Quasistationary states and coherent versus incoherent transitions for crossing diabatic potentials.

V.A.Benderskii
Institute of Problems of Chemical Physics, RAS
142432 Moscow Region, Chernogolovka, Russia and
Laue-Langevin Institute, F-38042, Grenoble, France

E.V.Vetoshkin
Institute of Problems of Chemical Physics, RAS
142432 Moscow Region, Chernogolovka, Russia

E. I. Kats
Laue-Langevin Institute, F-38042, Grenoble, France and
L. D. Landau Institute for Theoretical Physics, RAS, Moscow, Russia
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We investigate coherent and incoherent tunneling phenomena in conditions of crossing diabatic potentials. We consider a model of two crossing parabolic diabatic potentials (left (L) and right (R)) with an independent of coordinates constant adiabatic coupling $U_{12}$. As a result of the coupling and level crossing avoiding, we get the asymmetric double-well lower adiabatic potential with a variable shape depending on a value of a continuous parameter $b$ (which describes in the limit $b = 1$ two identical parabolic diabatic potential crossing 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 $H_{LR}$ (or tunneling splitting) is smaller than characteristic inter-level spacings $\Delta_R$ (the latter ones in own turn decrease upon increasing of a difference between the diabatic potential minima $\delta E_{LR}$). We calculate the non-adiabatic factor, i.e. $H_{LR}$ as a function of $U_{12}$. In the diabatic limit ($U_{12} \to 0$) $H_{LR}$ goes to zero, and 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 the 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. A new phenomenon emanated from this oscillating dependence of $H_{LR}$ on $U_{12}$, namely, multiple coherent - incoherent regime transitions for the upper adiabatic potential state evolution, is our main concern in this paper. 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 capture many of the features exhibited by experiment.

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I. 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 multidimensional more or less parabolic surfaces shifted relative to each other. Although the 1D asymmetric double-well model is idealized, it can be very useful for a qualitative discussion to gain more insight into complex multidimensional dynamic molecular properties for which exact or even approximate theoretical results are not available, thus throughout what follows 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 both, say L and R wells) which will be referred further on as the tunneling region, the behavior in the both wells are fully decoupled and therefore one well is independent from other. As it is a common wisdom nowadays 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 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, the tunneling is suppressed, except for certain critical values of model parameters for which the levels are brought in resonance again,
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 one-parameter dependent shape

\[ U_1(X) = \frac{1}{2} X^2 (1 - X) \left( 1 + \frac{1}{b^2} X \right). \tag{1.1} \]

\( U_1 \) is written in dimensionless form measuring energy in the characteristic frequency of the oscillations say around the left (L) minimum \( \Omega_0 \), and the coordinate \( X \) is measured in the units \( a_0 \) of the inter-well distance (and in "God given unit" we put \( \hbar = 1 \), except where explicitly stated to the contrary when it 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 \( b \to \infty \). Behavior in the latter limiting case is also well known, there is a continuum spectrum of eigenstates for \( X \to \infty \) and incoherent decay of quasi-stationary states from the \( L \) - well.

For a small asymmetry \( b \approx 1 \) the ground state doublet \( E_{0}^{\pm} \) in the potential (1.1)

\[ E_{0}^{\pm} = \pm \left[ \frac{(b-1)^2}{4} + \left( \frac{H_{LR}^{(0)}}{2} \right)^2 \right]^{1/2}, \tag{1.2} \]

where \( H_{LR}^{(0)} \) is the ground state splitting for the symmetrical double well potential.

It was shown in [2] that for any asymmetric double-well potential the behavior depends crucially on a dimensionless parameter \( \Lambda \) 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 so-called survival probability (i.e. the probability for a particle initially localized in one well to remain there) has coherent oscillations related to resonance splitting. However, for \( \Lambda \to \infty \) for any finite time scale, there are no oscillations for the survival probability, and there is almost an exponential decay with the characteristic relaxation time \( \propto H_{LR}^2 \) determined by Fermi golden rule. In the NMR language this relaxation time can be associated to the so-called dephasing \( T_2 \) time. Thus one can say that tunneling destroys coherent behavior and it can be associated with dephasing processes in the phenomenological Bloch theory of quantum relaxation. Explicitly for asymmetric double-well potentials

\[ T_2^{-1} = \frac{H_{LR}^2}{2\pi \Delta_R}, \tag{1.3} \]

where \( \Delta_R \) 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, by other words, instead of isolated pairs there appear the resonance regions containing the sets of strongly coupled levels. At the intermediate values of \( \Lambda \approx 1 \) one has a crossover between both limiting cases, namely the exponential decay with subsequent long period recurrent behavior (more longer the larger \( \Lambda \)). In this region, \( \Lambda \approx 1 \), and in the vicinity of quasi-stationary states of the \( L \)- well the doublet-like eigen-spectrum turns into the equidistant one.

It is particularly instructive to look to this result from a slightly different point of view related to a striking and still enigmatic phenomenon - quantum chaos. Perhaps the first successful quantitative criteria relating the classical ergodic theory to quantum molecular dynamics was 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.

Let us emphasize that the criteria claim that quantum manifestations of the classical chaos are related to specific spectral features of a system under consideration, and not to some kind of its irregular time evolution. From the first sight it might seem that ergodic behavior is impossible in one dimensional systems which are integrable in classical mechanics. However, in fact our model examples should be considered as two classically decoupled systems (\( L \) and \( R \) wells) interacting only via quantum tunneling. One can call this phenomenon as tunneling induced ergodicity, and for more details, see e.g. [2], (and also, [4], [5]). It turns out that the time evolution of the localized initial state is governed by the interplay of two physical parameters, recovering period time and decay rate. The both parameters depend on the spectral representation (or distribution function) of the initial state. It is shown in [2] that the both listed above 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. The condition to have this phenomenon (tunneling induced ergodicity of final states) reads in our notation as

\[ |H_{LR}| > \Delta_R. \tag{1.4} \]
In this paper we will show that similar phenomena can take place also for delocalized initial states, where non-adiabatic coupling gives rise to chaotic behavior. It will be referred to as non-adiabatic transitions induced ergodicity.

Of course an isolated double-well potential is only an idealization of any real molecular system. The applicability of such an idealization must be decided 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. But 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 the consideration of only the 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, evidently it is not the case for example if we are 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 potentials crossing 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 for these situations (see Fig. 1). In the most of the calculations of tunneling splittings in the ground and low excited vibrational states the coupling to the upper potential are neglected, what is certainly correct only for strong enough adiabatic coupling. The same situation takes place for systems undergoing the Jahn - Teller effect, where the interference of the diabatic states occurs [6]. 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 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 own 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 the both cases the non-adiabatic transitions should be taken into account, and the most of the non-radiative processes occur owing to this non-adiabicity. The typical examples investigated in the monography [7], are so-called pre-dissociation, singlet-triplet or singlet-singlet conversion, and vibrational relaxation phenomena.

To treat this kind of level crossing (Landau - Zener (LZ)) problems usual textbook consideration utilizes the outset within a limited electronic subspace which is completely spanned by a finite set of Born - Oppenheimer or adiabatic electronic states. However, because these states obey the noncrossing 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 with the construction and solution of a model for two asymmetric diabatic level crossing phenomena. The rest of our paper begins in section II with a formulation of our model and with a discussion of basic methodical details necessary for our study. Section III contains our main results. We derive the criteria for reversibility and coherent or incoherent tunneling for crossing diabatic potentials. Our conclusion section IV deals with miscellaneous subjects related to the diabatic level crossing phenomena.

II. MODEL POTENTIAL AND BASIC RELATIONS

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

\[ U_L = \frac{1}{2} (1 + X)^2; \quad U_R = \frac{1}{2} \left( 1 - 2X + \frac{X^2}{b} \right) \] (2.1)

with a symmetrical crossing in the point \( X = 0 \). Upon increasing the well asymmetry

\[ \delta E_{LR} = -\frac{b - 1}{2} \] (2.2)

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 (see Fig. 1).

At arbitrary values of the parameters \( U_{12} \) and \( b \) to find eigenstates and eigenfunctions for our model potential we should solve the coupled Schrödinger equations

\[ -\frac{d^2 \Theta_L}{dX^2} + \gamma^2 (U_L(X) - E) \Theta_L = \gamma^2 U_{12} \Theta_R; \quad \frac{d^2 \Theta_R}{dX^2} + \gamma^2 (U_R(X) - E) \Theta_R = \gamma^2 U_{12} \Theta_L, \] (2.3)
which can be written as one fourth order equation

\[
\frac{d^4 \Theta_L}{dX^4} - \gamma^2 (U_L(X) + U_R(X) - 2E) \frac{d^2 \Theta_L}{dX^2} - 2\gamma \frac{dU_L}{dX} \frac{d\Theta_L}{dX} + \gamma^4 \left[ (U_L - E)(U_R - E) - U_{12}^2 - \frac{1}{\gamma^2} \frac{d^2 U_L}{dX^2} \right] \Theta_L = 0. \tag{2.4}
\]

Here \( \gamma \gg 1 \) is the semiclassical parameter which is 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 a mass of a particle, \( a_0 \) is a characteristic length of the problem, e.g., the tunneling distance, \( \Omega_0 \) is a characteristic frequency, e.g., the oscillation frequency around the potential minimum).

Luckily the equation (2.4) admits semiclassical solutions by Fedoryuk method [8] - [10] since the coefficients at the \( n \)-th order derivatives proportional to \( \gamma^{-n} \), and therefore are small. Besides in the vicinity of the crossing point \( X = 0 \) the diabatic potentials (2.1) can be replaced by the linear ones counted from the barrier top \( U^\# \)

\[
U_{L/R}(X) = U^\# \pm fX, \tag{2.5}
\]

and eventually the equation (2.4) can be presented into a more compact and simple form

\[
\frac{d^4 \Theta_L}{dX^4} - 2\gamma^2 \frac{d^2 \Theta_L}{dX^2} - 2\gamma^2 f \frac{d\Theta_L}{dX} + \gamma^4 [\alpha^2 - f^2 X^2 - U_{12}^2] \Theta_L = 0, \tag{2.6}
\]

where \( \alpha = U^\# - E \).

Four roots of the characteristic polynomial of (2.4) or (2.6)

\[
F(\lambda, X) = \lambda^4 - \gamma^2 (U_L + U_R - 2E) \lambda^2 - 2\gamma^2 \frac{dU_L}{dX} \lambda + \gamma^4 \left[ (U_L - E)(U_R - E) - U_{12}^2 - \frac{1}{\gamma^2} \frac{d^2 U_L}{dX^2} \right] \tag{2.7}
\]

determine the four fundamental solutions to (2.6)

\[
y_j = (f^2 X^2 + U_{12}^2)^{-1/4} \exp \left( \int \lambda_j(X) dX \right), \quad j = 1, 2, 3, 4. \tag{2.8}
\]

The solutions (2.8) can be visualized as a motion with imaginary momenta in the upper and lower adiabatic potentials

\[
U^\pm = \frac{1}{2}(U_L + U_R) \pm \frac{1}{2}[(U_L - U_R)^2 + 4U_{12}^2]^{1/2}. \tag{2.9}
\]

As it was mentioned above in the vicinity of the crossing point one can replace (2.4) by (2.6). In the latter equation the coefficient at the first order derivative is small (\( \propto \gamma^{-1} \)), and by the substitution

\[
\Theta_L = \exp(\kappa_{1,2} X) \Phi_L^{1,2}, \tag{2.10}
\]

where

\[
\kappa_{1,2} = \pm \gamma \sqrt{\alpha} \left( 1 \pm \frac{\delta}{2} \right), \tag{2.11}
\]

and \( \delta \) is a first order correction (see [13]) \( \delta = (\gamma f/4\sqrt{\alpha}) \). Therefore the equation (2.6) is reduced to two independent Weber equations with the known fundamental solutions [11]

\[
\{\Theta_L\} = \left\{ \exp(\pm \gamma \sqrt{\alpha} X) D_{-\nu} \left( \pm \left( \frac{2 f^2}{\alpha} \right)^{1/4} X \right), \exp(\pm \gamma \sqrt{\alpha} X) D_{-1-\nu} \left( \pm \left( \frac{2 f^2}{\alpha} \right)^{1/4} X \right) \right\}, \tag{2.12}
\]

where \( \nu \equiv (\gamma U_{12}^2/4f\sqrt{\alpha}) \) is referred traditionally as the Massey parameter, and in fact it controls the main features of the behavior. The corrections to the indices of the parabolic cylinder functions \( D \) and to the arguments of these functions can be found from (2.11) and have been calculated in [13].

At the next step we should perform the asymptotically smooth matching of the solutions (2.8) and (2.12). The whole analysis can be brought into a more elegant form by introducing connection matrices which link on the complex plane the semiclassical solutions to the Schrödinger equation for the exact potential of the problem under study (e.g., (2.1) for our case) and the exact solutions of the so-called comparison equation (in our case (2.6)) which is valid near the crossing point. The explicit calculations of the connection matrices are rather involved since the LZ problem is characterized by the 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 $4 \times 4$ matrices. Although the generalization for our case of the known already $2 \times 2$ connection matrices (see e.g., [12], and for more recent references our publication [13]) is straightforward, it deserves some precaution as it implies quite different procedures for the energy, more accurately for $E/\gamma$ smaller (the tunneling region), larger (the over-barrier region), or of the order (the intermediate region) of the potential barrier, i.e. $U^\# - U_{12}$.

Indeed, in the case

$$\frac{E}{\gamma} \ll U^\# - U_{12},$$

(2.13)

the region near the crossing point is forbidden for the 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 $E/\gamma$, 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.

$$\frac{E}{\gamma} \gg U^\# + U_{12},$$

(2.14)

the whole region for the both potentials, is accessible for the classical motion. Therefore 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

$$U^\# + U_{12} \geq \frac{E}{\gamma} \geq U^\# - U_{12},$$

(2.15)

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

The tunneling path is one central 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 potential (1.1) in the symmetrical case the extremal action trajectory consists from so-called kink and anti-kink pairs corresponding $L \to R$ and $R \to L$ transitions, and the action for every part (i.e. kink or anti-kink) is $W^*$. More or less qualitatively the same 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 $L$) which does not reach the more deep $R$ minimum and comes back to $L$. Thus in this case the pair kink - anti-kink forms a single so-called bounce trajectory with the action $2W^*$. We will explore this issue in more details in what follows.

The double-well shape of the lower adiabatic potential and the influence of the upper adiabatic potential require that to find the solutions one has to take into account at least two instanton trajectories with the energies $E = 0$ and $E = \gamma U^\#$. Following the strategy, described above, one has to match smoothly the semiclassical (e.g., instanton) solutions known in the remote from the crossing point ($X = 0$) region with the solutions of the more simple comparison equation which is valid in the vicinity of the crossing point. This matching should be performed asymptotically, i.e. at small $|X|$ but for large enough $\sqrt{|X|}$.

Now we are in the position to find all needed connection matrices. In the tunneling region (2.13) for every well ($L$ or $R$) there exist increasing and decreasing exponentially real-valued solutions to the Schrödinger equation. The solutions are matched at the crossing point, therefore they are linked by the real-valued $4 \times 4$ connection matrix which should have two $2 \times 2$ 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 the 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 following form

$$\begin{pmatrix}
\Phi_R^- \\
\Phi_R^+
\end{pmatrix} = \begin{pmatrix}
\hat{M}_c^{(+)}
0
0
\hat{M}_c^{(-)}
\end{pmatrix}
U_c^{-1}
\begin{pmatrix}
\hat{F}_c^{(+)}
0
0
\hat{F}_c^{(-)}
\end{pmatrix}
\begin{pmatrix}
\phi_L^+
\phi_R^-
\phi_R^+
\phi_R^-
\end{pmatrix}.$$
Here \( \hat{U}_c \) is the \( 4 \times 4 \) connection matrix at the crossing point, which in the tunneling region has the following form

\[
\hat{U}_c = \begin{bmatrix}
p & 0 & 0 & -\cos(\pi \nu) \\
0 & (\sin^2(\pi \nu))/p - \cos(\pi \nu) & 0 & 0 \\
0 & \cos(\pi \nu) & -\cos(\pi \nu) & 0 \\
\cos(\pi \nu) & 0 & 0 & (\sin^2(\pi \nu))/p
\end{bmatrix}, \tag{2.17}
\]

where we designated

\[
p = \frac{\sqrt{2\pi} \exp(-2\chi)}{\Gamma(\nu)}, \tag{2.18}
\]

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

\[
\hat{M}_c^{(-)} = \begin{pmatrix} 1 & -i/2 \\ -i/2 & (1/2) \end{pmatrix}, \tag{2.19}
\]

and \( \hat{M}_c^{(+)} \) is the matrix Hermitian conjugated to (2.19). The \( \hat{L}_{L/R}^{(c)} \) and \( \hat{F}_c \) matrices are called shift matrices, and those 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). Explicitly we get

\[
\hat{F}_c = \begin{pmatrix} \exp(-\gamma W_{B}/2) & 0 \\ 0 & \exp(\gamma W_{B}/2) \end{pmatrix}. \tag{2.20}
\]

Here \( \gamma \) 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

\[
\hat{L}_{L/R}^{(c)} = \begin{pmatrix} \exp(i\gamma W_{L/R}^{*}) & 0 \\ 0 & \exp(-i\gamma W_{L/R}^{*}) \end{pmatrix}, \tag{2.21}
\]

where \( W_{L/R}^{*} \) is the action calculated by the integration between the turning points. We depicted the corresponding trajectories and matrices in Fig. 2.

The same manner can be treated the over-barrier region (2.14) (see Fig. 3). In this case the crossing point is in the classically accessible region for the both potentials. The fundamental diabatic solutions can be represented as the waves propagating in the opposite directions, and the complex-valued connection matrix has as it was for the tunneling region \( 2 \times 2 \) block structure, where the blocks link the waves in the \( L \) and in the \( R \) wells propagating in the same direction. Specifically the corresponding connection matrix at the crossing point \( \hat{U}_c' \)

\[
\hat{U}_c' = \begin{bmatrix} s \exp(-i\phi) & 0 & 0 & -\exp(-\pi \nu) \\ 0 & s \exp(i\phi) & -\exp(-\pi \nu) & 0 \\ 0 & 0 & s \exp(-i\phi) & 0 \\ -\exp(-\pi \nu) & 0 & 0 & s \exp(i\phi) \end{bmatrix}, \tag{2.22}
\]

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

\[
\begin{pmatrix} \Phi_{R}^{*} \\ \Phi_{R}^{*} \\ \Phi_{L}^{*} \\ \Phi_{L}^{*} \end{pmatrix} = \begin{pmatrix} \hat{M}_c^{(+)} & \hat{L}_c^{(c)} \\ 0 & \hat{M}_c^{(-)} \end{pmatrix} \hat{U}_c' \begin{pmatrix} \hat{L}_c^{(-)} & \hat{M}_c^{(+)} \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \Phi_{R}^{*} \\ \Phi_{R}^{*} \\ \Phi_{L}^{*} \\ \Phi_{L}^{*} \end{pmatrix}. \tag{2.23}
\]

Here we used the same notations as it was above for the tunneling region, and besides the matrices \( \hat{M}_c^{(\pm)} \) are transposed with respect to the matrices \( \hat{M}_c^{(\pm)} \) given in (2.19), and the new shift matrix \( \hat{L} \) is

\[
\begin{pmatrix} \exp(-i\gamma W_{L}/2) & 0 \\ 0 & \exp(i\gamma W_{L}/2) \end{pmatrix}, \tag{2.24}
\]
(remind that $W^*$ is the action in the upper adiabatic potential). Combining altogether (2.23), (2.22), (2.24), and (2.19) one can trivially find the full connection matrix for the over-barrier energy region (2.14).

More tricky task is to calculate the connection matrix in the intermediate energy region (2.15). 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 (see Fig. 3 for the illustration). Nevertheless even in this case the connection matrix has the $2 \times 2$ block structure, but these blocks determine the transitions between the adiabatic states (unlike the tunneling or the over-barrier regions, where the connection matrices (2.16), (2.23) link the diabatic states). To treat this kind of problems we have developed recently [13, 14] the semiclassical method for level quantization in the vicinity of the diabatic potential crossing point. The method enables to find all four exponentially increasing or decreasing solutions to the Schrödinger equation for an arbitrary shape of the crossing diabatic potentials, i.e. for any combination of the 1-st and 2-d order turning points, and of the crossing point. In this paper we generalize this method [13, 14] to study coherent-incoherent tunneling regimes in an asymmetric double well potential.

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

$$
\begin{pmatrix}
\Phi_L^+ \\
\Phi_L^-
\end{pmatrix} = \begin{pmatrix}
\hat{M}_L^{(+)} & 0 \\
0 & \hat{M}_L^{(+)}
\end{pmatrix} \hat{U}_c \begin{pmatrix}
\hat{M}_L^{(-)} & 0 \\
0 & \hat{M}_L^{(+)}
\end{pmatrix} \begin{pmatrix}
\Phi_L^+ \\
\Phi_L^-
\end{pmatrix}.
\tag{2.25}
$$

The matrices $\hat{M}_L^{(\pm)}$, have been introduced in [15] for the imaginary turning points (in the case under consideration the both adiabatic potentials have these turning points in the energy window $|\alpha| < U_{12}$) and they have a form

$$
\hat{M}_L^{(\pm)} = \begin{pmatrix}
\frac{1}{i/2} \exp(-\gamma W_i^{\pm}) & 0 \\
0 & 1
\end{pmatrix},
$$

where $\hat{M}_L^{(-)}$ is the matrix Hermitian conjugated to $\hat{M}_L^{(+)}$, and $W_i^{\pm}$ are so-called Euclidean actions in the turned over upper and lower adiabatic potentials

$$
W_i^{\pm} \simeq \frac{\pi q_{1,2}}{\gamma} ; q_{1,2} = \frac{U_{12}}{4f} \sqrt{U_{12} \pm \alpha} .
\tag{2.26}
$$

Since the matrices $\hat{M}_L^{(\pm)}$ become the unitary ones at $\alpha > U_{12}$ and at $\alpha < -U_{12}$, the intermediate region connection matrix (2.25) matches continuously the the connection matrices (2.16) and (2.23) in the tunneling and over-barrier regions, respectively.

The connection matrix in the intermediate energy region can be calculated using the known Weber function asymptotic expansions for large complex indices [16, 17]. Combining together these asymptotic expansions and all matrices entering (2.25) defined already above, we find at the crossing point, the matrix $\hat{U}_c^{\prime\prime}$ is

$$
\hat{U}_c^{\prime\prime} = \begin{pmatrix}
(\sqrt{2\pi}/\Gamma(q^*)) \exp(-2\chi(q^*)) & 0 & 0 \\
0 & (\Gamma(q)/\sqrt{2\pi}) \exp(2\chi(q))(1 - \exp(-2\pi q_2) \cos^2(\pi q_1)) \\
\exp(-2\pi q_2) \cos(\pi q_1) & 0 & 0
\end{pmatrix} \begin{pmatrix}
\frac{\exp(-2\pi q_2) \cos(\pi q_1)}{\Gamma(q^*)/\sqrt{2\pi}} \exp(2\chi(q^*))(1 - \exp(-2\pi q_2) \cos^2(\pi q_1))
\end{pmatrix} .
\tag{2.27}
$$

where as above we introduced the following abridged notations

$$
q = q_1 + iq_2 ; q_{1,2} = \frac{\gamma U_{12} \sqrt{U_{12} \pm \alpha}}{4f} ; q^* = q_1 - iq_2 ,
\tag{2.28}
$$

and, besides,

$$
\chi = \chi_1 + i\chi_2 ; 2\chi_1 = q_1 - \left( q_1 - \frac{1}{2} \right) \ln |q| + \varphi q_2 ,
\tag{2.29}
$$
and analogously
\[ 2\chi_2 = q_2 - q_2 \ln |q| - \varphi \left( q_1 - \frac{1}{2} \right). \] (2.30)

The phase factor \( \varphi \) is defined as
\[ \tan \varphi = \sqrt{\frac{U_{12} - \alpha}{U_{12} + \alpha}}. \] (2.31)

Now the full connection matrix in the intermediate energy region can be found easily simply collecting the given above expressions.

### III. RESULTS AND DISCUSSION

Our purpose in this section is to study how found in [2] coherent - incoherent tunneling relationships shortly described in the introduction section I for an isolated double-well potential, and in particularly the criterion (1.4) and the dephasing time \( T_2 \) (1.3) should be modified for more realistic situations when there is 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 first we should derive the quantization rules for the crossing diabatic potentials. It can be done using presented above the connection matrices. 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, we have calculated in the previous section. To apply this machinery within the instanton approach, the quantization rule can be formulated as a condition that the amplitudes of exponentially increasing solutions must be vanished. In terms of the matrix elements \( m_{ij} \) of the connection matrix this condition is
\[ m_{22}m_{33} - m_{23}m_{32} = 0. \] (3.1)

If made above assumptions are granted one can easily write down the Bohr - Sommerfeld [1] quantization equations applying shown in the Figs. 2, 3 the connection- and shift matrices (for the details of the calculation method, see [13], [14]), and we end up with
\[ \tan(\gamma W^*_L) \tan(\gamma W^*_R) = \frac{4}{p^2} \exp(2\gamma W^*_b) , \] (3.2)

where \( W^*_b \) is the action in the classically forbidden region in between the turning points, and \( W^*_L/R \) are the coordinate independent actions inside of the \( L \) (respectively \( R \)) well. This equation (3.2) can be solved to find energy levels in the wells.

Applying the same procedure to the over-barrier region (2.14) we find from (2.26)
\[ (1 - \exp(-2\pi \nu)) \cos(\gamma (W^*_L + W^*_R) - \phi) \cos(\gamma W^* + \phi) + \exp(-2\pi \nu) \cos \left( \gamma \left( \frac{W^*_L + W^*_R}{2} \right) \right) \cos \left( \gamma \left( \frac{W^*_L + W^*_R}{2} \right) \right) = 0. \] (3.3)

In the diabatic limit \( \nu \to 0 \) one get from (3.3)
\[ \cos \left( \gamma \left( \frac{W^*_L + W^*_R}{2} \right) \right) \cos \left( \gamma \left( \frac{W^*_L + W^*_R}{2} \right) \right) = 0, \] (3.4)

and therefore two independent quantization conditions
\[ \left( \gamma \left( \frac{W^*_L + W^*_R}{2} \right) \right) = \pi \left( n_L + \frac{1}{2} \right); \left( \gamma \left( \frac{W^*_L + W^*_R}{2} \right) \right) = \pi \left( n_R + \frac{1}{2} \right). \] (3.5)

On the other hand in the adiabatic limit, i.e. at \( \nu \to \infty \) and \( \phi \to 0 \) we have
\[ \cos(\gamma (W^*_L + W^*_R)) \cos(\gamma W^*) = 0, \] (3.6)
and therefore
\[ \gamma(W^+_L + W^+_R) = \pi \left( n + \frac{1}{2} \right); \quad (\gamma W^+) = \pi \left( n_0 + \frac{1}{2} \right). \]

(3.7)

And to conclude this part and to span a wide range of possibilities, the quantization condition in the intermediate energy region derived from the corresponding connection matrix can be represented in the following form
\[ \cos(\gamma(W^+_L + W^+_R) - \phi) = \frac{\exp(-\pi q_2)}{\sqrt{1 + \exp(-\pi q_2)}} \cos(\gamma(W^+_L - W^-_R)). \]

(3.8)

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. In own turn 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 reflected from the barrier waves acquire non trivial phase factor. The phenomonen is related to 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 which includes some integer numbers numerating and an exponentially small phase shift due to the existence of the barrier between two wells.

The second phase shift occurs in our case due to non-adiabatic behavior. Indeed the LZ case (even for the same asymmetric double well shape of the lower adiabatic potential) is quite different not only quantitatively due to coupling with the upper adiabatic potential but also qualitatively, since a novel and fundamental quantum effect will occur. 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 [21] - [22]. What is most characteristic for the concept of Berry phase is the existence of a continuous parameter space in which the state of the system can travel on a closed path. In our case the phase is determined by the non-adiabatic interaction. Coherent or incoherent kind of behavior for 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, is our main motivation for presenting this paper. The semiclassical wave functions of the bound states are linear combinations of (2.16), or (2.23), or (2.25) (respectively for the tunneling, over-barrier, and intermediate energy regions), which can be determined, provided we know the eigenvalues. The quantization rules (namely, conditions that coefficients at exponentially increasing and ingoing from the both infinities \( |X| \rightarrow \pm \infty \) waves are zero), and the wave function normalizations, define uniquely these linear combinations. The shift matrices have always the same form as (2.21), where one has to insert the action between a given point \( X \) and the nearest turning (or crossing) point \( X_k \). For the upper and the lower adiabatic potentials the action reads as
\[ W_{\pm}(X_k, X) = \int_{X_k}^{X} dX \sqrt{2 \left[ U_{\pm}(X) - \frac{E}{\gamma} \right]}. \]

(3.9)

We have illustrated the general connection matrix scheme in the Figs. 2 and 3.

Let us consider a general example describing two non-symmetric potentials crossing at \( X = 0 \) point (2.1). When the parameter \( b \) entering the potential (2.1) is varied from 1 to \( \infty \), we recover the two known in the literature limiting cases, and come from two identical parabolic potentials to the case one-well and linear diabatic potentials crossing. This kind of the diabatic potentials crossing leads to the lower adiabatic potential in the form investigated in [2], and has qualitatively the same features as the model potential (1.1). If one neglects for a moment the upper adiabatic factor, aiming to study crossover behavior from coherent to incoherent tunneling upon increase of the parameter \( b \), the larger is this parameter \( b \), the larger will be the density of final states. The criterion for coherent-incoherent crossover found in [2] based on comparison of the transition matrix elements and the inter level spacings in the final state. The analogous criterion should hold for LZ level crossing problem, however in the latter case the tunneling transition matrix elements has to be multiplied by the adiabatic factor. Therefore the coherent - incoherent tunneling crossover region moves towards the more dense density of final states, and the larger \( U_{12} \) is the smaller will be the region for incoherent tunneling. For the sake of the skeptical reader it is worth to emphasize that the tunneling matrix element dependence on the Massey parameter \( \nu \) found above is valid for an arbitrary magnitude of the diabatic coupling (cf. the recent publication [38] where this matrix element has been calculated in the frame work of the perturbation theory, and only in the adiabatic and diabatic limits).

Owing to the non-adiabatic behavior of the system the tunneling matrix element \( H_{LR} \) is renormalized by the adiabatic factor. In the tunneling region from (3.2) we find this renormalization as
\[ H_{LR} \rightarrow H_{LRp}(\nu), \]

(3.10)
where the function $p(\nu)$ (2.18) is associated with the transition amplitudes between the diabatic potentials in the crossing region.

This renormalization tunneling factor varies from 0 to 1 upon increasing of the Massey parameter $\nu$. Again as we have found for the isolated double-well potential, in the limit

$$H_{LRp}(\nu) \ll \Delta_R,$$  

the spectrum consists of the set of the tunneling doublets and $L - R$ transitions are coherent ones. This criterion (3.11) replaces (1.4) for our case of the finite adiabatic coupling $U_{12}$.

Quite different situation occurs for the excited states. In the diabatic limit, the transition matrix element is increased with the Massey parameter $\nu$, and therefore at a given $b$ value, 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. To illustrate it let us study dynamics of the initial state of the system, prepared somehow in the ground vibrational state of the upper adiabatic potential

$$U^{(+)} = \frac{1}{2} + \frac{1 + b}{4b} X^2 + \left[U_{12}^2 + X^2 \left(1 + \frac{b - 1}{4} X^2 \right)^2 \right]^{1/2}. \quad (3.12)$$

Evidently the wave function $\psi^{(0)}$ of this state should be close to the harmonic oscillator function $n = 0$, with its minimum at $X = 0$, and its eigen-state $E_0$ dependent of $U_{12}$. The real part of the $E_0$ gives the oscillator vibration frequency $\omega_0$, and the imaginary part determines the decay rate $\Gamma_0$ of the state.

The spectral expansion of $\psi^{(0)}$ over the diabatic state eigen-functions $\{\psi_n\}$ can be found by the method proposed long ago by Zeldovich [27] (see also [2], where the method has been applied to find semiclassical solutions of the Schrödinger equation for 1D asymmetric double well potential) well adapted for quasi-stationary state wave function expansion over continuum spectrum functions. Note that for $b \gg 1$ all the states of the upper adiabatic potential (3.12) are placed in the same energy range that the $R$-well excited states. Since, as it is well known [1], the harmonic oscillator wave functions for $n \gg 1$ coincide with the semiclassical ones, we can represent the $R$-well wave functions in the vicinity of $E_0$ in the following form

$$\psi_n(X) = \begin{cases}  
A(k_n)\psi^{(0)}_n(X), |X| \simeq \lambda_0 \\
\sqrt{\frac{\pi}{k_n}} \sin(k_nX + \varphi(k_n)), X \gg \lambda_0
\end{cases}, \quad (3.13)$$

where $\lambda_0 \equiv \hbar/m\omega_0$ is the de Broglie wave length, corresponding the ground state oscillator wave function, $\psi^{(0)}_n$ are harmonic oscillator eigen - functions, $k_n = \sqrt{2mE_n}/\hbar$ is the wave vector, and the phase factor $\varphi(k_n)$ is defined as

$$\varphi(k_n) = k''_n - k'_n, \quad k'_n = \sqrt{2mE_0}/\hbar, \quad k''_n = k'_n \frac{\Gamma_0}{4E_0}. \quad (3.14)$$

The entering (3.13) amplitudes $A(k_n)$ are determined by the condition that the probability density flow from the quasi-stationary state to infinity should be constant (in fact this condition plays the role of the normalization condition for the quasi-stationary states [27]):

$$A^2(k_n) = \frac{2\hbar}{\pi} \sqrt{\frac{2E_n}{m}} \frac{\Gamma_0}{(E_n - E_0)^2 + \Gamma_0^2}. \quad (3.15)$$

We have shown in the Fig. 4 (for a fixed value of the potential shape controlling parameter $b \gg 1$ and various coupling strengths $U_{12}$) the spectral density expansion

$$S(E) = \sum_n |<\psi|\psi_n>|^2 \delta(E - E_n). \quad (3.16)$$

The spectrum of final states for $b \gg 1$ is a discrete one (although dense), and the envelope of the spectrum has a Lorentzian shape with a width $\Gamma_0$, which is determined by the non-adiabatic transition matrix element. The latter quantity has an oscillating dependence on $U_{12}$. Since the final state spectrum at $b \gg 1$ has only weak dependence on the non-adiabatic coupling $U_{12}$ we have almost constant spectral distribution but the number of the final states (relevant for the transition) is determined by $\Gamma_0$, and it oscillates with $U_{12}$. Analogously to the adiabatic transitions considered
According to the criterion, coherent tunneling should be destroyed when the density of final states is so high that been done long ago by Jortner and Bixon [35]. In this paper the authors have formulated the irreversibility criterion.

One qualitative answer to this question has or incoherent) depend on more subtle specific features of the potential energy profiles than merely energies of the same order). A question of primary importance is the understanding of how these two tunneling regimes (coherent and incoherent) decay of an initially prepared seemingly equilibrium configuration. Thus experimental data signal that two distinct dynamic regimes exist in bistable molecular systems. Moreover, barrier heights and potential well asymmetries in the systems manifesting different dynamic behaviors, are quite similar by their magnitudes (of the two distinct dynamic regimes). 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 relations 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 provide that for the measurement time dephasing or relaxation processes are not essential [28], [29], [30], demonstrated tunneling doublets dependence on well defined vibrational excitations. Thus this low-temperature behavior can be attributed with the coherent tunneling, and the advent of ultrafast lasers has provided physical chemists with a tool for studying these systems under nonequilibrium conditions.

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On the other hand there are also numerous examples (see e.g. [31], [32], [33], [34]) clearly showing exponential (incoherent) decay of an initially prepared seemingly equilibrium configuration. Thus experimental data signal that two distinct dynamic regimes exist in bistable molecular systems. Moreover, barrier heights and potential well asymmetries in the systems manifesting different dynamic behaviors, are quite similar by their magnitudes (of the same order). A question of primary importance is the understanding of how these two tunneling regimes (coherent or incoherent) depend on more subtle specific features of the potential energy profiles than merely energies of the characteristic points (like for example, our model potential (1.1), (2.1)). One qualitative answer to this question has been done long ago by Jortner and Bixon [35]. 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. Our aim in this paper is to formulate quantitatively the analogous criterion. One methodical comment seems in order here. Usual technique to analyze radiationless transitions is based on the perturbation theory in the adiabatic representation, and the nonadiabatic coupling operator is treated as a perturbation (see, e.g., [41], [42]). It is easy to understand, however, that this kind of the adiabatic perturbation theory is equivalent to isolated two level systems approach, which is valid only when the level displacements (due to tunneling or non-adiabatic transitions) are smaller than the inter-level spacing. Analogously for quasi-stationary states the adiabatic perturbation theory works when the level broadening (or decay rate) is smaller than the level spacing. Clearly it is not the case for the intermediate energy region we have studied in our paper. Note also that our connection matrix approach can be also formulated in terms of the Liouville-von Neumann equation for the density matrix, where so-called relaxational matrix should be chosen phenomenologically to mimic decay rate dependences on the energy and on the Massey parameter. But anyway to find those one has to solve the Schrödinger equation for the potential under consideration.

Our model appears to be a simplest one demonstrating that relatively small variation of the adiabatic coupling (at a level spacing scale which is small in comparison with potential barrier heights or well asymmetries) enables to change qualitatively dynamic behavior. Therefore, we conclude that dynamic irreversibility in the systems under investigations crucially depends on the final states density (and not on potential energy profiles directly). We believe we are the first to explicitly address this issue. To illustrate these phenomena we investigated coherent and incoherent investigations crucially depends on the final states density (and not on potential energy profiles directly). We believe we are the first to explicitly address this issue. To illustrate these phenomena we investigated coherent and incoherent tunneling in the conditions of crossing diabatic potentials. As a result of the coupling and level crossing avoiding, we get the asymmetric double-well lower adiabatic potential with a variable shape depending on a value of a continuous parameter $b$ (which describes in the limit $b = 1$ two identical parabolic diabatic potential crossing and in the limit $b \rightarrow \infty$ one-well and linear diabatic potentials crossing). The doublet structure of levels (generic for double-well potentials) is remained valid as long as the renormalized by the adiabatic coupling transition matrix element $H_{LR}$ (or tunneling splitting) is smaller than characteristic inter-level spacings $\Delta R$. We calculated the non-adiabatic factor, and found in the diabatic limit ($U_{12} \rightarrow 0$) $H_{LR}$ goes to zero, and in the adiabatic limit ($U_{12} \rightarrow \infty$) 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 the 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.

In an apparently unrelated development researches studying the problem of intermolecular energy redistribution discovered purely quantum energy flow between modes which would be otherwise uncoupled. The mechanism for such classically forbidden energy flow between degenerate vibrational modes arose from non-adiabatic couplings involving a sequence of intermediate states. In the various existing in the nature molecular systems the non-adiabatic coupling strengths $U_{12}$ can have fairly different magnitudes, thus we anticipate realizations of the both kinds of dynamic behavior, coherent and incoherent ones. Our model of the non-adiabatic transitions from the initially prepared quasi-stationary state $\psi(t)$ can be directly confronted to experimental data on super fast non-linear optical spectroscopy (see e.g., the monographs [39], [40]). The developed in this area technique allows to prepare a given initial quasi-stationary state by a suitable optical pumping pulse shape.

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Figure Captions.

Fig. 1
Crossing asymmetric parabolic diabatic potentials (adiabatic potentials for $U_{12} = 0.5$) are shown by the dashed lines:
(a) bound initial and final states ($b = 3$);
(b) bound initial and decay final states ($b = \infty$).

Fig. 2
Connection matrices for the tunneling energy region:
(a) in the WKB approach, where the trajectory has 4 linear turning points, and one crossing point. $M_{L}^{(\pm)}$ are the connection matrices for the isolated linear turning points, $L_{L/R}^{(c)}$ are the shift matrices (2.21) in the classically accessible regions, $L_{c}$ is the shift matrix (2.20), and $U_{c}$ is the connection matrix at the crossing point;
(b) in the instanton method, where the trajectory $E = 0$ passes through the second order turning point (the $L$ well potential minimum). In the $L$ well the WKB connection matrix should be replaced by the energy dependent connection matrix $M_{L}^{(2)}$ at the second order turning point [15]), corresponding to kink-anti-kink pair. The same manner the connection matrix for the $R$ well $M_{R}^{(2)}$ corresponds to so-called bounce [25].

Fig. 3
Connection matrices for the over-barrier and intermediate energy regions (in the latter region the connection matrices for the imaginary turning points are not shown).

Fig. 4
Spectral distributions for the initial state wave function (chosen as the ground state of the upper adiabatic potential) over the eigenfunctions of the model potential (1.1): $b = 1500$, $\gamma = 12$, and $U_{12} = 0.09, 0.15, 0.21, 0.28, 0.40$ for (a) - (e) figures respectively.

Fig. 5
Survival probability for the same as in Fig. 4 initial state.
(a) - solid line corresponds to the Fig. 4a; dashed line - to the Fig. 4b;
(b) solid line corresponds to the Fig. 4c, dashed line - to the Fig. 4d.

Fig. 6
Averaged over the recovering period survival probability shown in Fig. 5.
Fig. 2
Fig. 3
Fig. 5
Fig. 6