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A model study of the wavepacket dynamics around a Jahn–Teller conical intersection in a symmetric charge-transfer system

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Abstract

A model system with a Jahn–Teller conical intersection is investigated. Two vibrational modes are considered: a tuning mode corresponding to a vibrational motion that reduces the symmetry, thus removing the degeneration between the electronic states and a coupling mode, which is responsible of the electronic coupling. While the above scheme may be quite general, we consider in particular a charge-transfer system, in which the charge (an electron) is exchanged between identical moieties and the hopping term is null for the reference geometry. A typical realization may be that in biphenyl-like compounds in which the two rings are held at 90° by bulky substituents. We perform calculations of the time-dependent populations of the two diabatic (charge separated) states, assuming that the system is initially distorted, being trapped in one of the two minima, while a short pulse excites the wave-packet vertically. We not only discuss the ordinary situation in which we deal with the response of an ensemble of molecules, but also the one in which an individual molecule is interrogated. In the latter case, mimicking what may happen in a molecular electronic device grounded on a single molecule, quantum jumps come out. The role of adding energy quanta in the coupling mode is also investigated, showing that this gives rise to an accelerated charge-transfer dynamics. From the observation that no electronic coherence is produced between diabatic states during the time evolution, we are led to try with a very simple model (in the spirit of surface hopping but working with diabatic surfaces) which is shown to reproduce quite well the exact results. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The dynamics involving coupled electronic states, in a region around a point or seam where two adiabatic Born–Oppenheimer potential energy surfaces are degenerate (conical intersection), plays a fundamental role in the understanding of several chemical reactions. In particular, the im-

portance of conical intersections for photochemistry is now well established from both the theoretical and the experimental point of view. Since in these reactions, the coupling between two electronic states often results in branching between energetically accessible product channels, the detailed study of the time-dependent behavior of an excited wave-packet crossing the critical region is of great practical as well as theoretical relevance. It is also the preliminary step for any attempt to control the reaction yields by suitable excitation mechanisms. In previous work [1–5] we have

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performed a systematic theoretical–numerical study on model systems to shed light on different aspects of the wave-packet motion around a conical intersection. Other relevant contributions in this field have been furnished by Domcke, Stock, Manthe and coworkers, as documented (up to the 1997) in the review [6]. Among the molecular systems investigated through *ab initio* calculations + quantum dynamics, we mention the pyrazine [7,8], the ethylene cation [9,10], the benzene cation [11,12], Na_3 [13,14], NO_2 [15]. Very recently Chachisvilllis and Zewail [16] have performed an experimental–theoretical study of the pyridine molecule in S_1 and S_2 states. In the latter state a conical intersection may lead to a valence isomer, a prefulvenic form. Furthermore, methods which allow to locate relevant conical intersections on the PES of chemical systems have been developed [17–21].

In the present paper, we examine in major detail the case of crossing of degenerate PES (Jahn–Teller effect), which takes place in a molecular system that for a certain reference nuclear configuration belongs to a symmetry group with degenerate species [22,23]. If one moves away from the high-symmetry reference geometry along suitable vibrational modes (tuning modes) the symmetry is reduced and the degeneracy is removed. The non-adiabatic coupling, which gives rise to jumps between the two PES, involves different modes (coupling modes). Many examples can be taken from very different contexts, from solid state to gas-phase (see Ref. [24] for references on systems as well as on recent *ab initio* calculations). The prototypical case is that of H_3 already mentioned in the seminal paper of Herzberg and Longuet-Higgins [25] and recently in [26], while similar systems are those with three alkali atoms [13,14, 24,27,28]. In these systems the electronic degeneration is accompanied by vibrational degeneration, in such a way that three (or more) vibrational modes have to be considered.

In the following, we will examine a particular kind of problem involving a conical intersection between electronically degenerate diabatic states, which, apart from its intrinsic interest, is also relevant for supra-molecular photochemistry and material science [29–31]. We will focus on the in-

tramolecular electron transfer as happens in molecules built by two identical and weakly coupled moieties, as, for example in biaryls and related molecules. As we will discuss, in some special cases one can assume that a single vibrational coordinate is relevant in modulating the electron hopping which is responsible of the coupling between the two diabatic surfaces. If the diabatic coupling vanishes (due to symmetry reasons) at a particular value of the coordinate, a typical Jahn–Teller situation is realized. To mimic the distortion of the charged moiety accompanying the electron transfer one needs in principle a further couple of vibrational modes, which are degenerate if one deals with identical moieties. In this latter case, however, as explained in the following, the whole process can be modeled by a minimal two-state, two-mode hamiltonian since only the antisymmetric combination of the localized modes is active. We will study the dynamical outcome of the model also from the point of view of the single molecule, an aspect that should be taken in mind when designing electronic devices on the molecular scale. Furthermore, the role of the vibrational excitation of selected modes, occurring before the electronic excitation will be discussed. In fact one expects that the region of the upper surface explored by the vertically excited wave packet may be quite different depending on the initial vibrational state and so the time spent in the region close to the conical intersection. This argument apply for the excitation along the vibrational coordinate that removes the degeneracy (tuning mode). What is less intuitive is the role of the vibrational excitation along the coupling mode. This also establishes a contact with various investigations on the role of the motion along modes orthogonal to the reaction coordinate, which in our example is identified with the tuning mode.

There are several theoretical and experimental works examining the influence of vibrational motion orthogonal to the reaction coordinate in reactive systems with either avoided crossings or conical intersections. The role of a statistical distribution of the excess of energy among several modes [32], as well as the effect of a specific vibrational excitation in a degree of freedom different from the reaction coordinate [7] have been theo-

retically studied. On the experimental side, the influence of an excess vibrational energy on both the product internal state distributions and the branching ratio between different products has been investigated [33–38].

As a last point we will comment on the fact that, due to the form of the diabatic coupling, no electronic coherence develops during the time evolution (i.e. the reduced electronic density matrix remains diagonal in the diabatic basis set).

2. The model Hamiltonian

The following model Hamiltonian involving two diabatic electronic states and two vibrational modes has been used for all the numerical investigations described in this paper

$$H = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix},$$

where

$$\begin{aligned} H_{11} &= \frac{1}{2}K_X(X - X_1^0)^2 + \frac{1}{2}K_Y Y^2 + T_X + T_Y, \\ H_{22} &= \frac{1}{2}K_X(X - X_2^0)^2 + \frac{1}{2}K_Y Y^2 + T_X + T_Y, \\ H_{12} &= H_{21} = \gamma Y \exp(-\alpha(X - X_{ci})^2) \exp(-\beta Y^2), \\ X_{ci} &= \frac{(X_1^0)^2 - (X_2^0)^2}{2(X_1^0 - X_2^0)}. \end{aligned} \quad (1)$$

Here K_X and K_Y are the harmonic constants of the oscillators, X_1^0 and X_2^0 are the equilibrium positions of the X oscillator in the two diabatic states, T_X and T_Y the kinetic energy operators. The relevant parameters are (in atomic units)

$$\begin{aligned} m_X &= 20000, & m_Y &= 6666.7, & K_X &= 0.02, \\ K_Y &= 0.1, & \alpha &= 3, & \beta &= 1.5, & X_1^0 &= -1, \\ X_2^0 &= 1, & \gamma &= 0.01. \end{aligned}$$

Since the aim of this work is to put in evidence some general features of the dynamical behavior of Jahn–Teller systems, no effort has been made to choose the parameters in order to mimic a particular molecule. As a consequence the emphasis has not to be posed on the specific examples pre-

sented, which are sensitive to the exact value of the parameters, but on the general trends that emerge from the calculations and are, in a loose sense, independent on the exact Hamiltonian. In this respect, it is worthwhile to stress that an element of specificity of our model Hamiltonian is the fact that the diabatic coupling H_{12} , Eq. (1), is damped out quite rapidly as one moves away from the conical intersection. In other model Hamiltonians used in the literature [8] this damping is not present and the effect of the linear coupling along the Y -coordinate extends far away from the critical region. We have not performed a systematic investigation on this point, but what clearly appears is that our curves showing transition probabilities (between diabatic states) vs. time (see Figs. 2 and 3, discussed below) exhibit marked jumps, which are quite smoothed with an undamped diabatic coupling [6,8]. The Fig. 1 gives a pictorial representation of both diabatic (a) and adiabatic (b) potential energy surfaces.

3. Electron transfer between identical moieties

A situation in which the coupling of two degenerate electronic states plays an important role is that realized in systems where a charge or an excitation may stay on two identical moieties. These are two physically well distinct cases that, however, share many similarities as far as their dynamical behavior is concerned. From now on we will refer specifically on charge transfer systems, which have been extensively studied for their intrinsic interest in chemistry and biology [39,40] as well as for their potential use as electronic devices on the molecular scale [41,42]. Here the two diabatic states corresponds quite naturally to charge-localized states. The site distortion induced by the charge localization may be well represented by a set of tuning oscillators, which are antisymmetric combination of couple of normal modes, representing identical vibrations on the different moieties. It can be shown that the symmetric combinations do not play any role [43–45]. The two charge transfer states are coupled by an hopping term, which in principle depends on the whole set of inter-site vibrational coordinates and is usually non-zero

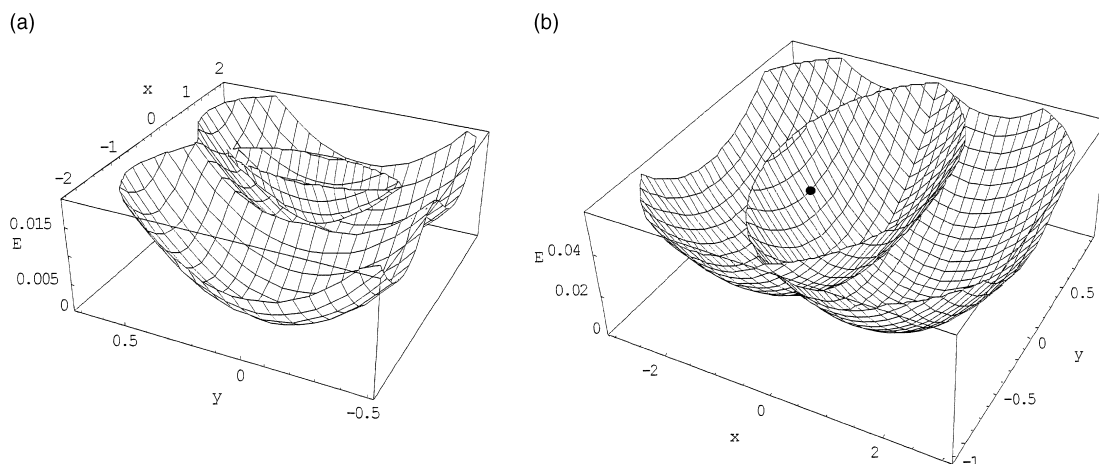


Fig. 1. (a) The two adiabatic surfaces obtained from the diagonalization of the Hamiltonian (1) with the neglect of kinetic energy. (b) The two diabatic surfaces, corresponding to the diagonal matrix elements of the same Hamiltonian. Also shown is the point at which the initial wave-packet is centered. Both energy and coordinates are in atomic units.

when the latter are in their equilibrium position. This coupling terms results in adiabatic surfaces exhibiting an avoided crossing. This kind of situation may occur frequently in symmetric charge transfer systems, and has been discussed in Refs. [45,46] for mixed-valence ions. Basically the same arguments are involved in the discussion of the small polaron problem, where however the emphasis is usually on extended systems [47].

In some particular cases the most relevant coordinate modulating the charge hopping process may be such that it gives rise to a null hopping term, at the equilibrium position. A typical situation is that of a biphenyl-like molecule [48] in which two aromatic rings are maintained at 90° , for example by steric hindrance. The hopping term may be modeled as $t = t_0^* \cos(90 - \phi)$ and for small deviation from the equilibrium position $t \sim t_0^* \phi$, so that a true Jahn–Teller conical intersection is realized. For this and similar systems the two-state two-mode model discussed in this paper may be utilized as an useful tool for obtaining general answers on the dynamical behavior.

The on site distortion induced by the charge localization may be strong enough to give rise to a symmetry breaking, which in dynamical terms means that if the charge is injected on one site, it will require a long time to be transferred on the other site (this is sometime referred as static Jahn–

Teller effect [24]). In this situation we can imagine that our initial wave-packet is on the bottom of one of the two diabatic states. The charge motion may be fired by exciting vertically up to the other diabatic state, after which the wave-packet motion through the conical intersection will provide the possibility of branching between the two localized states. The vertical excitation makes accessible an energy range where the Jahn–Teller effect manifests in a dynamical way.

It is worthwhile to notice here that the previously invoked vertical excitation from the bottom of one diabatic state up to the other diabatic state is not an easy step, since the two charge localized states corresponds to a good approximation to eigenstates of the dipole operator (assumed to be independent on nuclear coordinates) and as such only a very small transition moment is expected [45,49–51]. It can however be achieved using a sufficiently strong field. An alternative way can be offered by two-color, two-pulse techniques utilizing a third electronic state (it might be a delocalized Rydberg state).

The charge motion following the vertical excitation can in principle be probed by a second pulse. An elegant way could be that of probing the energy separation of a couple of levels on a chromophore placed somewhere on one side (say where the charge is initially placed) which should be es-

entially decoupled from the system undergoing the charge transfer, apart from the Stark modulation of the position of the energy levels on the chromophore, which is the crucial point. The light pulse to be used as a probe, in fact, has to be peaked at such a frequency that it can only be absorbed if the charge is localized on one site. The output of such an experiment (i.e. absorption vs. time delay of the pulse with respect to the time where the vertical excitation is realized) for an ensemble of molecular systems would then monitor the diabatic population.

It is interesting to notice, however, that a molecular electronic device is based on a single molecule. At this level our suggested experiment closely resembles those performed in quantum optics to show individual quantum jumps associated with photon emission [52,53]. It is interesting, then, to briefly discuss both the ensemble and single molecule results.

If an ensemble is taken, we can assume that each pulse interrogates a sub-ensemble of molecules, which it must have two fundamental properties: (i) it is a small fraction of the total (weak pulse); (ii) it is statistically significant, i.e. it reproduces the features of the total ensemble. Clearly, the point (i) is necessary to safely assume that the wavepacket reduction on the subensemble has no influence on a subsequent measurement, while point (ii) ensures us that our measurement reproduces the properties of the total ensemble. Under such assumptions the diabatic population at time t , as computed from the time-dependent Schrödinger equation, will represent the output of an experiment performed at such a time.

The results of our calculations, with the Hamiltonian of Eq. (1) are depicted in Figs. 2 and 3, all showing the population of the initial electronic state (here referred as 2) vs. the time (in units of the period of the tuning oscillator T_X). Each figure contains three curves, which refers to different number of quanta (ν) in the tuning oscillator: $\nu = 0$, continuous line; $\nu = 1$, long-dashed line; $\nu = 4$, short-dashed line. While Fig. 2 shows the fully time-resolved behavior, Fig. 3 gives a time average, as discussed below.

Let us first examine the time resolved curve for $\nu = 0$ (continuous line of Fig. 2). One can see that

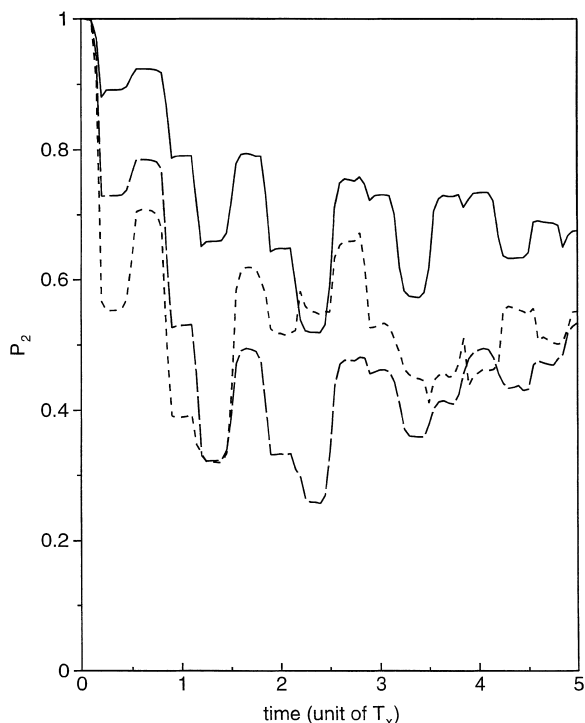


Fig. 2. The probability of being in the initial diabatic state as a function of time. The latter is in units of the period of the X -oscillator (T_X). The three curves refer to cases differing for the initial number of quanta (ν) in the Y -oscillator. Solid line, $\nu = 0$; long-dashed line, $\nu = 1$; short-dashed line, $\nu = 4$.

the charge move back and forth but, at difference with a degenerate two-level system, the memory of the initial situation is conserved, in the sense that the electron is never completely transferred to the other moiety (i.e. at no time the totality of molecules has the electron on the initially uncharged moiety). Even more, the fraction of molecules in the initial state is always greater than one half (which means that the dipole moment maintains its initial direction, while oscillating). The oscillations do not exhibit any clear damping, due to the fact that we have considered only two oscillators. However, even in the absence of additional decay channels one may expect that the oscillations will be damped out by dephasing processes leading to some asymptotic population distribution between the two diabatic states. This asymptotic behavior can be better seen looking at the time averaged population (charge) defined as

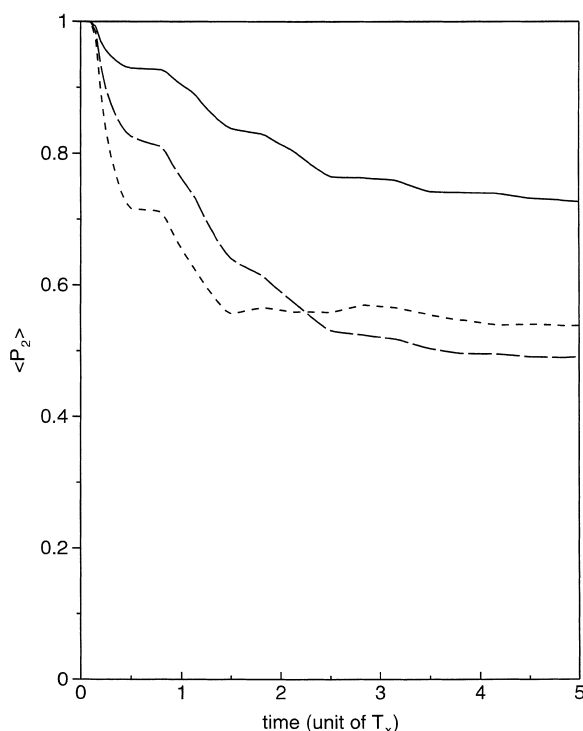


Fig. 3. The same as in Fig. 2 but taking an average over the time (see text).

$$\langle P_2^{\text{dia}}(t) \rangle = \frac{1}{t} \int_0^t P_2^{\text{dia}}(\tau) d\tau \quad (2)$$

by which rapid oscillations are washed out. As discussed by Heller and co-workers [54–56] time averages are useful for comparing classical and quantum dynamics and elucidating the degree of ergodicity of the system. We also used it in previous work [4,5] on the conical intersection dynamics. A direct physical interpretation of these quantities can also be done, since, as an example, a chemical process which starts from one of the two diabatic states but takes place on a slower time scale, can be better related to the time-averaged population of Eq. (2).

The time-averaged result for $v = 0$ is the continuous line of Fig. 3. It appears clearly that the asymptotic value of the population of the initial diabatic state is greater than 0.5. This may perhaps sound strange, but can be understood looking at the consequences of the choice of the initial state.

One may think that, although the latter is localized on the minimum of Fig. 1 (at $X = -1$ and $Y = 0$), the vertical excitation may furnish to the wavepacket a sufficient energy to reach a region where it can explore ergodically all the states, with the only constraint of energy conservation. This is not true, however, simply because there is also a symmetry constraint, as one can easily realize looking at the Hamiltonian (1). In fact, let us suppose that the initial state is $|1, n\rangle$ (1 is the diabatic state and n is the number of quanta in the coupling oscillator, while the state of the tuning oscillator is not relevant here) with n even. Then the evolving wavepacket can only visit states $|2, n'\rangle$ and $|1, n''\rangle$ with n' odd and n'' even. This parity requirement is the obstacle to an ergodic regime, that would result in an asymptotically democratic behavior of the wavepacket as far as the time spent on both diabatic states is concerned.

One expects that the oscillatory behavior shown by the diabatic population (i.e. the charge) in the non-averaged curves would be naturally smoothed by including further vibrational degrees of freedom, as required for a more realistic simulation of a polyatomic molecule. Several examples showing the role of additional modes as well of a weakly coupled bath on non-adiabatic dynamics, with different computational techniques, have been discussed in Ref. [6]. The photoinduced electron transfer in a three-mode model has been studied by Wolfseder and Domcke [57] (within the reduced density matrix approach).

Let us discuss now the effect of putting energy in the Y -oscillator, i.e. in a vibrational degree of freedom which is orthogonal to the “reaction coordinate” (the reaction being the intramolecular electron transfer). The fully time-resolved results and the corresponding time-averages for the cases with one (long-dashed line) or four quanta (short-dashed line) in the Y -mode are depicted in the same figures. (Figs. 2 and 3, respectively). A perusal of the figures suggests that the addition of quanta in the Y oscillator results in all cases in a more rapid population flow back and forth from the initial diabatic state. This accelerated behavior results also in a more rapid attainment of the asymptotic population distribution. This can be explained focussing on the role of the coupling

oscillator Y and considering that the diabatic coupling is essentially linear in Y (the damping factor has a minor role here). The tuning oscillator is assumed here to simply control at what time the diabatic coupling is switched on. If we start from state $|2, n\rangle$ we have that the hopping between the two electronic states is determined by the two matrix elements connecting the initial state to $|1, n-1\rangle$ and $|1, n+1\rangle$ (the Y -oscillator is harmonic), which are proportional to \sqrt{n} and $\sqrt{n+1}$, respectively, and thus grow up with n . The same kind of considerations hold for the back transfer rate, which is also a growing function of n , thus determining an increased mobility of the charge, as shown by Figs. 2 and 3.

Let us come to the simulation of the output of a single-molecule experiment in which the system is measured at regular time intervals to know where the charge is localized. We proceeded as follows, assuming that a wave-packet collapse occur at every step (for a discussion on the unitary approach according to which there is no collapse at all, see [52,53]). The initial state is propagated up to the time of the first measure, say t_1 . From the state at time t_1 , $|\psi(t_1)\rangle$, we compute the probability of permanence in the initial electronic state, $P_2(t_1)$, and then generate a random number, r_1 , between 0 and 1. The wave-packet reduction depends on the value of r_1 . For example, if $r_1 < P_2(t_1)$ we proceed projecting out the component on the state $|1\rangle$, i.e. taking as the initial state for the second propagation step $|2\rangle\langle 2||\psi(t_1)\rangle$ (after normalization) (if $r_1 > P_1(t_1)$ the projector is $|1\rangle\langle 1|$). The same procedure is repeated at any step, corresponding to a measurements by the light pulse, which asks to the system where the charge is localized. The result of a simulation is shown in Fig. 4. The quantum nature of the system is made now visible under the form of quantum jumps, since the answer of the system can only be 1 or 0 (meaning yes, the charge is where it was at the beginning or no it has been transferred to the other moiety). As previously mentioned these have been observed in the photon emission, performing suitable experiments on trapped atoms [58]. It would be interesting to detect the same behavior on individual systems undergoing charge transfer processes.

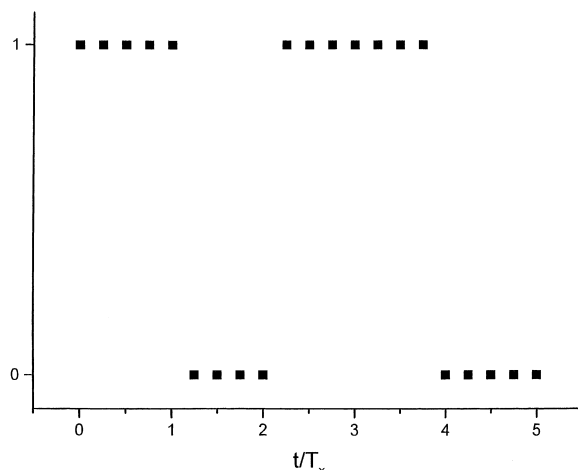


Fig. 4. The possible result of an experiment in which a single molecule is interrogated at regular time intervals τ on where the charge is localized (see the text). Here $\tau = T_x/5$.

As the last point we examine the behavior of our system, as far as the reduced density matrix over the diabatic electronic states is concerned

$$\rho^{\text{el}}(t) = \text{Tr}\{|\psi(t)\rangle\langle\psi(t)|\}_{X,Y}. \quad (3)$$

The diagonal elements are $\rho_{22} = P_2(t)$ (which is shown in Fig. 2) and $\rho_{11} = P_1(t) = 1 - P_2(t)$. The extradiagonal matrix element is always zero, in the present model, due to the fact that the diabatic coupling connects only vibrational states of opposite parity, as far as the Y -oscillator is concerned. This means that no electronic coherence develops during the time evolution and suggests that the ensemble behavior could be successfully investigated by a surface hopping method in the diabatic basis set (it is interesting to notice here that in the surface hopping method [59] the trajectory hops between adiabatic surfaces). In fact the main criticism against a surface hopping approach is that it neglects the electronic coherence, by constraining, so to speak, the classical trajectory to choose one or the other surface. The vanishing of the electronic coherence means that if one looks at the total electronic population, disregarding vibrational details, the system behaves as it were really in one or the other diabatic states. Hence, we decided here to try with an extreme simplification, that of considering the initial

wave-packet as a single classical point moving on the initial surface. When the point reaches the conical intersection point (see Fig. 1) we evaluate the transition probability as in the simplified vibronic model of conical intersection described in Section IV of Ref. [1]. This consists in treating semi-classically the motion along the tuning mode while taking into account the quantum nature of the coupling mode. In practice the transition probability is evaluated from a modified Landau–Zener formula:

$$P_{2 \rightarrow 1} = 1 - e^{-2\lambda} + e^{-3\lambda}, \quad (4)$$

where

$$\lambda = \frac{\pi\gamma^2}{v_X \Delta F m_Y \omega_Y} \quad (5)$$

and v_X is the velocity in the X direction at the moment of the crossing and ΔF is the slope difference between the diabatic curves (which is constant in our model).

We decide that a fraction of molecules proportional to the transition probability jumps on the other diabatic surface. The mother trajectory does not change at all, while the daughter one starts moving on the new surface with the same velocity it had at the moment of the transition. The same procedure is repeated whenever one of the trajectories goes through the conical intersection (the new weight factor associated to each trajectory is also computed and stored). The ensemble results for the probability of finding a molecule in a given diabatic electronic state is generated by summing all the corresponding weight factors. The results of such a simulation are shown in Fig. 5, together with the corresponding exact results, for comparison. In particular the curves refer to the fully time-resolved case (short-dashed line for the model and continuous line for the exact results) and to the time-averaged case (dotted line for the model and long-dashed line for the exact results). One can see that the average behavior of the full quantum computation (dotted line) is reproduced quite well, thus confirming the validity of the initial guess. The full time resolved curve, however, shows that the oscillations are quite smoothed in the model.

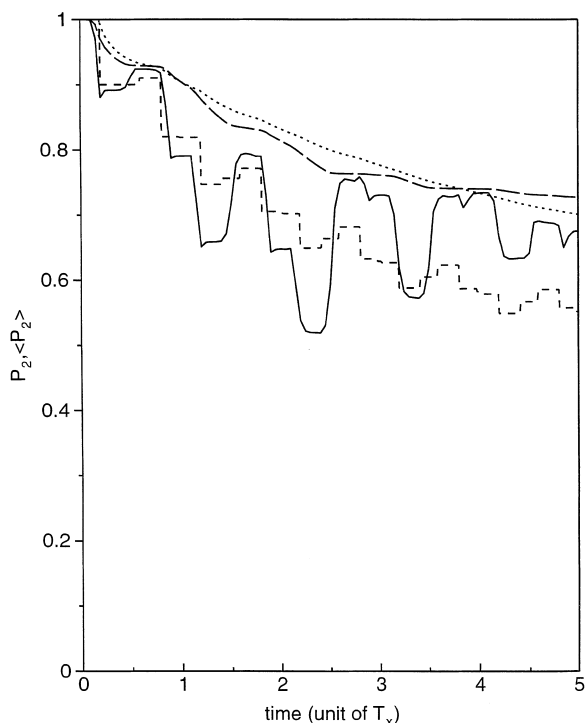


Fig. 5. The result of the simplified model described in the text for both the fully time resolved behavior (short-dashed line) and time-averaged behavior (dotted line). Also shown are the exact results, for comparison (continuous line for the fully time resolved case and long-dashed line for the time-averaged case).

4. Conclusions

We have performed a full quantum-mechanical study of the wave-packet dynamics in a system with a conical intersection between two degenerate electronic surfaces (Jahn–Teller effect), having in mind an intramolecular photo-induced electron transfer process in which the electron may hop between two identical moieties (as, for example in diarils). The diabatic electronic states, being characterized by a well-defined charge assignment (i.e. the charge is on one or the other moiety), are the natural candidates for describing such a charge transfer process. The probability of remaining in the initial state (say with the charge on the left side) is computed as a function of time after a vertical excitation. The curves exhibit marked oscillations but the charge is never completely transferred to the other moiety. According to the

widely accepted interpretation of Quantum Mechanics, these results mimic what can be obtained from an experiment on an ensemble of molecules. We have also investigated what could be the output of an experiment performed on a single molecule, which is interrogated at regular time intervals on where the charge is localized. Here the quantum nature of the process is made visible under the form of quantum jumps. The role of the vibrational excitation of the coupling oscillator has also been investigated, showing that it gives rise to an enhanced charge mobility.

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