HAIT Journal of Science and Engineering, Volume 1, Issue 2, pp. 386-406
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Quasi-ergodic behavior for crossing diabatic potentials *

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Received 3 November 2003, accepted 4 March 2004

Abstract

We investigate coherent and incoherent tunneling phenomena in crossing diabatic potentials (Landau - Zener (LZ) level crossing problem). We consider a model of two crossing parabolic diabatic potentials (left (L) and right (R)) with a constant adiabatic (i.e. independent of coordinates and difference of the diabatic potential minima δE_{LR}) coupling U_{12}. As a result of coupling and level repulsing, we get the asymmetric double-well lower adiabatic potential with a variable shape depending on a continuous parameter b (which describes for $b = 1$ two identical parabolic diabatic potential crossings and in the limit $b \to \infty$ one-well and linear diabatic potentials crossing). We show that the doublet structure of levels (generic for double-well potentials) is remained valid as long as the transition matrix element H_{LR} (tunnel splitting) is smaller than the characteristic inter-level spacings Δ_R (which, in turn, decreases upon δE_{LR} increasing). We calculate the non-adiabatic factor, H_{LR} as a function of U_{12}. In the diabatic limit ($U_{12} \to 0$) H_{LR} goes to zero while in the adiabatic limit ($U_{12} \to \infty$) the tunneling transitions do not depend on the upper potential. In the over-barrier energy region, H_{LR} is an oscillating function of U_{12}

[*] Presented at Russian-Israeli Conference *Frontiers in Condensed Matter Physics.* Shoresh, Israel, 19-24 October 2003

due to resonances between the states in the lower and upper adiabatic potentials. In the case $H_{LR} < \Delta_R$, any level from the shallow L-well is coupled by tunneling to several levels in the R-well, and the transitions lose their coherence. The problem is not only of intellectual interest but also of relevance to various molecular systems undergoing conversion of electronic states or isomerization reactions. Our model exhausts all cases practically relevant for spectroscopy of non-rigid molecules, and can explain many of the experimentally observed features.

PACS: 05.45.-a, 72.10.-d

1 Introduction

Double-well potentials appear in various contexts in physics and chemistry. For example, the simplest pattern of almost any molecular reactive system (with two stable configurations identified as a reactant and as a product) corresponds to the model potential energy formed by two multi-dimensional nearly parabolic terms shifted relative to each other. Although the 1D asymmetric double-well model is idealised, it can be very useful for a qualitative discussion to gain more insight into complex multi-dimensional dynamic molecular properties for which exact or even approximate theoretical results are not available, and in the whole description to follow we will consider 1D case only.

In the classical limit for the energy region $E < U_b$ (where U_b is the potential barrier, separating the left (L) and the right (R) wells), which will be referred further on as the tunneling region, the both wells are fully decoupled and therefore independent. As it is a common wisdom nowadays that in quantum mechanics even for $E < U_b$ the particle can tunnel between the wells. It admixes the L and R well localized states, thus allowing an under-barrier tunneling mechanism. The extent of this delocalization is larger in the states close to the top of the barrier, and it is maximal when the unperturbed levels on the opposite sides of the barrier are degenerate (the reason is immediately clear by looking at the standard textbook expressions for the tunneling probability and level splitting [1]). For the symmetric case this tunneling level splitting leads to coherent quantum oscillations typical for any two-level system. For asymmetric double-well potentials, pairs are not in coincidence any more, tunneling is suppressed, except for certain critical values of model parameters for which the levels are brought back in resonance, and the problem becomes more tricky. We have recently shown [2] that one can successfully attack this problem by a semiclassical solution

of the Schrödinger equation for 1D asymmetric double-well potential with a one-parameter shape

$$U_1(X) = \frac{1}{2}X^2(1-X)\left(1+\frac{1}{b^2}X\right) . \tag{1}$$

U_1 is written in the dimensionless form with energy measured in the units of characteristic oscillation frequency around the left (L) minimum Ω_0, and coordinate X measured in the units of the inter-well distance a_0 (using also the "God given unit" $\hbar = 1$, except for separate explicitly indicated cases when the opposite is necessary for understanding or estimations). The dimensionless parameter b allows us to change the shape of the R well and to consider both limiting cases, namely, a traditional symmetric double-well potential ($b = 1$) and a decay potential for $b \to \infty$. The latter limiting case is also well known, and is characterized by a continuum spectrum of eigenstates for $X \to \infty$ and incoherent decay of quasi-stationary states from the L-well.

Of course, the model potential (1) is only one particular example of the 1D asymmetric potentials with one-parameter shapes. A generalization of our results to other asymmetric potentials will be commented upon throughout the text. On equal base we could take, e.g.,

$$U_2(X) = \frac{1}{2}(1-X^2)^2 + \frac{3\beta}{2}X\left(1-\frac{1}{3}X^2\right) , \tag{2}$$

where β sets a scale of the double-well asymmetry. Although the both potentials (1) and (2) have different shapes, they share many common features. For a small asymmetry $\beta \ll 1$ or $b \simeq 1$ (let us remind that the energy scale is a characteristic one-well oscillation frequency) there is a trivial modification (with respect to the symmetrical double-well potential) of the tunneling splitting. For example, a straitforward calculation gives for the ground state doublet $E_0^{\pm}$ in the potential (2)

$$E_0^{\pm} = \pm(\beta^2 + \Delta_0^2)^{1/2} , \tag{3}$$

where Δ_0 is the ground state splitting for the symmetrical double-well potential (i.e. for $\beta = 0$ or $b = 1$).

It was shown in [2] that for any asymmetric double-well potential the behavior depends crucially on a dimensionless parameter Λ that is, roughly speaking, a ratio of characteristic frequencies for low-energy in-well oscillations and inter-well tunneling. For $\Lambda \ll 1$, there are well defined resonance pairs of levels, and the so-called survival probability (i.e. the probability for

a particle initially localized in one well to remain there) has coherent oscillations related to the resonance splitting. However, for $\Lambda \to \infty$ for any finite time scale, there are no oscillations for the survival probability, but almost exponential decay with the characteristic relaxation time $\propto H_{LR}^{-2}$ determined by Fermi golden rule. In NMR terms this relaxation time can be associated with the so-called dephasing time T_2. Thus one can say that tunneling destroys coherent behavior and can be associated with dephasing processes in the phenomenological Bloch theory of quantum relaxation. Explicitly, for asymmetric double-well potentials

$$T_2^{-1} = \frac{H_{LR}^2}{2\pi\Delta_R} \tag{4}$$

where Δ_R is a typical level spacing for the final states. In the case $\Lambda \gg 1$ one may not restrict himself to the only resonance pair levels. The number of levels perturbed by tunneling grows proportionally to $\sqrt{\Lambda}$ or, in other words, instead of isolated pairs there appear the resonance regions containing sets of strongly coupled levels. At the intermediate values of $\Lambda \geq 1$ one has a crossover between both limiting cases, namely, exponential decay with subsequent long period recurrent behavior (longer the larger is Λ).

It is particularly instructive to look at this result from a slightly different point of view related to the striking and still enigmatic phenomenon of quantum chaos. Perhaps the first successful quantitative criteria relating the classical ergodic theory to quantum molecular dynamics were formulated long ago by von Neumann and Wigner [3]. According to [3], a system has the ergodic behavior if it has:

(i) equidistant spectral distribution (i.e. no degenerate states);

(ii) time decay of correlations for any observable.

We will see that the both criteria are satisfied for strongly asymmetric double-well potentials where highly excited states in the R well are strongly perturbed by tunneling from the shallow L well. This phenomenon will be referred to what follows as tunneling induced ergodicity of final states and in our notation it corresponds to

$$|H_{LR}| > \Delta_R \,. \tag{5}$$

An isolated double-well potential is, of course, only an idealization of any real molecular system. The applicability of such an idealization must be analyzed separately for each system or process in question. However, even in the cases where such a model is not justifiable the calculations we performed are nonetheless instructive. Moreover, in this paper we make one step further.

In a typical problem of chemical dynamics or molecular spectroscopy, the double-well potentials can appear as a result of level crossing phenomena, and consideration of a single isolated double-well potential (lower adiabatic potential) can be justified only if the gap occurring in the spectrum at the avoided level crossing point is much larger than all other characteristic energy scales of the problem. However, it is not evidently the case if we are, for example, interested in the calculation of vibrational - tunneling spectra of non-rigid molecules, or reactive complexes with more than one stable configuration. The lowest multi-well potential of such systems is formed from one-well diabatic potential crossings corresponding to each stable configuration. Apart from the lowest potential, the upper adiabatic potential with its minimum above the maximum of the lowest potential should be also taken into account in these situations. Most of the calculations of tunneling splittings in the ground and low excited vibrational states neglect the coupling to the upper potential, what is certainly correct only for a strong enough adiabatic coupling. The same situation takes place for systems undergoing the Jahn - Teller effect, where the interference of the diabatic states occurs [4]. In all these situations the adiabatic coupling removes diabatic level crossing, and the diabatic levels are replaced by the adiabatic ones. Let us repeat that only in the case of a large adiabatic splitting one can restrict oneself to the only lower adiabatic potential and neglect any influence of the upper adiabatic potential. However, in a general case of arbitrary adiabatic splittings, intra-well and inter-wells dynamics depends on the both adiabatic potentials (i.e. on tunneling splittings and adiabatic interactions).

In the fundamental problems of chemical dynamics and molecular spectroscopy, the transitions from the initial to final states can be treated as a certain motion along the potential energy surfaces of the system under consideration. These surfaces, in turn, are usually determined within the Born - Oppenheimer approximation. However, the approximation becomes inadequate for the excited vibrational states, when their energies are of the order of electronic inter-level energy spacing or near the dissociation limit. In both cases the non-adiabatic transitions should be taken into account, and the most of the non-radiative processes occur owing to this non-adiabaticity. The typical examples investigated in the monography [5], include the so-called pre-dissociation, singlet-triplet or singlet-singlet conversion, and vibrational relaxation phenomena.

To treat this kind of Landau-Zener (LZ) level crossing problems, a usual textbook consideration utilises the outset within a limited electronic subspace, which is completely spanned by a finite set of Born - Oppenheimer or adiabatic electronic states. However, since these states obey the non-

crossing rule, it may be desirable technically to transform the states into the diabatic representation in which the diagonal matrix elements of the electronic Hamiltonian in the subspace can cross, and the off-diagonal interactions appear as scalar coupling potentials.

The major concern of this paper is the construction and solution of a model for two asymmetric diabatic level crossing phenomena. We begin with Section 2 containing a formulation of our model and a discussion of basic methodical details necessary for our study. Section 3 contains our main results. We derive the criteria for reversibility and coherent or incoherent tunneling for crossing diabatic potentials. The conclusive Section 4 deals with miscellaneous subjects related to the diabatic level crossing phenomena.

2 Model potential and basic relations

As a model for diabatic potentials in this paper we choose two non-equivalent parabolas:

$$U_L = \frac{1}{2}\,(1+X)^2\;;\; U_R = \frac{1}{2b}\,(X-b)^2 \tag{6}$$

with a symmetric crossing at $X = 0$. Upon increasing the well asymmetry

$$\delta E_{LR} = -\frac{b-1}{2} \tag{7}$$

the potential U_R is converted from a simple parabola at $b = 1$ to a linear potential at $b \to \infty$. Owing to the adiabatic coupling U_{12} (which we assume for simplicity independent of coordinates) we get the lower double-well and the upper one-well adiabatic potentials.

To find eigenstates and eigenfunctions for our model potential at arbitrary values of the parameters U_{12} and b, we should solve the system of coupled Schrödinger equations

$$-\frac{1}{2}\frac{d^2\Theta_L}{dX^2} + \gamma^2(U_L(X) - E)\Theta_L = \gamma^2 U_{12}\Theta_R\,; \tag{8}$$

$$-\frac{1}{2}\frac{d^2\Theta_R}{dX^2} + \gamma^2(U_R(X) - E)\Theta_R = \gamma^2 U_{12}\Theta_L\,, \tag{9}$$

which can be written as a single fourth-order equation

$$\frac{d^4\Theta_L}{dX^4} - 2\gamma^2(U_L(X) + U_R(X) - 2E)\frac{d^2\Theta_L}{dX^2} - 4\gamma^2\frac{dU_L}{dX}\frac{d\Theta_L}{dX} + 4\gamma^4\left[(U_L - E)(U_R - E) - U_{12}^2 - \frac{1}{2\gamma^2}\frac{d^2U_L}{dX^2}\right]\Theta_L = 0\,. \tag{10}$$

Here $\gamma \gg 1$ is the semiclassical parameter determined by the ratio of the characteristic potential scale over the zero oscillation energy (i.e., as above, $\gamma \equiv m\Omega_0 a_0^2/\hbar$ where m is the mass of a particle, a_0 is a characteristic length of the problem, e.g., the tunneling distance, Ω_0 is a characteristic frequency, e.g., the oscillation frequency around the potential minimum).

Luckily, the equation (10) admits semiclassical solutions by the Fedoryuk method [6 - 8] since the coefficients at the n-th order derivatives are proportional to γ^{-n}, and therefore are small. Besides, in the vicinity of the crossing point $X = 0$ the diabatic potentials (6) can be replaced by linear ones counted from the barrier top $U^{\#}$

$$U_{L/R}(X) = U^{\#} \pm \frac{1}{2} fX \,, \tag{11}$$

and eventually the equation (10) can be presented into a more compact and simple form

$$\frac{d^4\Theta_L}{dX^4} - 2\gamma^2\alpha\frac{d^2\Theta_L}{dX^2} - 2\gamma f\frac{d\Theta_L}{dX} + \gamma^4[\alpha^2 - X^2 - u_{12}^2]\Theta_L = 0 \,, \tag{12}$$

where $\alpha = (1/2) - E$, and $u_{12} \equiv 2U_{12}/\gamma$.

Four roots of the characteristic polynomial of (12)

$$F(\lambda, X) = \lambda^4 - 2\gamma^2(U_L + U_R - 2E)\lambda^2 - 4\gamma^2\frac{dU_L}{dX}\lambda + 4\gamma^4\left[(U_L - E)(U_R - E) - U_{12}^2 - \frac{1}{\gamma^2}\frac{d^2U_L}{dX^2}\right] \tag{13}$$

determine the four fundamental solutions to (12)

$$y_j = (f^2X^2 + u_{12}^2)^{-1/4}\exp(\int \lambda_j(X)dX) \,, \; j = 1, 2, 3, 4 \,. \tag{14}$$

The solutions (14) can be visualized as a motion with imaginary momenta in the upper and lower adiabatic potentials

$$U^{\pm} = \frac{1}{2}(U_L + U_R) \pm \frac{1}{2}[(U_L - U_R)^2 + 4U_{12}^2]^{1/2} \,. \tag{15}$$

As it was mentioned above, in the vicinity of the crossing point one can replace (10) by (12). In the latter equation the coefficient at the first order derivative is small ($\propto \gamma^{-1}$), and by the substitution

$$\Theta_L = \exp(\kappa_{1,2}X)\Phi_L^{1,2} \,, \tag{16}$$

where

$$\kappa_{1,2} = \pm\gamma\sqrt{\alpha}\left(1 \pm \frac{\delta}{2}\right), \tag{17}$$

and δ is a first order correction (see [11]), we obtain $\delta = (f/4\gamma)\alpha^{-3/2}$. Therefore the equation (12) is reduced to two independent Weber equations with the known fundamental solutions [9]

$$\begin{aligned}\{\Theta_L\} = \{ \quad & \exp(\pm\gamma\sqrt{\alpha}X) D_{-\nu}\left(\left(\tfrac{f^2\gamma^2}{\alpha}\right)^{1/4} X\right), \\ & \exp(\pm\gamma\sqrt{\alpha}X) D_{-1-\nu}\left(\left(\tfrac{f^2\gamma^2}{\alpha}\right)^{1/4} X\right)\}\end{aligned} \tag{18}$$

and $\nu = (\gamma u_{12}^2)/(4f\sqrt{\alpha})$ is the so-called Massey parameter. The corrections to the indices of the parabolic cylinder functions D and to the arguments of these functions can be found from (17) and have been calculated in [11].

At the next step we should perform the asymptotically smooth matching of the solutions (14) and (18). The whole analysis can be brought into a more elegant form by introducing connection matrices which link on the complex plane the semiclassical solutions of the Schrödinger equation with the exact potential of our problem (e.g. (6) in our case) and the exact solutions of the so-called comparison equation (in our case (12)) which is valid near the crossing point. Explicit calculations of the connection matrices are rather involved since the LZ problem is characterized by four fundamental solutions to the left and to the right regions with respect to turning or crossing points. Therefore the connection matrices we are looking for, are 4×4 matrices. Although the generalization for our case of the already known 2×2 connection matrices (see, e.g., [10] and our publication [11] for more recent references) is straightforward, it deserves some precaution as it implies quite different procedures for the energy, more accurately for E/γ smaller then (the tunneling region), larger then (the over-barrier region), or of the order (the intermediate region) of the potential barrier, i.e. $U^{\#} - U_{12}$.

Indeed, in the case

$$\frac{E}{\gamma} \ll U^{\#} - U_{12} - \frac{1}{2}\Omega^{\#}, \tag{19}$$

($\Omega^{\#}$ is the characteristic frequency of "oscillations" in the barrier of the lower adiabatic potential) the region near the crossing point is forbidden for both adiabatic potentials. However, four real-valued turning points of the lower adiabatic potential are far enough from the crossing point. The

upper adiabatic potential in this case is also higher than E/γ, and therefore for the instanton approach there are two imaginary turning points, which characterize the motion in the inverted upper adiabatic potential. Thus for the tunneling region we have four real-valued and two pure imaginary turning points.

In the over-barrier energy region, when the energy is larger than the upper adiabatic potential minimum, i.e.

$$\frac{E}{\gamma} \gg U^{\#} + U_{12} + \frac{1}{2}\Omega_0 \,, \tag{20}$$

(remind that Ω_0 is the characteristic frequency of one-well oscillations) the whole region for both potentials is accessible for the classical motion. Thus there are four real-valued turning points (two for the lower and two for the upper adiabatic potentials). Besides, there are two imaginary turning points corresponding to the quantum over-barrier reflection for the lower adiabatic potential. Finally in the intermediate energy region, i.e. for

$$U^{\#} + U_{12} + \frac{1}{2}(\Omega^{\#} + \Omega_0) \geq \frac{E}{\gamma} \geq U^{\#} - U_{12} - \frac{1}{2}(\Omega^{\#} + \Omega_0) \,, \tag{21}$$

there are two real-valued and four imaginary turning points.

The tunneling path is the key point to be considered within the instanton method, and the determination of the tunneling trajectory (or trajectories) is, in a general case, a nontrivial task. However, for our model 1D potentials (1), (2) in the symmetrical case the extremal action trajectory consists of the so-called kink and anti-kink parts corresponding to the $L \to R$ and $R \to L$ transitions, and the action for every part (i.e. kink or anti-kink) is W^*. More or less qualitatively, it is also is the tunneling path for a small potential asymmetry. However, when the asymmetry is larger than the tunneling splitting in the symmetric double-well potential, there is only one classical trajectory starting from the less deep well (say, R) and returning to R not reaching the deeper L minimum. Thus in this case the pair kink - anti-kink forms a single (so-called bounced) trajectory with the action $2W^*$. We will explore this issue below in more detail.

The double-well shape of the lower adiabatic potential and the influence of the upper adiabatic potential require taking into account at least two instanton trajectories with the energies $E = 0$ and $E = \gamma E^{\#}$ during the solution. According to this strategy, one has to match smoothly the semi-classical (e.g., instanton) solutions far from the crossing point ($X = 0$) with the solutions of the more simple comparison equation valid in the vicinity of

the crossing point. This matching should be performed asymptotically, i.e. at small $|X|$ but large enough $\sqrt{\gamma}|X|$.

Now we are in the position to find all needed connection matrices. In the tunneling region (19) for every well (L or R) there exist both increasing and exponentially decaying, real-valued solutions of the Schrödinger equation. The solutions are matched at the crossing point, being linked by the real-valued 4×4 connection matrix, which should have two 2×2 blocks linking the increasing (decreasing) diabatic solution in the L-well with the decreasing (increasing) diabatic solution in the R-well, in the agreement with the standard Landau scheme of tunneling transitions [1]. Omitting a large amount of tedious algebra we can represent the connection matrix linking the "asymptotic" (i.e. in the left/right (L, R) wells and for the upper/lower ($+$, $-$) adiabatic potentials) solutions in the tunneling energy region in the form

$$\begin{pmatrix} \Phi_R^- \\ \Phi_R^+ \\ \Phi_L^+ \\ \Phi_L^- \end{pmatrix} = \begin{pmatrix} \hat{M}_c^{(+)} \hat{L}_R^{(c)} \hat{M}^{(-)} \hat{F}_c & 0 \\ 0 & \hat{1} \end{pmatrix} \hat{U}_c \begin{pmatrix} \hat{F}_c \hat{M}_c^{(+)} \hat{L}_L^{(c)} \hat{M}_c^{(-)} & 0 \\ 0 & \hat{1} \end{pmatrix} \begin{pmatrix} \Phi_L^+ \\ \Phi_L^- \\ \Phi_R^- \\ \Phi_R^+ \end{pmatrix}. \tag{22}$$

Here $\hat{U}_c$ is the 4×4 connection matrix at the crossing point, which in the tunneling region has the form

$$\hat{U}_c = \begin{bmatrix} p & 0 & 0 & -\cos(\pi\nu) \\ 0 & (\sin^2(\pi\nu))/p & -\cos(\pi\nu) & 0 \\ 0 & \cos(\pi\nu) & p & 0 \\ \cos(\pi\nu) & 0 & 0 & (\sin^2(\pi\nu))/p \end{bmatrix}, \tag{23}$$

where we designated

$$p = \frac{\sqrt{2\pi}\exp(-2\chi)}{\Gamma(\nu)}, \tag{24}$$

and $\chi = (\nu/2) - (1/2)\,(\nu - (1/2))\ln\nu$. The matrices $\hat{M}_c^{(+)}$ and $\hat{M}_c^{(-)}$ are the 2×2 connection matrices at the corresponding turning points, which are determined by the phase shifts at these points:

$$\hat{M}_c^{(-)} = \begin{pmatrix} 1 & -i \\ -(i/2) & (1/2) \end{pmatrix}, \tag{25}$$

and $\hat{M}_c^{(+)}$ is the matrix Hermitian conjugated to (25). The $\hat{L}_{L/R}^{(c)}$ and $\hat{F}_c$ matrices, called shift matrices, are related to the variations of the coefficients of increasing and decaying semiclassical solutions in the regions between the turning points ($\hat{F}_c$ is the shift matrix when one moves from the crossing to the turning point in classically forbidden region, and $\hat{L}_{L/R}^{(c)}$ are the shift matrices in the classically accessible regions). Explicitely we get

$$\hat{F}_c = \begin{pmatrix} \exp(-\gamma W_B^*/2) & 0 \\ 0 & \exp(\gamma W_B^*/2) \end{pmatrix}. \tag{26}$$

Here γ is the semiclassical parameter and W_B^* is the action in the lower adiabatic potential barrier. Finally, the structure of the shift matrices $\hat{L}_{L/R}^{(c)}$ is

$$\hat{L}_{L/R}^{(c)} = \begin{pmatrix} \exp(i\gamma W_{L/R}^*) & 0 \\ 0 & \exp(-i\gamma W_{L/R}^*) \end{pmatrix}, \tag{27}$$

where $W_{L/R}^*$ is the action calculated by integration between the turning points.

The over-barrier region (20) can be treated in the same manner. In this case the crossing point is in the classically accessible region for both potentials. The fundamental diabatic solutions can be represented as the waves propagating in the opposite directions, and the complex-valued connection matrix has, similarly to the tunneling region, a 2×2 block structure where the blocks link the waves in the L and R wells propagating in the same direction. Specifically, the corresponding connection matrix at the crossing point $\hat{U}_c'$

$$\hat{U}_c' = \begin{bmatrix} s\exp(-i\phi) & 0 & 0 & -\exp(-\pi\nu) \\ 0 & s\exp(i\phi) & -\exp(-\pi\nu) & 0 \\ 0 & \exp(-\pi\nu) & s\exp(-i\phi) & 0 \\ \exp(-\pi\nu) & 0 & 0 & s\exp(i\phi) \end{bmatrix} \tag{28}$$

where we denoted $s = \sqrt{1-\exp(-2\pi\nu)}$, $\phi = \arg\Gamma(-i\nu) + \Im(2\tilde{\chi})$, and $\tilde{\chi} = -(i/2)((\pi/4) + \nu(1-\ln\nu)) + (1/4)(\pi\nu + \ln\nu))$ should be multiplied by two blocks: the left block gives the contribution at the turning point and includes the shift matrix to the crossing point in L and R wells of the lower adiabatic potential; the right block is related to the turning point and to the shift matrix to the crossing point in the upper one-well adiabatic potential.

Thus in the over-barrier region we finally get

$$\begin{pmatrix} \Phi_R^- \\ \Phi_R^+ \\ \Phi_L^+ \\ \Phi_L^- \end{pmatrix} = \begin{pmatrix} \hat{M}_c^{(+)}\hat{L}_R^{(c)} & 0 \\ 0 & \hat{M}^{(+)}\hat{L} \end{pmatrix} \hat{U}'_{cross} \begin{pmatrix} \hat{L}_L^{(c)}\hat{M}_c^{(-)} & 0 \\ 0 & \hat{L}\hat{M}^{(-)} \end{pmatrix} \begin{pmatrix} \Phi_L^+ \\ \Phi_L^- \\ \Phi_R^- \\ \Phi_R^+ \end{pmatrix}. \tag{29}$$

Here we used the same notations as above for the tunneling region. The matrices $\hat{M}^{(\pm)}$ are also transposed with respect to the matrices $\hat{M}_c^{(\pm)}$ given by (25), and the new shift matrix $\hat{L}$ is

$$\begin{pmatrix} \exp(-i\gamma W^*/2) & 0 \\ 0 & \exp(i\gamma W^*/2) \end{pmatrix}, \tag{30}$$

(remind that W^* is the action in the upper adiabatic potential). Combining altogether (29), (28), (30), and (25), one can trivially find the full connection matrix for the over-barrier energy region (20).

More tricky task is to calculate the connection matrix in the intermediate energy region (21). In this region the crossing point is close to the internal linear turning points of the diabatic potentials. Therefore the two fundamental diabatic solutions are in the classically accessible region and two others are in the forbidden region. Nevertheless, even in this case the connection matrix has the 2×2 block structure but these blocks determine the transitions between the adiabatic states (unlike the tunneling or the over-barrier regions where the connection matrices (22), (29) link the diabatic states).

Following the same line as above, we first present the general structure of the connection matrix in the intermediate energy region:

$$\begin{pmatrix} \Phi_R^- \\ \Phi_R^+ \\ \Phi_L^+ \\ \Phi_L^- \end{pmatrix} = \begin{pmatrix} \hat{M}_c^{(+)}\hat{L}_R^{(c)} & 0 \\ 0 & 1 \end{pmatrix} \hat{U}''_{cross} \begin{pmatrix} \hat{L}_L^{(c)}\hat{M}_c^{(-)} & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \Phi_L^+ \\ \Phi_L^- \\ \Phi_R^- \\ \Phi_R^+ \end{pmatrix}. \tag{31}$$

All matrices in (31) have been already defined, and at the crossing point, the matrix $\hat{U}''_c$ is

$$\hat{U}''_c = \begin{bmatrix} \tilde{s}\exp(-i\phi) & i\exp(-\pi q_2) & 0 & 0 \\ -i\exp(-\pi q_2) & \tilde{s}\exp(i\phi) & 0 & 0 \\ 0 & 0 & \tilde{p} & \sin(\pi q_1) \\ 0 & 0 & -\sin(\pi q_1) & \cos^2(\pi q_1)/\tilde{p} \end{bmatrix} \tag{32}$$

where $\tilde{s} = \sqrt{1+\exp(-2\pi q_2)}$, $\phi = \arg\Gamma((1/2) - iq_2) + \Im(2\chi_2)$, and $\tilde{p} = \sqrt{2\pi}$ $\exp(-2\chi_1)/\Gamma((1/2)+q_1)$. We have introduced the following notations

$$q_1 = \gamma\frac{u_{12}+\alpha}{2}\,;\; q_2 = \gamma\frac{u_{12}-\alpha}{2}, \tag{33}$$

$$\chi_1 = \frac{1}{2}\left(q_1+\frac{1}{2}\right) - \frac{q_1}{2}\ln\left(q_1+\frac{1}{2}\right)\,, \tag{34}$$

and similarly

$$\chi_2 = \frac{1}{2}\left(iq_2-\frac{1}{2}\right) - \frac{iq_2}{2}\left[\ln\left(q_2+\frac{i}{2}\right) - i\frac{\pi}{2}\right]\,. \tag{35}$$

Now the full connection matrix in the intermediate energy region can be easily found by simply collecting the given above expressions (31), (32), and (25).

3 Results and discussion

The purpose of this section is to study how the coherent - incoherent tunneling relationships found in [2] and shortly described in Section 1 for an isolated double-well potential, particularly, the criterion (5) and the dephasing time T_2 (4), should be modified for more realistic situations with a finite adiabatic coupling between the diabatic potentials forming the asymmetric double-well lower adiabatic potential, and the one-well upper adiabatic potential.

However, to investigate this problem, we should first derive the quantization rules for crossing diabatic potentials. In spite of the fact that instanton trajectories are rather simple objects and can be relatively easy found analytically, calculations of the quantization rules within the instanton approach are rather intricate and require the knowledge of all connection matrices, calculated in the previous section. To apply this machinery within the instanton approach, the quantization rule can be formulated as a condition of vanishing the amplitudes of exponentially increasing solutions. In terms of the connection matrix elements m_{ij} this condition is

$$m_{22}m_{33} - m_{23}m_{32} = 0\,. \tag{36}$$

If the above-made assumptions are fulfilled, one can easily write down the Bohr - Sommerfeld [1] quantization equations for the tunneling region

$$\tan(\gamma W_L^*)\tan(\gamma W_R^*) = \frac{4}{p^2}\exp(2\gamma W_b^*) \tag{37}$$

where W_b^* is the action in the classically forbidden region between the turning points and $W_{L/R}^*$ are the coordinate-independent actions inside L (or R) well. This equation (37) can be solved to find energy levels in the wells.

Applying the same procedure to the over-barrier region (20), we find from (33)

$$(1-\exp(-2\pi\nu))\cos(\gamma(W_L^*+W_R^*)-\phi)\cos(\gamma W^*+\phi)+ \\ \exp(-2\pi\nu)\cos\left(\gamma\left(W_L^*+\frac{W^*}{2}\right)\right)\cos\left(\gamma\left(W_R^*+\frac{W^*}{2}\right)\right)=0\,. \tag{38}$$

In the diabatic limit ($\nu \to 0$) one get from (38)

$$\cos\left(\gamma\left(W_L^*+\frac{W^*}{2}\right)\right)\cos\left(\gamma\left(W_R^*+\frac{W^*}{2}\right)\right)=0\,, \tag{39}$$

and, therefore, two independent quantization conditions

$$\left(\gamma\left(W_L^*+\frac{W^*}{2}\right)\right)=\pi\left(n_L+\frac{1}{2}\right)\;;\;\left(\gamma\left(W_R^*+\frac{W^*}{2}\right)\right)=\pi\left(n_R+\frac{1}{2}\right)\,. \tag{40}$$

On the other, hand in the adiabatic limit, i.e. at $\nu \to \infty$ and $\phi \to 0$, we have

$$\cos(\gamma(W_L^*+W_R^*))\cos(\gamma W^*)=0\,, \tag{41}$$

and therefore

$$\gamma(W_L^*+W_R^*)=\pi\left(n+\frac{1}{2}\right)\;;\;(\gamma W^*)=\pi\left(n_0+\frac{1}{2}\right)\,. \tag{42}$$

To conclude this part and span a wide range of possibilities, the quantization condition in the intermediate energy region derived from the connection matrix can be represented in the following form:

$$\cos(\gamma(W_L^*+W_R^*)-\phi)=\frac{\exp(-\pi q_2)}{\sqrt{1+\exp(-\pi q_2)}}\cos(\gamma(W_L^*-W_R^*))\,. \tag{43}$$

Now it seems appropriate to take a fresh look at the results presented above. What can we learn from the performed calculations? First, we can go one step further to analyze the phase factors calculated above. In our system (two crossing diabatic potentials) there are two types of phases. The first phase factor occurs since the tunneling results in the phase shift related to the change of eigenvalues. It leads to a certain kind of one-well phase (T_2)

relaxation. The physical argument leading to T_2 relaxation at the tunneling in the asymmetrical double-well potentials may be rationalized as follows. The fact is that waves reflected from the barrier acquire a non-trivial phase factor. The phenomenom is related to the interference of incident, reflected and transmitted waves. One can look to this phase factor from a slightly different point of view since tunneling results in the phase shift related to the change of eigenvalues. The quantization rules can be rewritten in the form including some integers numerating an exponentially small phase shift due to the existence of a barrier between two wells.

The second phase shift in our case is related to non-adiabatic processes. The LZ case (even for the same asymmetric double-well shape of the lower adiabatic potential) is, indeed, quite different not only quantitatively due to coupling with the upper adiabatic potential but also qualitatively, due to a novel and fundamental quantum effect. Namely, in addition to the described above tunneling phase (existing even in an isolated double-well potential), a quantum mechanical wave function acquires upon a cyclic evolution some geometrical, or Berry phase, factor [12 - 16]. The most characteristic for the concept of Berry phase is the existence of a continuous parametric space in which the state of the system can travel along a closed path. In our case the phase is determined by the non-adiabatic interaction. Coherent or incoherent kind of crossing diabatic potentials crucially depends on a quite tricky interplay between the both (i.e. tunneling and Berry) phase factors. Two new results which have emanated from our study of these phenomena, were our stimuli for presenting this paper.

Let us consider a general example describing two non-symmetric potentials crossing at $X = 0$ (6). When the parameter b determining the potential (6) is varied from 1 to ∞, we recover the two known in the literature limiting cases and come from two identical parabolic potentials to a crossing of one-well and linear diabatic potentials. This kind of crossing leads to the lower adiabatic potential in the form investigated in [2] and has qualitatively the same features as the model potentials (1) and (2). If one neglects for a moment the upper adiabatic potential, aiming to study the crossover from coherent to incoherent tunneling upon increase of the parameter b, then the density of final states will increase with the parameter b. The criterion for coherent-incoherent crossover found in [2] is based on comparison of the transition matrix elements and the inter-level spacings in the final state. A similar criterion should hold for LZ level crossing problem, but in the latter case the tunneling transition matrix elements has to be multiplied by a small adiabatic factor. Therefore the coherent - incoherent tunneling crossover region moves to the higher density of final states, and the larger is U_{12} the

smaller will be the region for incoherent tunneling.

Quite different situation occurs for the excited states. In the diabatic limit, the transition matrix element increases with the Massey parameter ν and therefore at a given b, the system moves to more incoherent behavior. In the adiabatic limit, the transition matrix element is exponentially small and coherence of the inter-well transitions should be restored. However, since the matrix elements are oscillating functions of U_{12} for the intermediate range of this coupling (U_{12}), coherent - incoherent tunneling rates are also non-monotonically varying functions.

Owing to non-adiabatic behavior of the system, the tunneling matrix element H_{LR} is renormalized by the adiabatic factor. In the tunneling region (37) we find this renormalization as

$$H_{LR} \rightarrow H_{LR} p(\nu) \tag{44}$$

where the function $p(\nu)$ (24) is associated with the transition amplitudes between diabatic potentials in the crossing region.

This renormalization tunneling factor varies from 0 to 1 upon increasing of the Massey parameter ν. As we have already found for the isolated double-well potential, in the limit

$$H_{LR} p(\nu) \ll \Delta_R \,, \tag{45}$$

the spectrum consists of a set of tunneling doublets and $L - R$ transitions are coherent ones. The criterion (45) replaces (5) for our case of the finite adiabatic coupling U_{12}.

The expressions for the connection matrices enable us to find the renormalization factor in the over-barrier and intermediate energy regions as well. To do it, one has to compute the integral

$$\int_{-\infty}^{\infty} dX \left| \Psi \frac{d\Psi}{dX} \right| .$$

We do not present here calculations of this renormalization factor. It might be an interesting task to compare them with detailed experimental data on spectroscopy of non-rigid molecules but in the absence of these data we mention only that the renormalization factor turns out to be an oscillation function of the well asymmetry and therefore the phase space contains several regions of coherent and incoherent tunneling. To illustrate these unusual phenomena, we show in Fig. 1 time dependence of the average survival probability P for the initially prepared state $n = 0$ localized in the left well.

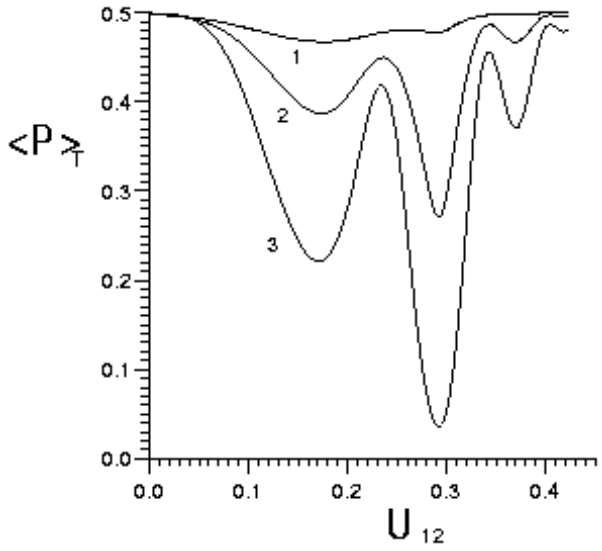

Figure 1: Survival probability for the localized $n = 0$ state; (a) $b = 1500$, dashed lines $U_{12} = 0.15$; solid lines $U_{12} = 0.21$; (b) $b = 1500$, dashed lines $U_{12} = 0.28$; solid lines $U_{12} = 0.21$.

4 Conclusion

In conclusion, let us first comment on our motivation. In principle, potentials with two stable equilibrium configurations are widely used in chemistry and physics, for description of molecular spectroscopy data. Analyzing these data, one must distinguish between two types of states, which require a set of different theoretical and experimental methods, each one with specific strengths and weaknesses on certain length and time scales. Low-energy states localized near the minima of such potentials, are experimentally studied by vibrational spectroscopy methods. These low-energy states can be characterized by well-defined quantum numbers describing the normal vibration excitations. Quite different approaches should be used to study highly excited states near the top of potential barrier. Just these states determine the probability of thermo activated molecular transitions. These phenomena are essentially, so that theoretical descriptions of these states usually assume their ergodicity. This ergodic behavior can be easily understood since the excited states near the barrier top have so high density that even very small coupling to environment (thermal reservoirs) can provide fast mixing and

thermalization of the states.

However, applying these approaches (and the model potentials) to real chemical dynamic problems of low-temperature reactions and transitions of relatively small molecules or atomic clusters (attracting much attention in relation with chemical reactions in upper Earth atmosphere layers and high precision laser spectroscopy techniques), one should take care whether these two relevant regions of energy are not overlapped. Measurements of molecules with two stable configurations performed in the temperature interval $(10 - 20$ K) low enough to ensure irrelevance of dephasing or relaxation processing for the measurement time [21 - 23], demonstrated tunneling doublets dependence on well-defined vibrational excitations. Thus such a low-temperature behavior can be attributed to coherent tunneling, and the advent of ultrafast lasers has provided physical chemists with a tool for studying these systems under nonequlibrium conditions.

On the other hand, there are also numerous examples (see, e.g., [24 - 27]) clearly showing exponential (incoherent) decay of an initially prepared seemingly equilibrium configuration. The question of a primary importance is the understanding of how these two tunneling regimes (coherent and incoherent) depend on specific features of the potential energy profiles (like, for example, our model potentials (1), (2), (6)). One qualitative answer to this question was given long ago [28]. In this paper the authors have formulated the irreversibility criterion. According to the criterion, coherent tunneling should be destroyed when the density of final states is so high that typical inter-level spacings become smaller than characteristic transition matrix elements. The aim of this paper is to formulate a similar criterion quantitatively.

To illustrate these phenomena, we investigated coherent and incoherent tunneling the under conditions of crossing diabatic potentials. As a result of coupling and level repulsion, we get the asymmetric double-well lower adiabatic potential with a variable shape depending on a continuous parameter b (which describes in the limit $b = 1$ a crossing of two identical parabolic diabatic potentials, crossing and in the limit $b \to \infty$ a crossing of one-well and linear diabatic potentials). The doublet structure of levels (generic for double-well potentials) is valid as long as the renormalized by the adiabatic coupling transition matrix element H_{LR} (or tunnelling splitting) is smaller than characteristic inter-level spacings Δ_R. We calculated the non-adiabatic factor and found that in the diabatic limit ($U_{12} \to 0$) H_{LR} goes to zero while in the adiabatic limit ($U_{12} \to \infty$) the tunneling transitions do not depend on the upper potential. In the over-barrier energy region H_{LR} is an oscillating function of U_{12}, due to resonances between the states in the lower and in

the upper adiabatic potentials. In the case $H_{LR} < \Delta_R$, any level from the shallow L-well is coupled by the tunneling to several levels in the R-well, and the transitions lose their coherence.

There is also one more message of our paper. We have shown that transitions between two levels take place only in the presence of interaction between, e.g., the reaction coordinate and other degrees of freedom. Even if the levels are in resonance, i.e. very close or coinciding, as in symmetrical systems, the interaction with environment is required to ensure energy dissipation and destruction of the transition coherence, which are necessary conditions for irreversibility. In asymmetrical systems, the interaction with environment is also necessary in order to compensate the resonance misfit (i.e. the energy difference between the levels involved in the transition takes place) by means of the inter-mode energy exchange. Thus, double-well transitions are, in essence, multidimensional even in the case where the potential structure seems to allow the reaction mode to be considered as an independent one-dimensional variable.

The research described in this publication has become possible partially due to RFFR Grants. One of us (E.K.) is indebted to INTAS Grant (under No. 01-0105) for partial support.

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