabilities for the crossing of a conical intersection, and in the present context is only useful for testing purposes. We consider again the $\hat{H}_{\text{vib}}$ Hamiltonian, Eqs. (26)–(28), but this time $X$ is just a constant parameter which determines a shift $\Delta E$ between the vibrational levels belonging to state $|\eta_i\rangle$ and state $|\eta_j\rangle$:

$$\Delta E = \langle 2,0| \hat{H}_{\text{el}} | 2,0 \rangle - \langle 1,1| \hat{H}_{\text{el}} | 1,1 \rangle = \Delta + \frac{i}{2} k \left( x_2^2 - x_1^2 - 2 x_2 x + 2 x_1 x \right). \quad (33)$$

The initial state, $|2,0\rangle$, is only coupled with $|1,1\rangle$; if one neglects the coupling of the latter with other states, a safe approximation for short times, the transition probability is given by Rabi’s formula (which is the exact solution of a two-state problem with a time-independent coupling):

$$P_1^{(XFM,q)}(t) = \frac{\gamma^2}{2 M_y \omega_y \Omega_q} \sin^2(\Omega_q t), \quad (34)$$

with

$$\Omega_q = \frac{1}{2} \sqrt{\frac{2 \gamma^2}{M_y \omega_y} + (\Delta E - \omega_y)^2}. \quad (35)$$

Here the index $q$ stands for quantum mechanical treatment. Notice that $P_1^{(XFM,q)}(t)$ is the probability of being in the diabatic state $|\eta_1\rangle$. We do not attempt to translate this result in the adiabatic basis. The same model can be solved semiclassically. Instead of considering the vibrational levels for the $Y$ motion, we have a representative point which oscillates in the upper potential with a frequency $\omega_y$ and an amplitude $(M_y \omega_y)^{-1/2}$, corresponding to the zero point energy. Because the $Y$ coordinate oscillates, the electronic coupling in this case is time dependent:

$$H_{12}^{(2)} = \frac{\gamma}{\sqrt{M_y \omega_y}} \cos(\omega_y t). \quad (36)$$

The separation between the two potential curves is constant, $\Delta E$, therefore the solution of the semiclassical equations (18) is again a Rabi formula, but with some important differences:

$$P_1^{(XFM,c)}(t) = \frac{\gamma^2}{4 M_y \omega_y \Omega_c} \sin^2(\Omega_c t), \quad (37)$$

with

$$\Omega_c = \frac{1}{2} \sqrt{\frac{\gamma^2}{M_y \omega_y} + (\Delta E - \omega_y)^2}. \quad (38)$$

Notice that Rabi’s formula for a time-dependent perturbation incorporates the rotating wave approximation. The semiclassical formulas [(37)–(38)] are identical to the quantum mechanical ones [(34)–(35)], except that in the former the coupling strength $\gamma$ is everywhere multiplied by a factor 1/$\sqrt{2}$. It can be concluded that the semiclassical treatment undervalues the importance of the transitions induced by the $Y$-electronic coupling. This is not due to any particular option in our implementation of the trajectory surface hopping method: It seems rather to be a basic feature of the semiclassical equations. In Fig. 11 we compare the quantum and semiclassical results for the XFM model, with a reasonable choice of the parameters: $\Delta E = 0.01$ and $\gamma = 0.01$. Because both the quantum and the semiclassical solutions given in Eqs. (34)–(38) contain some approximations, in the same figure we also show the results of numerically exact calculations: The agreement with the analytic solutions is good, at least for the short times we are interested in (40 fs). The same figure shows the semiclassical trajectory distributions, which do not follow the corresponding probabilities, at least after the first oscillation. This can be easily explained if one considers that, once in the lower potential curve, a trajectory can reach values of the $Y$ coordinate where a jump to the upper state is impossible because of the energy conservation: Therefore, an increase in the probability of state 2 is not matched by an equal increase of the fraction of trajectories in that state.

V. CONCLUSIONS

We have brought out the main features of the dynamics of a wave packet which goes through a two-dimensional conical intersection, traveling along the symmetric coordinate $X$ and almost stationary in the antisymmetric one, $Y$. 

The crossing is essentially diabatic, in the sense that the transition probability from the upper to the lower adiabatic surface is always large (>0.8), for any coupling strength. This result pertains to a single passage through the strong coupling region: For longer times, one expects oscillations, unless dissociation or dissipative processes prevail. A simple vibronic model accounts for this behavior, and for other qualitative properties of the time-dependent wave packet. The same model allows to introduce a single parameter to define the coupling strength of the conical intersection, depending on the properties of the surfaces and on the velocity along the X coordinate.

We have compared a quantum mechanical and a semiclassical treatment. We find a good agreement between the two sets of results for small coupling strengths, less so for large couplings. The reduction to one-dimensional models, with X-electronic or Y-electronic couplings only, shows that the semiclassical treatment underestimates the transition probabilities induced by the motion along the antisymmetric coordinate Y. An improvement of the performance of semiclassical methods in such circumstances is considered to be important for the application to multidimensional conical intersections and to other problems where the electronic coupling oscillates in time along a trajectory.

ACKNOWLEDGMENTS

We gratefully acknowledge the permission to employ the VENUS program by W. L. Hase et al. This research was supported by the C.N.R. and M.U.R.S.T.

31 A. Lami and F. Santoro, unpublished results.