Instanton versus traditional WKB approach to Landau - Zener problem.

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Different theoretical approaches to the famous two state Landau - Zener problem are briefly discussed. Apart from traditional methods of the adiabatic perturbation theory, Born - Oppenheimer approximation with geometric phase effects, two-level approach, and momentum space representation, the problem is treated semiclassically also in the coordinate space. Within the framework of the instanton approach we present a full and unified description of 1D Landau-Zener problem of level crossing. The method enables us to treat accurately all four transition points (appearing at two levels crossing), while the standard WKB approach takes into account only two of them. The latter approximation is adequate for calculating of the transition probability or for studying of scattering processes, however it does not work for finding corresponding chemical reactions rates, where very often for typical range of parameters all four transition points can be relevant. Applications of the method and of the results may concern the various systems in physics, chemistry and biology.

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I. INTRODUCTION

At first sight, the title of this paper might sound perplexing. What else can be said about Landau - Zener (LZ) problem after numerous descriptions in both research and textbook literature? However, although theoretical (and experimental) investigations of different LZ systems began more than seventy years ago, it is still remains an active area of research. Various approaches to LZ problem have appeared separately in the literature (see e.g. by no means not a complete list of publications [1] - [67]), these references are not fully consistent with each other. We, therefore, think that it is important to collect and discuss all these approaches in one place. We will study the 1D LZ problem [1] of quantum mechanical transitions between the levels of a two-level system at the avoided level crossing. LZ theory treats a quantum system placed in a slowly varying external field. Naturally in such a condition the system adiabatically follows variation of an initially prepared discrete state until its time dependent energy level crosses another one. Near the crossing point evidently the adiabaticity condition is violated (like a semiclassical behavior is violated near turning points). The slow variation of the perturbation means that the duration of the transition process is very long, and therefore the change in the action during this time is large. In this sense the LZ problem is a semiclassical one (but with respect to time instead of a coordinate for standard semiclassical problems).

As is well known the problem presents the most basic model of non-adiabatic transition which plays very important role in many fields of physics, chemistry, and biology. Not surprisingly therefore that numerous monographs and uncountable papers have been devoted to this subject. In the literature there are roughly speaking three kinds of semiclassical modelling of LZ problem, namely:

- (i) two level system approach [2] - [8];
- (ii) adiabatic perturbation theory [9] - [21] (see also review paper [6]) ;
- (iii) momentum space representation [22] - [25].

Because different approaches have been proposed to study the LZ problem one of the immediate motivation of the present paper is to develop an uniform and systematic procedure for handling the problem. We will show that all three methods are equivalent for treating tunneling and over-barrier regions of parameters, and no one of them can be applied to study say intermediate region of parameters, where all four of the involving into LZ system states are relevant. To study this region is our main concern in this paper. A second question addressed here concerns so-called
connection matrices. At usual textbook treatment of the LZ problem, only the transition probabilities are calculated and expressed in terms of the genuine two-level LZ formula successively applied at each diabatic level intersection. Evidently such a procedure is an approximation for the general LZ problem including even in the simplest case at least 4 energy levels. To solve many important physical or chemical problems one must find the $4 \times 4$ (not only $2 \times 2$) connection matrices related these 4 states.

While our paper is not intended as a comprehensive review we detail here key results of the standard WKB and instanton approaches from our own researches and literatures within the context of different factors that we feel are important to studying LZ problem. Specifically we focus in the next section (II) on the Born - Oppenheimer approximation which is a benchmark to test semiclassical approximations. In section (III) we lay the foundation for treating LZ problem, namely - adiabatic perturbation theory. Section (IV) is devoted to the generalization of the instanton method enables us to investigate LZ problem in the momentum space. It is shown in this section that for a linear (in a $1D$ coordinate under consideration) potential WKB semiclassical wave functions in the momentum space coincide with the instanton wave functions. For the quadratically approximated (parabolic) potentials the instanton wave functions are exact and have no singularities (unlike WKB wave functions; remind that the same kind of relations hold for the WKB and instanton wave functions in the coordinate space [26] - [29]).

In this paper we are advocating for the instanton approach, but it is worth noting that, nevertheless, many important results have been obtained in the frame work of the WKB approach [1] -[8]. For example, one of the very efficient technique (so-called propagator method) was proposed and elaborated by Miller and his coworkers [34], [35], [36] (see also [26]). This approach uses semiclassic (van Fleck - Gutzwiller types) propagators, taking into account automatically in terms of the general WKB formalism, the contribution coming from the contour around a complex turning point. The accuracy of the WKB method can be improved considerably, [30] [2], [31], [5] (more recent references on so-called Laplace contour integration can be found also in [32]) by the appropriate choice of the integration path around the turning point, and it appears to be quite accurate for the tunneling and over-barrier regions, but it becomes nonadequate in the intermediate energy region. It has been overlooked in the previous investigations treating this region by a simple interpolation from the tunneling (with monotonic decay of the transition probability) to the over-barrier (with oscillating behavior) regions.

We present all details of the LZ problem for two electronic states in section V using the instanton description of LZ problem in the coordinate space. In the section the basic two second order differential (Schrödinger) equations to be dealt with are written in the so-called diabatic state representation (i.e. in the basis of "crossed" levels). Neglecting higher order space derivatives we find asymptotic solutions, and using adiabatic - diabatic transformation we match the solutions in the intermediate region. The complete scattering matrix for the LZ problem is derived in the section VI. In the section VII we derive the quantization rules for crossing diabatic potentials and discuss shortly the application of the obtained results to some particular models of level crossings which are relevant for the interpretation and description of experimental data on spectroscopy of non-rigid molecules, on inelastic atomic collisions [33], non-radiative transitions arising from "intersystem" crossings of potential energy surfaces in molecular spectroscopy and chemical dynamics (see e.g. [26] and references herein). In the last section VIII we draw our conclusions.

Throughout what follows we will consider $1D$ case only. The LZ problem for 1D potentials coupled with the thermal bath of harmonic oscillators is shown to reduced to a certain renormalization of the Massey parameter, where entering the expression for this parameter longitudinal velocity is decreased due to coupling to transverse oscillations (see [26] and references herein, and for more recent references also [66], [67]). Of course the energetic profile of any real system is characterized by a multidimensional surface. However, it is often possible to identify a reaction coordinate, such that the energy barrier between initial and final states is minimized along this specific direction, and, therefore, effectively one can treat the system under consideration as $1D$. In certain systems, the physical interpretation of the reaction coordinate is immediate (e.g. the relative bond length in two diatomic molecules), but sometimes it is not an easy (if possible at all) task, because of the many possibilities involved. The latter (multidimensional) case will be studied elsewhere. Unfortunately the accuracy of the WKB method near the barrier top is very poor to make any numbers realistic and it is one more motivation to use the alternative to WKB semiclassical formalism - extreme tunneling trajectory or instanton technique.

II. BORN - OPPENHEIMER APPROXIMATION.

It may be useful to illustrate the essential physics of the LZ problem starting with a very well known picture corresponding to the Born - Oppenheimer approximation [37], [1] which leads to the separation of nuclear and electronic motions, and the approximation is valid only because electrons are so much lighter than nuclei and therefore move so
much faster. Thus the small parameter of the Born - Oppenheimer approximation is
\[
\lambda = \left( \frac{m_e}{m} \right)^{1/4} \ll 1,
\] (2.1)
where \( m_e \) and \( m \) are electronic and nuclear masses respectively. On the other hands the semiclassical parameter
\[
\gamma = \frac{m\Omega a^2}{\hbar} \gg 1,
\] (2.2)
where \( a \) is a characteristic length of the problem, and the characteristic nuclear vibration frequency \( \Omega \propto m^{-1/2} \), therefore \( \gamma \propto \lambda^{-2} \). From this simple fact important conclusions are arrived at. Indeed one can satisfy the semiclassical condition \( \gamma \gg 1 \) by assuming formally \( \hbar \to 0 \) or equivalently \( \lambda \to 0 \). This correspondence allows us to apply on the same footing the separation of scales for nuclear and electronic motions either the Born - Oppenheimer or the semiclassical approximation.

In the traditional Born - Oppenheimer approach the solution \( \Psi \) to the full (i.e. including electronic Hamiltonian \( H_e \), depending on electronic coordinates \( r \), and nuclear Hamiltonian depending on nuclear coordinates \( R \) ) Schrödinger equation is presented in the form of an expansion over the electronic Hamiltonian eigen functions \( \phi_n \)
\[
\Psi = \sum_n \Phi_n(R)\phi_n(r, R).
\] (2.3)
The electronic eigen values \( E_n \) depends on the nuclear coordinates, and the expansion coefficients \( \Phi_n(R) \) is determined by the Born - Oppenheimer equations
\[
\left[ -\frac{\hbar^2}{2m} \nabla_r^2 + E_n(R) + \frac{\hbar^2}{2m} \sum_{k \neq n} A_{nk} A_{kn} - E \right] \phi_n = -\frac{\hbar^2}{2m} \sum_{k, m \neq n} (\delta_{nk} \nabla R - i A_{nk}) (\delta_{km} \nabla R - i A_{km}) \phi_m,
\] (2.4)
where for \( m \neq k \)
\[
A_{mk} = i \langle \phi_m | \nabla R | \phi_k \rangle,
\] (2.5)
and all the diagonal matrix elements \( A_{nn} = 0 \).

Thus from (2.4) we can find that in the electronic eigen state \( E_n \), the nuclei are moving in the effective potential
\[
U_n(R) = E_n(R) + \frac{\hbar^2}{2m} \sum_{k \neq n} A_{nk} A_{kn},
\] (2.6)
and transitions between the electronic states \( n \) and \( m \) are related to the non-adiabatic operator in the r.h.s. of (2.4).

This simple observation allows us to rewrite the effective potential (2.6) as
\[
U_n(R) = E_n(R) - \frac{\hbar^2}{2m} \sum_{m \neq n} \frac{\langle \phi_n | \nabla R H_e | \phi_m \rangle \langle \phi_m | \nabla R H_e | \phi_n \rangle}{(E_n - E_m)^2},
\] (2.7)
and from this seemingly trivial expression we arrive at the following important conclusions:

(i) corrections to \( E_n \) have the same order \( \mathcal{O}(\gamma^{-2}) \) as the ratio of the nuclear kinetic energy to the potential;

(ii) off-diagonal matrix elements of the non-adiabatic perturbation operator are also small (\( \propto \mathcal{O}(\gamma^{-2}) \)), and the fact is formulated as the so-called adiabatic theorem stating that at the adiabatic perturbations (\( \lambda \to 0 \)) there are no transitions between unperturbed states.

Since the non-adiabatic effects are characterized by the only small parameter \( \gamma^{-1} \) (the semiclassical parameter), the effects can be described in the frame work of semiclassical approaches (e.g. WKB or instanton ones). However, one has to bear in mind the main drawback problem of the Born - Oppenheimer method. Indeed the approximation assumes that the electronic wave functions are real valued ones and formed the complete basis, but it is impossible to construct such a basis in the whole space including classically accessible and forbidden regions.

If one relaxes the requirement to have a real valued basis, the diagonal matrix elements \( A_{nn} \neq 0 \), and the effective adiabatic part of the Born - Oppenheimer Hamiltonian takes the form
\[
\hat{H}_n = U_n(R) + \frac{\hbar^2}{2m} (\nabla R - i A_{nn}(R))^2
\] (2.8)
analogously to the Hamiltonian of a charged particle in a magnetic field \( B \propto \nabla R \times A_{nn} \). Therefore one can change the phases of the electronic and nuclear wave functions

\[
\phi_n \rightarrow \phi_n \exp(i\chi_n(R)) \quad \Phi_n \rightarrow \Phi_n \exp(-i\chi_n(R)),
\]

by changing respectively the "vector potential"

\[
A_{nn}(R) \rightarrow A_{nn}(R) + \nabla R \chi_n(R).
\]

Thus we confront to an important and, at times, mysterious concept of the geometrical (or Berry) phase factor that a quantum mechanical wave function acquires upon a cyclic evolution [38] - [47]. 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 (for more details related to the geometric phase for the Born - Oppenheimer systems, see e.g. the review article [48]). The phenomenon (which was manifested itself originally as a certain extra phase shift, appearing upon some external parameter cyclic evolution) has been generalized for the non-adiabatic, non-cyclic, and non-unitary cases [49], [50], although the most of the Berry phase applications concern the systems undergoing the adiabatic evolution (see e.g. the review article [51]). Note also that apart from the Berry phase some higher order corrections to the Born - Oppenheimer approximation (traditionally slightly confusing referred as geometric magnetism or deterministic friction, see [52]) also occur. The practically useful application of the Berry phase conception is the energy level displacements predicted in [53] and observed by NMR [54].

The essential physics of the phenomena can be illustrated as follows. There are two subsystems, the fast and the slow ones. The fast subsystem acquires the Berry phase due to the evolution of the slow subsystem. In own turn, there is say a feedback effect of the geometric phase on the slow subsystem. As a result the latter one is framed by a gauge field affecting its evolution. The gauge field produces additional forces (Lorentz-like and electric field-like ones) which have to be included into the classical equation of motion. In the case of stochastic external forces (e.g. from surrounding thermal fluctuation media), the Berry phase produces some level broadening for the fast subsystem. In the limit of low temperatures and strong damping, the slow subsystem dynamics can be described by the Langevin type equations [55]. The general message we can learn from this fact, is that the geometric phases are sources of the dissipative processes for LZ systems.

Thanks to its fundamental origin, this geometric phase has attracted considerable theoretical and experimental attention, however, its experimentally observable consequences until now have been scarce. Therefore each opportunity of improving this situation is worth trying. In this respect the Born - Oppenheimer geometrical phase provides a unique opportunity for its observation since it must appear as a non-adiabatic contribution in a standard Bohr - Sommerfeld quantization rule

\[
S_n^0 + \chi_n = 2\pi \hbar,
\]

where \( S_n^0 \) is the adiabatic action.

Note that care must be taken when \( |E_n(R) - E_m(R)| \) becomes smaller with respect to the characteristic nuclear oscillation energy \( \hbar \Omega \). It means that in the adiabatic representation (2.4) one may not consider the non-adiabatic interaction energy as a small perturbation. Fortunately in the limit

\[
|E_n(R) - E_m(R)| < \hbar \Omega
\]

we can start from the other limit with crossing weakly coupled diabatic states, and consider the adiabatic coupling as a perturbation. Thus we need the adiabatic - diabatic transformations enabling us to perform the procedure explicitly, which read for the wave functions

\[
\tilde{\Phi}(R) = \exp(i\theta \sigma_y)\Phi(R),
\]

and for the Hamiltonians

\[
\tilde{H} = \exp(i\theta \sigma_y)H \exp(-i\theta \sigma_y),
\]

where \( (H, \Phi) \) and \( (\tilde{H}, \tilde{\Phi}) \) are the adiabatic and diabatic representations respectively, \( \sigma_y \) is the corresponding Pauli matrix, and \( \theta \) is the parameter of the adiabatic - diabatic transformation (so-called adiabatic angle).

To illustrate how it works let us consider two coupled \( (U_{12} \) is the coupling energy) crossing effective electronic potentials \( U_1(R) \) and \( U_2(R) \). The corresponding adiabatic and diabatic Hamiltonians are

\[
H = -\frac{\hbar^2}{2m} (\nabla R)^2 + \frac{1}{2}(U_1 + U_2) + \\
\left( \frac{1}{2}(U_1 - U_2) \cos 2\theta(R) + U_{12} \sin 2\theta(R) \right) \sigma_3 + \frac{1}{2} \left( -\frac{1}{2}(U_1 - U_2) \sin 2\theta(R) + U_{12} \cos 2\theta(R) \right) \sigma_1,
\]

\[
\tilde{H} = \exp(i\theta \sigma_y)H \exp(-i\theta \sigma_y),
\]
and

\[ \hat{H} = -\frac{\hbar^2}{2m}(\nabla_R)^2 + \frac{1}{2}(U_1 + U_2) + \frac{1}{2}(U_1 - U_2)\sigma_3 U_{12}\sigma_1, \]  

(2.15)

where \( \sigma_{1,2,3} \) are the Pauli matrices, and the adiabatic angle is chosen to eliminate the principle interaction term between the adiabatic states

\[ \cot 2\theta(R) = \frac{U_1 - U_2}{2U_{12}}. \]  

(2.16)

The adiabatic - diabatic transformation can be brought also into more elegant form [16], [56]

\[ (\nabla_R - i\hat{A})\hat{T} = 0, \]  

(2.17)

where \( \hat{T} \) is the sought for transformation matrix, and the matrix \( \hat{A} \equiv A_{nn} \) was introduced above (see (2.5)). The formal solution of Eq. (2.17) can be represented as a contour integral

\[ \hat{T}(s) = \hat{T}(s_0) \exp \left( -\int_{s_0}^s \hat{A}(s')ds' \right), \]  

(2.18)

where \( s_0 \) and \( s \) stem for the initial and final points of the contour, and the solution (2.18) determines uniquely the transformation matrix \( \hat{T} \) for the curl-less field \( \hat{A} \)

\[ \hat{T}(t_0) = \hat{D}\hat{T}(0), \]  

(2.19)

and the diagonal matrix \( \hat{D} \) can be found from (2.17) and can be expressed in terms of the geometric phase factor

\[ D_{kn} = \delta_{kn} \exp(i\chi_k). \]  

(2.20)

These two relations (2.11) and (2.20) provide a complete account of the non-adiabatic transitions, the cornerstone of the LZ problem. Besides (2.11), (2.20) show that the geometrical Born - Oppenheimer phases occur from the diabatic potentials crossing points, and enter quantization rules additively with the contributions from the turning points. Therefore, our main conclusion from this section is that non-adiabatic phenomena should be (and can be) included into the general semiclassical approach scheme by use of the corresponding connection matrices [57] (see also [29]) for the appropriate combinations of crossing and turning points of the problem.

### III. ADIABATIC PERTURBATION THEORY.

It is almost a common student wisdom nowadays that any solution to the adiabatically time dependent Schrödinger equation can be represented as an expansion over the complete set of stationary (time independent) eigen functions [1]. For the case under investigation (two level crossing for the electronic Hamiltonian \( H_e(r, t) \)), this expansion reads

\[ \Psi(r, t) = c_1(t)\phi_1(r) + c_2(t)\phi_2(r), \]  

(3.1)

where \( \phi_{1,2} \) are the stationary with respect to a nuclear motion wave functions. The time dependent Schrödinger equation can be rewritten exactly in the form of two first order (over time derivatives) equations for \( c_1 \) and \( c_2 \)

\[ i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix} = \begin{pmatrix} \hat{H}_{11} & \hat{H}_{12} \\ \hat{H}_{21} & \hat{H}_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \]  

(3.2)

where

\[ \hat{H}_{kk'} = \langle \phi_k | \hat{H}(t) | \phi_{k'} \rangle, \quad k, k' = 1, 2 \]  

(3.3)

are the matrix elements for the diabatic Hamiltonian.

The following phase transformation (see, [10], [6], [8])

\[ c_k(t) = a_k(t) \exp \left( -\frac{i}{\hbar} \int \hat{H}_{kk}(t)dt \right) \]  

(3.4)
reduces (3.2) to the coupled first order equations

\[ i\hbar \dot{a}_1 = \tilde{H}_{12} a_2 \exp \left( i \int \Omega_{12}(t) dt \right), \quad i\hbar \dot{a}_2 = \tilde{H}_{21} a_1 \exp \left( -i \int \Omega_{12}(t) dt \right), \tag{3.5} \]

where

\[ \Omega_{12} = \frac{1}{\hbar} (\tilde{H}_{22} - \tilde{H}_{11}). \tag{3.6} \]

However the slightly different phase transformation

\[ c_k(t) = \tilde{\Phi}_k(t) \exp \left( \frac{i}{2\hbar} \int (\tilde{H}_{11} + \tilde{H}_{22}) dt \right) \tag{3.7} \]

keeps the second order Schrödinger like equations forms for the diabatic functions \( \tilde{\Phi}_{1,2} \)

\[ \hbar^2 \frac{d^2 \tilde{\Phi}_1}{dt^2} - \left( \frac{(\tilde{H}_{11} - \tilde{H}_{22})}{2} + \tilde{H}_{12} \tilde{H}_{21} + \frac{i\hbar}{2} \frac{d}{dt} (\tilde{H}_{11} - \tilde{H}_{22}) \right) \tilde{\Phi}_1 = 0, \tag{3.8} \]

To clarify the mapping of this time dependent perturbation theory to the two level crossing problem, and the Born-Oppenheimer approach described in the previous section II, let us consider the two states Born-Oppenheimer equations in the diabatic representation. From (2.15) for one active space coordinate \( X \), we have

\[ -\frac{\hbar^2}{2m} \frac{d^2 \tilde{\Phi}_1}{dX^2} + (\tilde{H}_{11} - E) \tilde{\Phi}_1 = \tilde{H}_{12} \tilde{\Phi}_2 = 0, \tag{3.9} \]

and

\[ -\frac{\hbar^2}{2m} \frac{d^2 \tilde{\Phi}_2}{dX^2} + (\tilde{H}_{22} - E) \tilde{\Phi}_2 = \tilde{H}_{21} \tilde{\Phi}_1 = 0. \tag{3.10} \]

The change of the variables

\[ \tilde{\Phi}_{1,2} = \exp(i k_0 X) c_{1,2}, \quad k_0^2 = \frac{2mE}{\hbar^2}, \tag{3.11} \]

transforms the two Born-Oppenheimer equations (3.9), (3.10) into the two level crossing equation (3.2) for the slow time dependent perturbations if one could neglect the second order derivatives \((\hbar^2/2m)d^2c_{1,2}/dX^2\) and to replace the time derivative by \(vd/dX\) \((v = \sqrt{2E/m}\) is velocity). Obviously we recognize the standard semiclassical approach in the afore-described procedure.

The same kind of the mapping can be performed also for the adiabatic amplitudes \( C_{1,2}(t) \) which are related with the diabatic amplitudes \( c_{1,2}(t) \) by the adiabatic-diabatic transformation matrix depending on the adiabatic angle \( \theta \)

\[ \begin{pmatrix} C_1(t) \\ C_2(t) \end{pmatrix} = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}, \tag{3.12} \]

The corresponding to (3.2) set of the first order equations in the adiabatic basis

\[ \begin{pmatrix} \dot{C}_1 \\ \dot{C}_2 \end{pmatrix} = \begin{pmatrix} H_{11} & -i\dot{\theta} \\ i\dot{\theta} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}, \tag{3.13} \]

where the non-adiabatic coupling coefficient \( \dot{\theta} \) can be related to the off-diagonal operator \( A_{12} \) (2.5) (or to the geometrical phase, see the previous section II)

\[ i\dot{\theta} = A_{12} \equiv i\langle \phi_1 | \dot{\phi}_2 \rangle. \tag{3.14} \]

The transformation (3.11) enables to reduce the Born-Oppenheimer equations (for the nuclear wave functions \( \Phi_{1,2} \) in the adiabatic representation) to (3.13) if and only if: (i) in the spirit of the semiclassical approach to neglect the second order derivatives ; (ii) to keep only \( \propto k_0 \) terms in the non-adiabatic matrix elements (i.e. neglecting higher
order over $1/k_0$ contributions). Expressions (3.12) - (3.14) do allow an entry point into the adiabatic perturbation theory developed by Landau [1] and Dykhne [10], [11] (see also [15], [16]). We will closely follow the same method.

One can make one step further and to find the combination of the two level system amplitudes $a_{1,2}$ (3.4), (3.5)

$$Y(t) = \Omega_{12}^{-1/2} \exp \left( -\frac{i}{2} \int \Omega_{12} dt \right) a_1 + i \Omega_{12}^{-1/2} \exp \left( \frac{i}{2} \int \Omega_{12} dt \right) a_2,$$

(3.15)
satisfying to the simple equation

$$\ddot{Y}(t) + \frac{\Omega_{12}^2}{4} Y = 0,$$

(3.16)

identical to (3.8), and the both describe oscillations around the crossing point in the adiabatic potential (inverted adiabatic barrier). Therefore formally the adiabatic perturbation theory reduces the level crossing problem to the well known quantum mechanical phenomenon - over-barrier reflection. Moreover for the latter problem the reflection coefficient in a full agreement with the adiabatic theorem is 1.

Since in $1D$ case evidently two adiabatic potentials have no real crossing points, the crossing is possible only at complex values $X$ or $t$

$$\Omega_{12}(\tau_c) = 0; \quad U_1 - U_2 = \pm iiU_{12}|_{t=\tau_c}.$$

(3.17)

In the vicinity of these points from (3.6)

$$\Omega_{12} \propto (t - \tau_c)^{1/2},$$

(3.18)

therefore

$$\int \Omega_{12} dt \simeq \frac{2}{3} (t - \tau_c)^{3/2},$$

(3.19)
i.e. the crossing points are square root bifurcation points for the function $\Omega_{12}(t)$. Using Exp. (3.19) we depicted in the Fig. 1 the Stokes and anti-Stokes lines for the equation (3.16). The diagram shown in this figure is identical to that corresponding to the treated semiclassical over-barrier reflection problem with the linear turning points. The transition probability $P_{12}$ in the main approximation is determined by the integration over the contour $C(\tau_c)$ going around the bifurcation point $\tau_c$

$$P_{12} \simeq \exp \left( \frac{2}{\hbar} \oint_{C(\tau_c)} (H_{11} - H_{22}) dt \right).$$

(3.20)

In the simplest form of the LZ problem the diabatic potentials are assumed as the linear functions of $t$ or (what is the same because $t = X/v$) $X$ (see Fig. 2 for the illustration)

$$U_{1(2)} = U^\# \pm FX.$$

(3.21)

Putting (3.21) into the general expression for the transition probability (3.20) we find for this case

$$P_{12} \simeq \exp(-2\pi\nu),$$

(3.22)

where $\nu = U_{12}^2/2\hbar v F$ is so-called Massey parameter, and the velocity $v = \sqrt{2|E - U^#|/m}$.

Some comments about the range of the validity of the approximation seem in order. A question of primary importance for the LZ problem is related to the semiclassical nature of the phenomenon. To illustrate it let us note that for $\Omega_{12}^2 = U_{12}^2 + v^2 F^2 X^2$, the Eq. (3.16) is the Weber equation with respect to the reel point $X = 0$ (diabatic potentials crossing point). Evidently, this correspondence of two complex conjugated linear crossing points $\pm \tau_c$ and one reel $X = 0$ crossing point for the Weber equation is the same as that (in the standard semiclassical treatment of the Schrödinger equation) for two linear and one second order turning points. Thus by the same manner as for any semiclassical problem, one can apply to LZ problem WKB or instanton methods. Let us compare the accuracy of the both approaches. If $|E - U^#| \gg \hbar \Omega$ (remind that $\Omega$ is a characteristic frequency of the adiabatic potentials), the WKB method considering for this problem two isolated linear turning points works quite well (it is the limit of $k_0 a \gg 1$, corresponding to the adiabatic approximation). If it is not the case we have to use the diabatic representation.
IV. INSTANTON METHOD IN MOMENTUM SPACE.

This is not the place to explain the instanton method in details. However, in a stripped down version the approach can be viewed as follows (see [26] - [29], [58], [59]). The recipe to find the instanton is based on the minimization of the functional of classical action in the space of paths connecting the minima in the upside-down potential. As it is well known [1] the expansion of an arbitrary wave function $\Psi(x)$ in terms of the momentum eigenfunctions is simply a Fourier integral

$$\Psi(x) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \exp(\frac{ipx}{\hbar})\Phi(p)dp.$$  \hspace{1cm} (4.1)

The wave function in the momentum representation $\Phi(p)$ in own turn can be written down in the semiclassical form

$$\Phi(p) = A(p) \exp(-\frac{iW(p)}{\hbar}),$$  \hspace{1cm} (4.2)

where the action $W(p)$ is determined by a classical trajectory $x_0(p)$ according to the definition

$$\frac{dW}{dp} = x_0(p).$$  \hspace{1cm} (4.3)

We use dimensionless variables: for the energy $\epsilon = E/\Omega_0$, for the potential $V = U/\gamma\Omega_0$, and for the coordinate $X = x/a_0$, where $E$ and $U$ are corresponding dimensional values for the energy and for the potential, $a_0$ 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. The dimensionless momentum can be defined as

$$P = \frac{pa_0}{\gamma\hbar},$$  \hspace{1cm} (4.4)

where $\gamma$ is semiclassical parameter (remind that $\gamma \equiv m\Omega_0a_0^2/\hbar$, where $m$ is a mass of a particle, and we believe that $\gamma \gg 1$).

Introducing the semiclassical form of the wave function in momentum representation (4.2) into the standard one particle 1D Schrödinger equation, one can transform it into the form

$$\left[ \frac{d^2}{dp^2} + 2\hat{V}\left(X_0 + \frac{1}{\gamma} \frac{d}{dP}\right) - \frac{2}{\gamma} \epsilon \right] A(P) = 0.$$  \hspace{1cm} (4.5)

In the momentum space $\hat{V}$ is a potential energy operator and it can be expanded into a semiclassical series over $1/\gamma$ (or what is the same, over $\hbar$, and further we will set everywhere $\hbar = 1$, measuring energies in the units of frequency, except at some intermediate equations where it is necessary for understanding). The expansion allows us to consider $\hat{V}$ as a function $V$ of two independent variables $X_0$ and $d/dP$, and one can get finally

$$V\left(X_0 + \frac{i}{\gamma} \frac{d}{dP}\right) = V(X_0) + \frac{i}{\gamma} \left( \frac{dV}{dX_0} \frac{d}{dP} + \frac{1}{2} \frac{d^2V}{dX_0^2} \frac{d^2}{dP^2} \right) + \left( \frac{i}{\gamma} \right)^2 \left[ \frac{d^3V}{dX_0^3} \frac{d^3}{dP^3} - \frac{1}{3} \frac{d^2V}{dX_0^2} \frac{d^2}{dP^2} \right] + ....,$$  \hspace{1cm} (4.6)

where the ellipsis represents all higher order expansion terms.

Accordingly to the general semiclassical rules from (4.5) and (4.6) one can easily find that the first and the second over $\gamma^{-1}$ order terms become identically zero, if the energy dependent trajectory $X_0(P)$ is determined by the equation

$$P^2 + 2V(X_0) = \frac{2\epsilon}{\gamma},$$  \hspace{1cm} (4.7)

and so-called transport equation (TE)

$$\frac{dV}{dX_0} \frac{dA}{dP} + \frac{1}{2} \frac{d^2V}{dX_0^2} \frac{d^2W}{dP^2} A,$$  \hspace{1cm} (4.8)
is also satisfied. The solution of TE (4.8) can be found explicitly, and it reads

$$A = \left( \frac{dV}{dX_0} \right)^{-1/2}.$$  \hspace{1cm} (4.9)

It follows from (4.9) that the semiclassical WKB wave function (4.2) has singularities in all stationary points of the potential $V$, i.e. these points are the turning points in the momentum space. It illustrates fundamental difficulties of the WKB procedure, i.e. how to match the solutions which become singular on caustic lines separating manifolds in phase space with real and imaginary momenta.

To illustrate also the second drawback of the WKB method let us consider the linear $(V = FX)$ and harmonic $(V = X^2/2)$ potentials. The trajectories $X_0(P)$ can be trivially determined from (4.7). For the linear potential, $X_0(P)$ is the inverted parabola with the maximum (the top of the inverted parabola) $X_{0m} = \epsilon F/\gamma$ at $P = 0$. The left and the right branches of the parabola correspond to the opposite motion directions in the classically accessible region $X_0 < X_{0m}$. The semiclassical WKB wave function in the momentum space for the linear potential

$$\Phi(P) = \frac{1}{\sqrt{F}} \exp\left( -i \frac{P}{F} \left( \epsilon P - \gamma \frac{P^3}{6} \right) \right),$$  \hspace{1cm} (4.10)

is the Fourier transform of the coordinate space Airy function. For the harmonic potential the corresponding trajectories (4.7) are the ellipses and the wave functions in the both spaces (momentum and coordinate) have the same functional form. It is worthwhile to note that although the WKB functions are not exact, the corresponding eigenvalues coincide with the exact quantum mechanical ones.

As we have recently shown [27] - [29], one can successfully attack many important semiclassical problems by the instanton method. Having in mind in this section momentum space let us remind for the sake of convenience the main ideas of the instanton approach. The first step of the approach derived in [58] and [59] is so-called Wick rotation of a phase space corresponding to a transformation to imaginary time $t \rightarrow -it$. At the transformation, the both, potential and kinetic, energies change their signs, and Lagrangian is replaced by Hamiltonian in the classical equation of motion. In the momentum space the low energy instanton wave functions can be constructed using Wick rotation in the momentum space (i.e. the transformation $P \rightarrow iP$) and besides the term with the energy $\epsilon$ in (4.7) should be removed from this equation and taken into account in the TE (4.8). The trajectory $X_0(P)$ in the instanton formalism describes zero energy motion in the classically forbidden region of the momentum space where the wave function has a form

$$\Phi(P) = \left( \frac{dV}{dX_0} \right)^{-1/2} Q(P) \exp(-\gamma W(P)), $$  \hspace{1cm} (4.11)

and additional prefactor $Q(P)$ which has appeared in (4.11) can be represented as

$$\ln Q(P) = \epsilon \int \left( \frac{dV}{dX_0} \right)^{-1} dP. $$  \hspace{1cm} (4.12)

In the particular case of a linear over 1D space coordinate potential $(V(X) = FX)$ the instanton and WKB functions have the same form. For an arbitrary (n-order) anharmonic potential, the Schrödinger equation in the momentum space is reduced to the n-th order differential equation. However the derivatives of the n-th order decrease proportional to $\gamma^{-n}$, and therefore corresponding terms can be taken into account perturbatively. A rigorous mathematical method to perform this procedure (we will use in our paper) has been developed by Fedoryuk [68] - [70].

To illustrate the instanton approach let us consider the simplest form of the LZ problem depicted in the Fig. 3 (see all notation in the figure caption). For the linear with arbitrary line slopes potentials in the diabatic state representation one has two second order coupled equations

$$-\frac{d^2 \Theta_1}{dX^2} = \gamma^2 (\alpha + f_1 X) \Theta_1 = \gamma^2 v \Theta_2;$$  \hspace{1cm} (4.13)

$$-\frac{d^2 \Theta_2}{dX^2} = \gamma^2 (\alpha + f_2 X) \Theta_2 = \gamma^2 v \Theta_1,$$

where $\Theta_{1,2}$ are the eigenfunctions of the corresponding states and all other notation are introduced according to the Fig. 3, namely

$$\Omega^2 = \frac{a^2 F^2}{mU_{12}}, \ F = \sqrt{F_1 F_2}, \ \gamma = \frac{a^3 F m^{1/2}}{U_{12}^{1/2}}, \ \alpha = 2 \frac{U_0 - E}{\gamma \Omega}, \ f_{1,2} = 2 \frac{a F_{1,2}}{\gamma \Omega}, \ v = 2 \frac{U_{12}}{\gamma \Omega}.$$
The equations (4.13) can be transformed into the momentum space (they formed a coupled linear differential equation system) and after that can be rewritten as one second order equation

\[
\frac{d^2 \Psi_1}{dk^2} + q(k) \Psi_1(k) = 0,
\]

(4.14)

where we introduced

\[
\Psi_1 = \Phi_1 \exp \left[ \frac{\gamma \alpha^{3/2}}{2} \left( \frac{1}{f_1} + \frac{1}{f_2} \right) \left( k + \frac{k^3}{3} \right) \right],
\]

(4.15)

and \( \Phi_1 \) is the Fourier transformed of \( \Theta_1 \), \( k = P/\gamma \sqrt{\alpha} \), and \( q(k) \) is a fourth order characteristic polynomial

\[
q(k) = \lambda^2 (1 + k^2)^2 + 2\lambda (ik - 2\nu),
\]

(4.16)

dependent on two parameters

\[
\lambda = \frac{1}{2} \gamma \alpha^{3/2} \left( \frac{1}{f_1} - \frac{1}{f_2} \right), \quad \nu = \frac{\gamma \nu^2}{2(f_1 - f_2)\sqrt{\alpha}}.
\]

(4.17)

The first parameter \( \lambda \) in the momentum representation plays the role of the new semiclassical parameter, the second one is the known (and already defined in (3.22)) Massey parameter.

Fortunately all roots of the characteristic polynomial (4.16) can be found analytically quite accurately in the most interesting physically region of parameters. To simplify expressions (keeping complete physical content) we present results only for the simplest case (symmetric slopes of the diabatic potentials) \( f_1 = -f_2 = f \). In the classically forbidden region \( U^\# - E > 0, \alpha > 0 \), at \( \lambda \gg 1 \) (i.e. equivalently at \( \alpha \gg (f/\gamma)^{2/3} \)), all the four roots of the polynomial are close to \( \pm i \)

\[
k_1^\pm = i \left( 1 \pm \sqrt{\frac{1 + \nu}{2\lambda}} \right), \quad k_2^\pm = \pm \sqrt{\frac{1 - \nu}{2\lambda}} - i.
\]

(4.18)

In the classically accessible region \( (U^\# - E < 0, \alpha < 0) \), the roots are close to \( \pm 1 \), if \( \lambda \gg 1 \) (or if \( -\alpha \gg (f/\gamma)^{2/3} \))

\[
k_1^\pm = \pm \frac{\sqrt{1 + \nu^2 + \tilde{\nu}}}{4\lambda}^{1/2}, \quad k_2^\pm = -1 \pm \left( \frac{\sqrt{1 + \nu^2 - \tilde{\nu}}}{4\lambda} \right)^{1/2},
\]

(4.19)

(the tilde sign means that in the corresponding quantity \( \alpha \) should be taken by its modulus, i.e. at \( |\alpha| \)).

Found above the set of the roots of the characteristic polynomial (4.16) in the classically forbidden (4.18) and in the classically accessible (4.19) regions is formally equivalent to the corresponding transition or turning points for the system of two potential barriers or two potential wells respectively. Thus we can use all known for these cases WKB and instanton results (see e.g. for all details our recent publications [29] and references herein). Since in the semiclassical treatment we usually concerned only with the asymptotic solutions and their connections via transition or turning points on the complex plane, the famous Stokes phenomenon [57], [30] of asymptotic solutions plays an essential role, and the distribution of the transition points (which are nothing but the zero points of the characteristic polynomial) and Stokes and anti-Stokes lines, dictates the phenomenon. We show all the lines emanating from linear turning points in Fig. 2. In the case when the roots formed a pair of close linear turning points, one can replace each such a pair by one second order turning points. The corresponding Stokes and anti-Stokes lines are depicted in the Fig. 4.

In the classically forbidden region the instanton wave functions can be found using the roots (4.18)

\[
\Phi_1^+ = \frac{(1 - ik)^{\nu - 1}}{(1 + ik)^{\nu + 1}} \exp \left( i\gamma \left( k + \frac{k^3}{3} \right) \right), \quad \Phi_1^- = \frac{(1 - ik)^{-\nu}}{(1 + ik)^{-\nu}} \exp \left( -i\gamma \left( k + \frac{k^3}{3} \right) \right).
\]

(4.20)

At \( |k| \to \infty \) the function \( \Phi_1^+ \) decreases proportional to \( |k|^{-2} \), and \( \Phi_1^- \) is reduced to the Airy function [71], [73]. In the vicinity of the second order turning points \( k = \pm i \), the fourth order characteristic polynomial is reduced to the second order one, and the equation (4.14) is reduced to the Weber equation with the known fundamental solutions [71]

\[
D_{-\nu}(\pm 2\sqrt{\lambda}(k + i)),
\]
at $|k + i| \to 0$ and

$$D_{-\nu-1}(\pm 2\sqrt{\lambda}(k-i)), \quad \text{at } |k - i| \to 0.$$  

The same procedure applied to the classically accessible region leads to the solutions

$$\Phi^+_i = \frac{(1-k)^{i\nu-1}}{(1+k)^{i\nu+1}} \exp \left( i\gamma \left( k - \frac{k^3}{3} \right) \right), \quad \Phi^-_i = \frac{(1+ik)^{i\nu}}{(1+ik)^{i\nu}} \exp \left( -i\gamma \left( k - \frac{k^3}{3} \right) \right), \quad (4.21)$$

and it is reduced to the Weber equation fundamental solutions too

$$D_{i\nu}(\pm 2\sqrt{\lambda}\exp(i\pi/4)(k+1)), \quad \text{at } |k + 1| \to 0$$

$$D_{i\nu-1}(\pm 2\sqrt{\lambda}\exp(i\pi/4)(k-1)), \quad \text{at } |k - 1| \to 0.$$  

The same solutions can be obtained for LZ problem in the two level approximation using the instanton method in the coordinate space. The reason for it is fairly transparent and based on the fact that for linear diabatic potentials the limit $k \to \pm \infty$ corresponds to the limit $x \to \pm \infty$, and therefore the asymptotic of the solutions are the same in the momentum and in the coordinate space.

The whole analysis can be brought into a more compact form by introducing so-called connection matrices. In the instanton approach we have deal with the asymptotic solutions and their connections on the complex coordinate plane. Thus it is important and significant to know the connection matrices. The needed connection matrices can be found easily by matching of the solutions (4.20) or (4.21) at the second order turning points through the corresponding fundamental solutions of the Weber equation. It gives the following connection matrices

$$\tilde{M}_1 = \left( \begin{array}{c} \frac{-\cos(\pi\nu)}{\Gamma(\nu) \exp(2\chi) \sin^2(\pi\nu) / \sqrt{2\pi}} \sqrt{2\pi} \exp(-2\chi) / \Gamma(\nu) \\ \frac{\sqrt{2\pi} \exp(-2\chi) / \Gamma(\nu)}{\cos(\pi\nu)} \end{array} \right),$$

(4.22)

where $\chi = (\nu - (\nu - 1/2) \ln \nu)/2$, and

$$\tilde{M}_2 = \left( \begin{array}{c} -\exp(-\pi\tilde{\nu}) \\ 2\Gamma(-i\tilde{\nu}) \exp(-\pi\tilde{\nu}/2) \exp(2\tilde{\chi}) s\chi(\pi\tilde{\nu}) / \sqrt{2\pi} \sqrt{2\pi} \exp(-2\tilde{\chi}) / \Gamma(-i\tilde{\nu}) \\ -\exp(-\pi\tilde{\nu}) \end{array} \right),$$

(4.23)

where $\tilde{\chi} = (i((\pi/4) + \tilde{\nu}(1 - \ln(\tilde{\nu}))) + (1/4) \ln \tilde{\nu}.$

As a note of caution at the end of this section we should also remind that initially for the linear diabatic potentials we had two corresponding Schrödinger equations, and each of them possesses two fundamental solutions. Thus the full LZ problem is characterized by the four fundamental solutions to the left with respect to a given turning point asymptotic and four fundamental solutions to the right (with respect to the same turning point) asymptotic. Therefore generally speaking the connection matrices should be $4 \times 4$ ones. However owing to the symmetry of the potentials these $4 \times 4$ matrices have two blocks $2 \times 2$ structures for the functions $\Phi_1$ and $\Phi_2$. The latter ones are given in (4.22) and in (4.23) respectively.

V. LZ PROBLEM FOR TWO ELECTRON STATES (INSTANTON APPROACH IN THE COORDINATE SPACE).

In the previous sections II - IV we investigated LZ problem in the frame work of the adiabatic perturbation theory, two level approximation and momentum representation. The all three methods are equivalent and semiclassical by their nature. Correspondingly the approaches do work properly for the tunneling and over-barrier transmission energy regions, but become non-adequate within the intermediate region (of the order of $\gamma^{-2/3}$) near the level crossing point. The fact is that the accuracy of these methods depends on the ”renormalized” (energy dependent) semiclassical parameter $\lambda$ (4.17) which can be small in the intermediate region ($\lambda \leq 1$ even for $\gamma \gg 1$). To treat this region we have to use the coordinate space presentation, since we need to know the connection matrices for non-adiabatic transitions. For the latter problem the wave functions outside the level crossing point, happen to be more convenient (and, besides, have a more compact mathematical form) in the coordinate space.
A. Tunneling and over-barrier regions

To move further on smoothly we start here reproducing in the coordinate space the results found in the previous sections for the tunneling and over-barrier energy regions. In the diabatic representation we can rewrite two second order LZ differential equations (4.13) as the following fourth order linear differential equation with the constant coefficients at the derivatives (for the sake of simplicity we consider the symmetric slope case $f_1 = - f_2 = f$)

$$\frac{d^4 \Phi_1}{dX^4} - 2\gamma^2 \frac{d^2 \Phi_1}{dX^2} - 2\gamma^2 f \frac{d\Phi_1}{dX} + \gamma^4 (\alpha^2 - v^2 - f^2 X^2) \Phi_1 = 0. \tag{5.1}$$

Mathematical formalism elaborated by Fedoryuk [68] - [70], we are about to recall, reduces (5.1) by a semiclassical substitution to a set of equations of the order $\gamma^n$. Characteristic polynomial for (5.1)

$$F(\lambda) = \lambda^4 - 2\alpha \gamma^2 \lambda^2 - 2\gamma^2 f \lambda + \gamma^4 (\alpha^2 - v^2 - f^2 X^2), \tag{5.2}$$

where by the definition $\lambda = dW/dX$.

Solving the equation $F(\lambda) = 0$ perturbatively over $\gamma^{-1} \ll 1$ we find

$$\lambda_j = \lambda_j^0 + u_j, \tag{5.3}$$

where

$$\lambda_j^0 = \pm \left[ \gamma (\alpha \pm \sqrt{v^2 + f^2 X^2}) \right]^{1/2}, \tag{5.4}$$

and

$$u_j = \frac{\gamma f}{2} \left[ (\lambda_j^0)^2 - \alpha \right]^{-1}. \tag{5.5}$$

Four asymptotic solutions of (5.1) thus can be represented as

$$\{ y_j \} \equiv \{ \Phi_+^+, \Phi_-^+, \Phi_+^-, \Phi_-^- \} = (v^2 + f^2 X^2)^{-1/4} \exp \left[ \int_{X_0}^X \lambda_j(X') dX' \right], \tag{5.6}$$

and these describe a motion with imaginary momentum in the upper and lower adiabatic potentials

$$\frac{2ma^2}{\hbar^2} (U^\pm - E) = \gamma^2 (\alpha \pm \sqrt{v^2 + f^2 X^2}).$$

The subscripts in (5.6) corresponds to the upper or lower adiabatic levels, and the superscripts are referred to the sign of the action.

Before turning on the connection matrices let us use the substitution

$$\Phi_1 = \exp(\kappa X) \phi, \tag{5.7}$$

and choose $\kappa$ value to vanish the first derivative in (5.1), i.e.

$$\kappa^3 - \gamma^2 \alpha \kappa - \frac{1}{2} \gamma^2 f = 0. \tag{5.8}$$

At $\alpha > 3(f/4\gamma)^{2/3}$ one can expand the roots of (5.8) in terms of the parameter

$$\delta = \frac{f}{4\gamma} \alpha^{-3/2} < \frac{1}{3\sqrt{3}}. \tag{5.9}$$

Thus we find

$$\kappa_1 = \gamma \sqrt{\alpha} \left( 1 + \frac{\delta}{2} \right), \kappa_2 = \gamma \sqrt{\alpha} \left( -1 + \frac{\delta}{2} \right), \kappa_3 = \gamma \sqrt{\alpha} \delta. \tag{5.10}$$
At the condition (5.8) the coefficients at the fourth and at the third order derivatives in (5.1) are small (proportional to $\delta$ and to $\sqrt{\delta}$ respectively) and the fourth order equation (5.1) can be rewritten as two second order Weber equations with the solutions

$$D_{p(1,2)}(\beta_{(1,2)} X),$$

where

$$p^1 = -1 + \delta \frac{\alpha}{2} - \nu \left(1 - \frac{3\delta}{2}\right), \quad p^2 = \frac{\delta}{2} - \nu \left(1 + \frac{3\delta}{2}\right), \quad \beta_{(1,2)} = \left(\frac{\gamma^2 f^2}{\alpha}\right)^{1/4} \left(1 \pm \frac{3\delta}{4}\right). \quad (5.11)$$

The leading terms of these solutions are the same as found in the previous section IV. But the Fedoryuk method we used, gives us also in the tunneling region (5.8) the higher order over the parameter $\delta$ corrections.

In the over-barrier energy region where $\alpha < -3(f/4\gamma)^{2/3}$, the roots of the equation (5.8) are complex - conjugated

$$\frac{\kappa_{(1,2)}}{\gamma \sqrt{\alpha}} = -\frac{\delta}{2} \mp i \left(1 + \frac{3\delta^2}{8}\right), \quad (5.12)$$

and $\delta$ plays the role of the small parameter in this region

$$\delta = \frac{f}{4\gamma |\alpha|^{3/2}}. \quad (5.13)$$

Again as above for the tunneling region, the coefficients at the higher order derivatives are small, and therefore, the function $\phi$ (5.7) satisfies the Weber equation with the fundamental solutions

$$D_{p(1,2)}(\tilde{\beta}_{(1,2)} X),$$

where

$$\tilde{p}^1 = -1 + i \frac{3\tilde{\delta}}{2} + i \nu \left(1 + \frac{3\tilde{\delta}}{4}\right), \quad \tilde{p}^2 = \frac{3\tilde{\delta}}{2} + i \nu \left(1 - \frac{3\tilde{\delta}}{4}\right), \quad (5.14)$$

$$\tilde{\beta}_1 = \exp(i\pi/4) \left(\frac{\gamma^2 f^2}{|\alpha|}\right)^{1/4}, \quad \tilde{\beta}_2 = \exp(-i\pi/4) \left(\frac{\gamma^2 f^2}{|\alpha|}\right)^{1/4}.$$ 

Like it was for the tunneling region (5.11), the leading terms of the expansion (5.14) coincide with the results found in the previous sections, but from (5.14) we are able to compute the corrections to the main terms.

Now we are in the position to find the connection matrices. To do it for the tunneling region we have to establish the correspondence between the solutions of the fourth order differential equation (5.1) and those for the localized in the left ($L$) and in the right ($R$) wells states. In the case $\alpha \gg f |X|$ for the diabatic potentials, the action can be computed starting from the both wells ($R$ and $L$)

$$\gamma W^L \simeq \gamma W_0^L + k_0 X + \frac{\beta^2}{4} X^2, \quad \gamma W^R \simeq \gamma W_0^R - k_0 X + \frac{\beta^2}{4} X^2, \quad (5.15)$$

where $k_0 = (2ma^2(U^# - E)/\hbar^2)^{1/2} \equiv \sqrt{\alpha}$ is imaginary momentum, and $W_0^{L,R}$ are the actions computed from an arbitrary distant point in the $L$ or in the $R$ wells, respectively to the point $X = 0$. From the other hand in the adiabatic potentials $U^\pm = U^# \pm \sqrt{U_{12}^2 + a^2 f^2 X^2}$ the corresponding actions can be represented

$$\gamma W^\pm - \gamma W_0^\pm = k_0 X \pm \frac{\beta^2}{4} X^2 \text{sign}(X). \quad (5.16)$$

Explicitly comparing the semiclassical wave functions in the both representations (adiabatic and diabatic ones) it is easy to see that the adiabatic functions in the potential $U^-$ coincide with the diabatic functions for localized $L$ and $R$ states at $X < 0$ and $X > 0$ respectively. The adiabatic functions for the upper potential $U^+$ correspond to the tails of the diabatic wave functions localized in the opposite wells. Therefore in the level crossing region the $L/R$ diabatic functions are transformed into the $R/L$ functions, and the interaction entangles the diabatic states with the same sign of $k_0 X$. Thus we have only four non-zero amplitudes of the following transitions

$$\langle \Phi^+_L | \Phi^-_R \rangle, \quad \langle \Phi^+_L | \Phi^+_R \rangle, \quad \langle \Phi^-_R | \Phi^-_L \rangle, \quad \langle \Phi^+_R | \Phi^-_L \rangle. \quad (5.17)$$
Recalling that
\[
\gamma W^\pm = \gamma \int \left( \alpha \pm \sqrt{\nu^2 + f^2(X^2)} \right)^{1/2} \sim k_0 X \pm \frac{\beta^2}{4} X^2 \pm \frac{\nu}{2} (1 - \ln \nu),
\]
we come to the conclusion that the quantum solutions (5.11), valid in the vicinity of the level crossing point asymptotically, match smoothly increasing and decreasing solutions (5.6), and it leads to the Landau description [1] of the level crossing transitions depicted in the Fig. 5.

Using expressions (4.22), (4.23) relating the fundamental solutions of the Weber equation, we can find the corresponding to (5.17) 4 × 4 connection matrix
\[
\begin{pmatrix}
\Phi_R^+ \\
\Phi_R^- \\
\Phi_L^+ \\
\Phi_L^-
\end{pmatrix} =
\begin{pmatrix}
\sqrt{2\pi} \exp(-2\chi)/\Gamma(\nu) & 0 & 0 & -\cos(\pi \nu) \\
0 & \Gamma(\nu) \exp(2\chi) \sin^2(\pi \nu) & -\cos(\pi \nu) & 0 \\
0 & \cos(\pi \nu) & \sqrt{2\pi} \exp(-2\chi)/\Gamma(\nu) & 0 \\
\cos(\pi \nu) & 0 & 0 & \Gamma(\nu) \exp(2\chi) \sin^2(\pi \nu)/\sqrt{2\pi}
\end{pmatrix}
\begin{pmatrix}
\Phi_L^- \\
\Phi_L^+ \\
\Phi_R^- \\
\Phi_R^+
\end{pmatrix},
\]
where as above
\[
\chi = \frac{\nu}{2} - \frac{1}{2} \left( \nu - \frac{1}{2} \right) \ln \nu.
\]
The matrix (5.19) has a 2 × 2 block structure, and each of the identical blocks connects increasing and decreasing diabatic solutions. However these diagonal blocks do not correspond to the \( L \rightarrow R \) transitions separately for the lower and upper adiabatic potentials. Indeed the corresponding to these transitions 2 × 2 matrix is
\[
\begin{pmatrix}
\Phi_R^+ \\
\Phi_R^-
\end{pmatrix} =
\begin{pmatrix}
\sqrt{2\pi} \exp(-2\chi)/\Gamma(\nu) & -\cos(\pi \nu) \\
\cos(\pi \nu) & \Gamma(\nu) \exp(2\chi) \sin^2(\pi \nu)/\sqrt{2\pi}
\end{pmatrix}
\begin{pmatrix}
\Phi_L^- \\
\Phi_L^+
\end{pmatrix},
\]
In the diabatic limit (i.e. \( \nu \to 0 \)) the diagonal matrix elements are small (\( \propto \nu^{1/2} \), and \( \nu^{3/2} \) respectively), and the off-diagonal elements approach to ±1, as it should be since by the definition there are no transitions between the diabatic potentials.

In the adiabatic limit \( \nu \gg 1 \), the diagonal matrix elements tend to 1, and it means that the decreasing \( L \) solution transits only into the increasing \( R \) solution, and vice versa. Thus the connection matrix in the tunneling region depends only on the Massey parameter \( \nu \). One has to bear in mind here that the blocks of the 4 × 4 connection matrix (5.19) correspond to the two isolated second order turning points with the Stokes constant (see e.g. [29])
\[
T_2 = \frac{\sqrt{2\pi}}{\Gamma(\nu)} \exp(-2\chi).
\]
Analogously one can study the over-barrier region. Repeating again the procedure described above for the tunneling region (with evident replacements \( k_0 \to -ik_0 \) and \( \beta^2 \to i\beta^2 \)) we end up with the following 4 × 4 connection matrix
\[
\hat{U} =
\begin{pmatrix}
\sqrt{2\pi} \exp(-2\chi)/\Gamma(-i\nu) & 0 \\
0 & 2\Gamma(-i\nu) \exp(-\pi \nu) \exp(2\chi) \sinh(\pi \nu)/\sqrt{2\pi} \\
0 & \exp(-\pi \nu) \\
\sqrt{2\pi} \exp(-2\chi)/\Gamma(-i\nu) & -\exp(-\pi \nu) \\
0 & 0 \\
\end{pmatrix}
\]
where
\[
\chi = \frac{i}{2} \left( \frac{\pi}{4} + \nu(1 - \ln \nu) \right) + \frac{1}{4} (\pi \nu + \ln \nu).
\]
The same manner (as it was already mentioned for the tunneling region), the blocks in (5.22) correspond to the two isolated second order turning points with the Stokes constant \[29\]

\[
\tilde{T}_2 = \frac{\sqrt{2\pi}}{\Gamma(-i\nu)} \exp(-2\tilde{\chi}).
\] (5.24)

Thus we arrive at the important conclusion that the main peculiarity of the LZ level crossing (in comparison with the standard say one-potential problems) is that the second order turning points characterizing the diabatic levels crossing for the LZ problem, possesses the different Stokes constants \(T_2\) (5.21) and \(\tilde{T}_2\) (5.24) in the tunneling and in the over-barrier regions.

**B. Intermediate energy region**

We can now reap the fruits of the previous subsection consideration efforts. First, let us note that from the relations (5.11) and (5.14) one can see that when the energy approaches to the top of the barrier, the exponents \(p^{(i)}\) and \(\tilde{p}^{(i)}\) of the parabolic cylinder functions are increased and thus, more and more deviated from the value prescribed by the Massey parameter \(\nu\). Second, increasing of \(\beta^{(i)}\) upon \(|\alpha|\) decreasing, decreases the values of \(|X|\) where the asymptotic smooth matching of the solutions should be performed. For \(\delta \to 0\) these \(|X|\) values are located deeply in the classically forbidden region, where the potentials are close to the diabatic potentials, while for \(\delta \geq 2\sqrt{3}/3\), these coordinates \(|X|\) are of the order of the quantum zero-point oscillation amplitudes, and therefore to find the solution in this region, we have to use the adiabatic representation.

These two simple observations give us a conjecture how to treat LZ problem in the intermediate energy region. To do it first of all we should find the energetical “window” for the intermediate region. It is convenient to chose the adiabatic potential frequency \(\Omega = F/\sqrt{mU_{12}}\) as the energy scale, and in terms of this scale the inequality \(|\alpha| < 3f/(4\gamma)|^{2/3}\) reads as

\[
|U^* - E| \leq \frac{3}{2} U_{12}^{1/3} \left( \frac{\Omega}{2} \right)^{2/3} = U_{12}^{*}. \tag{5.25}
\]

By the other words the characteristic interaction energy at the intermediate region boundaries does not depend on \(U_{12}\). However, the positions of the linear turning points \(|X^*|\) corresponding to the energies \(U^* \pm U_{12}^*\) depend on the ratio \(U_{12}/U_{12}^*\). These points are located inside or outside of the interval \([-a_0 \gamma^{-1/2} + a_0 \gamma^{-1/2}\) at \(U_{12}/U_{12}^* < 1\) and at \(U_{12}/U_{12}^* > 1\), respectively. Accordingly for the both cases the matching conditions in the intermediate energy region are different. In the former case for the asymptotic matching region the potentials can be reasonably approximated by parabola, and therefore we should work with the Weber equations, and for the latter case the matching are performed in the region where the potentials are linear ones, thus the equations are reduced to the Airy equations.

Let us investigate first the case \(U_{12}/U_{12}^* > 1\). Using Born-Oppenheimer approach of the section II, the Schrödinger equations in the adiabatic representation with the accuracy up to \(\gamma^{-2}\) are decoupled for the wave functions \(\Psi_{\pm}\)

\[-\frac{d^2\Psi_{\pm}}{dX^2} + \gamma^2 (\alpha \pm \sqrt{\nu^2 + f^2X^2})\Psi_{\pm} = 0.\] (5.26)

The equations (5.26) at \(|X| < v/f\) are reduced to the Weber equations with the fundamental solutions \(D_{-1/2-q_1}(\pm \sqrt{\nu}X)\), and \(D_{-1/2+iq_2}(\pm \exp(-i\pi/4)\sqrt{\nu}X)\), where

\[
q_1 = \gamma \frac{v + \alpha}{2}, \quad q_2 = \gamma \frac{v - \alpha}{2}, \tag{5.27}
\]
do not depend on the Massey parameter \(\nu\). Two real solutions of (5.26) correspond to the upper adiabatic potential (classically forbidden region), and two complex solutions correspond to the classically allowed motion under the lower adiabatic potential.

The argument of the Weber functions is \(\propto X\sqrt{\nu}\), and at the condition \(X < v/f\) their asymptotic expansions determine the interval where the matching should be done

\[
\gamma^{-1/2} \left( \frac{U_{12}}{\Omega} \right)^{1/2} > \gamma^{-1/2}. \tag{5.28}
\]

Thus this inequality (5.28) can be fulfilled only at \(U_{12}/U_{12}^* > 1\), when the intermediate region is sufficiently broad in comparison with \(\Omega\). In this case the exponents \(q_1, q_2\) (5.27) are large, and our aim is to find explicitly the asymptotic
expansions of the solutions in this case. We will closely follow the method we borrowed from Olver paper [72] (see also his monograph [73]), which is in fact an expansion over small parameters $1/|q_i|$ (where $|q_i|$ are the exponents (5.27)) of the fundamental Weber solutions, and it leads to the following asymptotic solution to Eq. (5.26) at $X > 0$

$$
\Psi^-(X) \simeq Y_+^{-1/2}(X + Y_+)^{-q_1} \exp(-\gamma X Y_+) \ , \ \Psi^+(X) \simeq Y_-^{-1/2}(X + Y_-)^{q_2} \exp(i \gamma X Y_-) ,
$$

(5.29)

where $Y_{\pm} = \sqrt{v \pm \alpha + X^2}$. Using the known relation between the fundamental solutions of the Weber equation [71], [73]

$$
D_\mu(z) = \exp(-i \pi \mu) D_\mu(z) + \frac{\sqrt{2\pi}}{\Gamma(-\mu)} \exp \left(-i \pi \frac{\mu + 1}{2} \right) D_{-\mu-1}(iz) ,
$$

we can find two other (complimentary to (5.29) solutions

$$
\Psi^\pm(X) = Y_+^{-1/2} \left(-\sin(\pi q_1)(X + Y_+)^{-q_1} \exp(-\gamma X Y_+) + \exp(-2\chi_1) \frac{\sqrt{2\pi}}{\Gamma((1/2) + q_1)} (X + Y_+)^{q_1} \exp(\gamma X Y_+) \right) (5.30)
$$

and

$$
\Psi^\mp(X) = Y_+^{-1/2} \left(-i \exp(-\pi q_2)(X + Y_-)^{q_2} \exp(i \gamma X Y_-) + \exp(-2\chi_2) \frac{\sqrt{2\pi}}{\Gamma((1/2) - i q_2)} (X + Y_-)^{q_2} \exp(-i \gamma X Y_-) \right) ,
$$

(5.31)

where we introduce the notation

$$
\chi_1 = \frac{1}{2} \left( q_1 + \frac{1}{2} \right) - \frac{q_1}{2} \ln \left( q_1 + \frac{1}{2} \right) , \ \chi_2 = -\frac{1}{2} \left( i q_2 - \frac{1}{2} \right) + \frac{i q_2}{2} \left(-i \frac{\pi}{2} + \ln \left( q_2 + \frac{i}{2} \right) \right) .
$$

Not surprisingly but it is worth to noting that these solutions (5.29) - (5.31) can be represented as a linear combination of the semiclassical solutions (5.6) $\Phi^\pm_\mp$ with the coefficients

$$
cos 2\theta_{(1,2)} = \frac{X}{\sqrt{v \pm \alpha + X^2}} .
$$

(5.32)

These energy dependent angles $\theta_{(1,2)}$ coincide with the adiabatic angles (see (2.12) and (3.12)) introduced above in sections II and III in the level crossing point at $\alpha = 0$, and $f|X| < v$, and the both angles acquire only slightly different values over the whole intermediate region $|\alpha| < v$.

Now we can find all needed connection matrices for these functions. Although the calculation is straightforward it deserves some precaution (e.g. the $X$-dependent matrices have different functional form at the positive and negative $X$). At $X > 0$ we get

$$
\begin{pmatrix}
\Phi^-

\Phi^+

\Phi^-

\Phi^+

\end{pmatrix} =
\begin{pmatrix}
\cos \theta_2 & 0 & -i \exp(-\pi q_2) \cos \theta_2 & \sqrt{2\pi} \exp(-2\chi_2) \cos \theta_2 / \Gamma((1/2) - i q_2) \\
0 & 0 & \sqrt{2\pi} \exp(-2\chi_2) \cos \theta_2 / \Gamma((1/2) - i q_2) & 0 \\
0 & 0 & 0 & 0 \\
\sin \theta_1 & 0 & 0 & \sin \theta_1 \\
\end{pmatrix}
\begin{pmatrix}
\Phi^-

\Phi^+

\Phi^-

\Phi^+

\end{pmatrix} ,
$$

(5.33)

and for $X < 0$ it reads as

$$
\begin{pmatrix}
\Phi^-

\Phi^+

\Phi^-

\Phi^+

\end{pmatrix} =
\begin{pmatrix}
\sqrt{2\pi} \exp(-2\chi_2) \cos \theta_2 / \Gamma((1/2) - i q_2) & 0 & -i \exp(-\pi q_2) \cos \theta_2 & \cos \theta_2 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\sin \theta_1 \sqrt{2\pi} \exp(-2\chi_1) / \Gamma((1/2) + q_1) & 0 & -\sin(\pi q_1) \sin \theta_1 & \sin \theta_1 \\
\end{pmatrix}
\begin{pmatrix}
\Phi^-

\Phi^+

\Phi^-

\Phi^+

\end{pmatrix} .
$$

(5.34)
The product of the inverse to (5.33) matrix and the matrix (5.34) determines the connection matrix, we have sought for, to relate the semiclassical solutions in the intermediate energy region (cf. (5.20) and (5.22) presenting the connection matrices for the tunneling and over-barrier energy regions). Performing this simple algebra one ends up with

\[
U_{\text{cross}} = \begin{pmatrix}
\sqrt{2\pi} \exp(-2\chi_2)/\Gamma((1/2) - i q_2) & i \exp(-\pi q_2) \\
-i \exp(-\pi q_2) & 2 \exp(2\chi_2)/\Gamma((1/2) - i q_2) \cosh(\pi q_2) \\
0 & 0 \\
0 & 0 \\
\sqrt{2\pi} \exp(-2\chi_1)/\Gamma((1/2) + q_1) & \sin \pi q_1 \\
-\sin \pi q_1 & \cos^2(\pi q_1)/\Gamma((1/2) + q_1) \exp(2\chi_1)
\end{pmatrix}
\]  

(5.35)

The matrix (5.35) has two \(2 \times 2\) blocks structure, the same as the connection matrices (5.19) and (5.22) for the tunneling and over-barrier regions. However, unlike (5.19), (5.22) describing the transitions between the diabatic states, the matrix (5.35) corresponds to the transitions between the adiabatic states. Indeed, at a strong level coupling (\(U_{12} > U_{12}^*\)) the eigenfunctions are close to the adiabatic functions and only non-adiabatic perturbations induce the transitions. Respectively, the off-diagonal matrix elements in (5.35), having meaning of the probability to keep the same diabatic state after the transition, are zero. The block with the real-valued matrix elements corresponds to the minimum of the upper adiabatic potential, i.e. it is to the isolated second order turning point, where [29]

\[
q_1 + \frac{1}{2} = \frac{U^* - E + U_{12}}{\Omega} + \frac{1}{2}.
\]  

(5.36)

The complex-valued block is associated with the maximum of the lower adiabatic potential, and analogously to (5.36) one can find the following relation for the turning point

\[
i q_2 + \frac{1}{2} = -i \frac{U^* - E + U_{12}}{\Omega} + \frac{1}{2}.
\]  

(5.37)

In the case of weak level coupling, namely at \(|U^* - E| < U_{12}^*\) and \(U_{12} < U_{12}^*\), for the intermediate energy region, the adiabatic potentials everywhere (except a small neighbourhood \(|X| < v/f \to 0\) of the level crossing point) can be linearized, i.e. represented as \(\alpha \pm f|X|\), and the asymptotic solutions (5.6) are reduced to a linear combination of the following functions

\[
\Phi^\pm \propto (f|X|)^{-1/2} \exp(\pm \xi_\pm \text{sign} X), \quad \Phi^\pm \propto (f|X|)^{-1/2} \exp(\pm \xi_- \text{sign} X), \quad \xi_\pm = \frac{2}{3 f} (f|X| \pm \alpha)^{3/2}.
\]  

(5.38)

Now all needed matrix elements can be calculated in the framework of the Landau perturbation theory [1], which can be formulated to avoid divergency of the parameter \(\nu\) at \(\alpha \to 0\) in terms of the dimensionless variables

\[
\hat{\alpha} = 3 \cdot 2^{-4/3} \frac{U^* - E}{U_{12}}; \quad \hat{\nu} = 3 \cdot 2^{-4/3} \frac{U_{12}}{U_{12}^*}.
\]

The results of our analysis is shown in Fig. 6. The tunneling and the over-barrier regions are separated from the intermediate energy region by the lines \(|U_{12}^* - E| = U_{12}^*\). In own turn the intermediate region is also separated into two parts by the line \(\nu = \nu^* = 0.325\), where \(\nu^*\) is the value of the Massey parameter \(\nu\) at \(U_{12}/U_{12}^* = 1\) and \(|U^* - E| = U_{12}^*\).

In the \(\nu < \nu^*\) region the perturbation theory is the adequate tool for the problem, and the transition matrix elements are proportional to \(U_{12}/U_{12}^*\). At \(\nu > \nu^*\) one can use the connection matrix (5.35). To illustrate the accuracy of the approximations we have computed the matrix element \(M_{11}\). The results are shown in the Fig. 7. Our computations demonstrate quite good precision, secured up to two stable digits. The accuracy of the results on the boundaries between the intermediate and over-barrier or tunneling regions is not worse than \(3 - 5\%\), and can be even easily improved using interpolation approaches.

VI. SCATTERING MATRIX.

LZ kind of phenomena can be considered as (and applied to) scattering processes. Found in the previous section \(V\) expressions for \(4 \times 4\) connection matrices can be used to calculate the scattering operator (or matrix) \(\hat{S}\), which converts an ingoing wave into an outgoing one.
Let us consider first the over-barrier region for two linear potentials crossing problem. For this case besides the crossing point which we chose as \( X = 0 \), there are two linear (first order) turning points \( X_0 = \pm |\alpha| / f \) (each turning point for each of the diabatic potentials, we designate by \( L \) and \( R \)). The scattering matrix which relates the asymptotic solutions at \( X \ll -X_0 \) and at \( X \gg X_0 \) is the product of the \( 4 \times 4 \) connection matrix \((5.22)\) calculated in the section V (subsection V A) and known \([57]\) (see also \([29]\)) two semiclassical connection matrices describing wave function evolution from the turning point \(-X_0\) to the crossing point \(0\), and from this point to the turning point \(+X_0\), respectively. Thus we end up with \( 2 \times 2 \) matrix having the following block matrix elements

\[
\begin{align*}
T_{11} &= A_{if} \begin{bmatrix} \exp(i(\phi - \phi_0) & 0 \\ 0 & \exp(-i(\phi - \phi_0)) \end{bmatrix}; \\
T_{12} &= T_{21} = (1 - A^2_{if}) \exp(i\gamma W^*/2) \begin{bmatrix} i & -1/2 \\ -\exp(-i\gamma W^*) (i/2) & \exp(-i\gamma W^*) \end{bmatrix} \\
T_{22} &= A_{if} \begin{bmatrix} 2\cos(\gamma W^* - (\phi - \phi_0)) & -\sin(\gamma W^* - (\phi - \phi_0)) \\ \sin(\gamma W^* - (\phi - \phi_0)) & (1/4) \cos(\gamma W^* - (\phi - \phi_0)) \end{bmatrix},
\end{align*}
\]

where \( A_{if} = (1 - \exp(-\pi\nu))^{1/2} \) is the LZ amplitude of the transition between the diabatic states, \( \phi - \phi_0 = \tilde{\chi} \) (see \((5.23)\)), and \( W^* \) is the action between the linear turning points.

The diagonal elements of \((6.1)\), proportional to the transition amplitude \( A_{if} \), describe the propagating waves (i.e. the solutions of the Schrödinger equation in the lower adiabatic potential), and oscillating blocks correspond to the solutions in the upper adiabatic potential. Off-diagonal blocks proportional to the probability to keep unchanged the initial diabatic states, describe the waves reflected from the linear turning points. Interesting for physical applications reflection \( R \) and transmission \( T \) coefficients can be found from \((6.1)\) by a straightforward calculation, and the results read as

\[
R = -i(1 - A^2_{if})[A^2_{if} \exp(i\gamma W^* - 2i(\phi - \phi_0)) + \exp(-i\gamma W^*)]^{-1};
\]

\[
T = 2A_{if} \cos(\gamma W^* - (\phi - \phi_0))[A^2_{if} \exp(i\gamma W^* - 2i(\phi - \phi_0)) + \exp(-i\gamma W^*)]^{-1}.
\]

The poles of the scattering matrix can be also easily found from \((6.1)\), and the corresponding resonance condition is

\[
\cos(2(\gamma W^* - (\phi - \phi_0))) = -\left(1 - \frac{1}{2} \exp(-2\pi\nu)\right) \left(1 - \exp(-2\pi\nu)\right)^{-1/2}.
\]

The action in the resonance points is complex-valued

\[
Re(\gamma W^* - (\phi - \phi_0)) = \left(n + \frac{1}{2}\right) \pi; \quad Im(\gamma W^* - (\phi - \phi_0)) = -\frac{1}{2} \ln(1 - \exp(-2\pi\nu)).
\]

The poles of the scattering matrix are placed on the lower complex \( E \) half plane at the vertical lines corresponding to conventional Bohr - Sommerfeld quantization rules \((\gamma W^* = \pi(n + (1/2))\) for the upper adiabatic potential. In the diabatic limit \((\nu \to 0)\) the imaginary part of the pole positions tends to infinity, and in the adiabatic limit \((\nu \to \infty)\) the poles move to the real axis. Thus we see that the eigenstates of the upper adiabatic potential are always quasistationary ones. The resonance widths are determined by the residues of the scattering matrix elements at the poles, and it can be shown the resonance widths are monotonically decreasing functions of \( \nu \). In the Fig. 8 we show the energy dependence of the transmission coefficient \( T \). In the diabatic limit \( T \to 0 \), and it is increased when \( U_{12} \) is increased, and in the over-barrier region there appear the resonances with the widths \( \Gamma_n \) increasing with the energy increase, since in these conditions the Massey parameter is decreased and \( \Gamma_n \propto \exp(-2\pi\nu) \).

We illustrate the energy dependence of the transmitted wave phase in the Fig. 9. In accord to the general scattering theory \([1]\), there are \( \pi \) - jumps of the phase at each quasi-discrete energy level of the upper adiabatic potential. At \( U_{12}/U_{22} < 1 \), the resonance widths are of the order of the inter-level spacings. The amplitudes of the decaying solutions (localized in the well formed by the upper adiabatic potential) are increased near the resonances, and this behavior is depicted in the Fig. 10. One note of primary importance concerning the issue is that the information about decaying solutions existing in the \( 4 \times 4 \) connection matrix, e.g. \((5.22)\) is lost when we use \( 2 \times 2 \) scattering matrix \((6.1)\).

Except for a slight natural modification the presented above results, one can find the scattering matrix for the
tunneling region merely by recapitulating the already derived expressions. Thus instead of the matrix (6.1) we get

\[
T_{11} = \begin{bmatrix}
(1/4)M_{11} \exp(-\gamma W^*) + M_{22} \exp(\gamma W^*) & i((1/4)M_{11} \exp(-\gamma W^*) - M_{22} \exp(\gamma W^*)) \\
-\frac{i}{2}(1/4)M_{11} \exp(-\gamma W^*) - M_{22} \exp(\gamma W^*) & (1/4)M_{11} \exp(-\gamma W^*) + M_{22} \exp(\gamma W^*)
\end{bmatrix};
\]
\[
T_{12} = T_{21}^* = \cos(\pi \nu) \exp(i\gamma W^*/2) \begin{bmatrix}
i & -1/2 \exp(-\gamma W^*) \\
-1 & (i/2) \exp(-\gamma W^*)
\end{bmatrix}
\]
\[
T_{22} = \begin{bmatrix}
M_{11} & 0 \\
0 & M_{22}
\end{bmatrix},
\]

where \(M_{11}\) and \(M_{22}\) are the corresponding matrix elements from (5.19).

The same as above we compute the reflection and transmission coefficients

\[
R = -i \left( \exp(\gamma W^*) - \frac{1}{4} M_{11}^2 \exp(-\gamma W^*) \right) \left( \exp(\gamma W^*) + \frac{1}{4} M_{11}^2 \exp(-\gamma W^*) \right)^{-1};
\]
\[
T = M_{11} \left( \exp(\gamma W^*) + \frac{1}{4} M_{11}^2 \exp(-\gamma W^*) \right)^{-1}.
\]

In the intermediate energy region the only block matrix element \(T_{11}\) requires the special calculations taking into account the contributions from the complex turning points

\[
T_{11} = \begin{bmatrix}
\sqrt{2\pi} \exp(-\pi q_2^2/2)/\Gamma((1/2) - iq_2) & i \exp(-\pi q_2^2) \\
-i \exp(-\pi q_2^2) & 2\Gamma((1/2) - iq_2) \exp(-\pi q_2^2/2) \text{ch}(\pi q_2)\sqrt{2\pi}
\end{bmatrix};
\]

and all other matrix elements are the same as in the matrix (5.34). Finally we find also in the intermediate energy region the reflection and the transmission coefficients

\[
R = \frac{\exp(-\pi q_2^2)}{\sqrt{1 + \exp(-2\pi q_2^2)}} \exp[-i(\phi - (\pi/2))];
\]
\[
T = \frac{1}{\sqrt{1 + \exp(-2\pi q_2^2)}} \exp(-i\phi),
\]

where \(\phi = \text{arg}[\Gamma((1/2) - iq_2)]\).

**VII. 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 involved and intricate and require the knowledge of the scattering matrix and all connection matrices, we have calculated in the previous sections. In this section we apply this machinery to find the quantization rules for the crossing diabatic potentials depicted in Fig. 11. Depending on the Massey parameter the shown on the figure situations exhaust all cases practically relevant for spectroscopy of non-rigid molecules (symmetric or asymmetric double - well and decay potentials).

Within the instanton approach the quantization rule can be formulated as a condition that the amplitudes of the tunneling splitting \(\Delta_0\) at finite values of the Massey parameter \(\nu\) can be represented as a product

\[
\tan(\gamma W_B) = \pm \frac{2}{p} \exp(\gamma W_B^*),
\]

where \(W_B^*\) is the action in the barrier formed in the lower adiabatic potential, and \(p \equiv U_{11}\) is the corresponding matrix element of the connection matrix (5.19).

Only the factor \(1/p\) varying from 0 to 1 in the diabatic and in the adiabatic limits, respectively, makes this quantization condition (7.1) different from the well known [1] quantization rule for the symmetric double-well potential. Correspondingly, the tunneling splitting at finite values of the Massey parameter \(\nu\) can be represented as a product

\[
\Delta_n = \Delta_0^\nu p(\nu),
\]

of the tunneling splitting \(\Delta_0^\nu\) in the adiabatic potential and the factor

\[
p(\nu) = \frac{\sqrt{2\pi}}{\Gamma(\nu)} \nu^{-1/2} \exp(-\nu),
\]
associated with the transition amplitudes between the diabatic potentials in the crossing region.

It is particularly instructive to consider (7.1) as the standard [1] Bohr-Sommerfeld quantization rule, where in the r.h.s. the both, geometrical \( \varphi_n \) and the tunneling \( \chi_n \) phases are included additively. In the adiabatic limit when \( p(\nu) \to 1 \), we find that \( \varphi_n \to 0 \) and (7.1) is reduced to the quantization of the symmetric double-well potential. In the diabatic limit \( \varphi_n = -\chi_n \) and the geometric phase compensates the tunneling one. The physical argument leading to this compensation may be easily rationalized as follows. Indeed, at the reflection in the crossing point \( X = 0 \), the trajectories in the classically forbidden energy region are the same as those for the tunneling region but with a phase shift \( \pi \).

We focus now on the quantization rules for the over-barrier energy region. Closely following the consideration performed above for the tunneling region (replacing the connection matrix (5.19) by the matrix (5.22), and making some other self-evident replacements) we end up after some tedious algebra with the quantization rule

\[
(1 - \exp(-2\pi \nu)) \cos(2\gamma W_L^* + (\phi - \phi_0)) \cos(\gamma W^* - (\phi - \phi_0)) + \exp(-2\pi \nu) \cos^2\left(\frac{\gamma W_L^* + \gamma W^*}{2}\right) = 0, \quad (7.4)
\]

where \( W^* \) is the action in the well formed by the upper adiabatic potential, and \( \phi - \phi_0 = \tilde{\chi} \) is determined according to (5.23). From the Eq. (7.4) follows that the eigenstates are determined by the parameter

\[
B = \frac{\exp(-2\pi \nu)}{1 - \exp(-2\pi \nu)}. \quad (7.5)
\]

In the diabatic limit \( \nu \to 0 \), and therefore, \( B \to 1/(2\pi \nu) \) in (7.4) the main contribution is due to the second term, and it leads to a splitting of degenerate levels in the diabatic potentials. Moreover since

\[
\gamma \left( W_L^* + \frac{W^*}{2} \right) = \pi \left( n + \frac{1}{2} \pm 2\nu \sin \left[ \gamma \left( W_L^* + \frac{W^*}{2} \right) - \phi + \phi_0 \right] \right), \quad (7.6)
\]

the splitting increases when the Massey parameter \( \nu \) increases, and it is an oscillating function of the interaction \( U_{12} \).

In the adiabatic limit, when \( \nu \to \infty \), \( \phi - \phi_0 \to 0 \), and, therefore, from (7.5) \( B \approx \exp(-2\pi \nu) \), the main contribution to (7.4) comes from the first term which determines the quantization rule for the upper one-well potential and for the lower double-well potential in the over-barrier energy region, and in this limit the parameter \( B \) plays a role of the tunneling transition matrix element. For \( B \) smaller than nearest level spacings for the lower and for the upper potentials, one can find from (7.4) two sets of quantization rules leading to two sets of independent energy levels

\[
\gamma W^* = \pi \left( n_1 + \frac{1}{2} \right); \quad 2\gamma W_L^* = \pi \left( n_2 + \frac{1}{2} \right). \quad (7.7)
\]

Since the eigenstate energy level displacements depend on \( U_{12} \) the resonances can occur at certain values of this parameter, where the independent quantization rules (7.7) are not correct any more. The widths of these resonances are proportional to \( \exp(-2\pi \nu) \) and therefore are strongly diminished upon the Massey parameter \( \nu \) increase. This behavior is easily understood, since in the limit the wave functions of the excited states for the lower potential are delocalized, and their amplitudes in the localization regions for the low-energy states of the upper potential, are very small.

More tricky task is to derive the quantization rule in the intermediate energy region. One has to use the connection matrix (5.35), and to bear in mind the contributions from the imaginary turning points. Nevertheless, finally the quantization rule can be written in the simple and compact form as

\[
\cos(2\gamma W_L^*) = -\exp(-\pi q_2), \quad (7.8)
\]

where \( q_2 = \gamma(\nu - \alpha)/2 \) is determined by the relation (5.27).

It is useful to illustrate the essence of the given above general result by simples (but yet non trivial) examples. First, let us consider two identical parabolic potentials with their minima at \( X = \pm 1 \) and with the coupling which does not depend on \( X \). Since the symmetry, the solutions of the Hamiltonian can be represented as symmetric and antisymmetric combinations of the localized functions

\[
\Psi_{\pm} = \frac{1}{\sqrt{2}}(\Phi_L \pm \Phi_R). \quad (7.9)
\]

The functions are orthogonal, and, besides, two sets of the functions \( (\Psi_0^+, \Psi_0^-) \), and \( (\Psi_0^+, \Psi_e^-) \) (where the subscripts 0 and \( e \) stand for the ground and for the first excited states respectively) correspond to the two possible kinds of level crossings.
In Fig. 12 we depicted schematically the dependence of the level positions on the coupling $U_{12}$. In the energy region $E \leq U^* + U_{12}$ where only there exist the discrete levels of the lower adiabatic potentials, there are the pairs of the alternating parity levels ($\Psi_+^1, \Psi_0^2$), and ($\Psi_0^1, \Psi_-^2$). The tunneling splittings are increased monotonically since the Massey parameter $\nu$ is increased, and the barrier is decreased with $U_{12}$. The same level and parity classification is remained correct for the energy region above the barrier of the lower adiabatic potential where the spectrum becomes almost equidistant one. However, in the over-barrier region, the resonances are occurred between the levels of the same parity, and this sequence of the odd and of the even levels is broken, and level displacements are not monotonic almost equidistant one. However, in the over-barrier region, the resonances are occurred between the levels of the lower adiabatic potential where the spectrum becomes. The same level and parity classification is remained correct for the energy region above the barrier of the lower adiabatic potential where the spectrum becomes almost equidistant one. However, in the over-barrier region, the resonances are occurred between the levels of the same parity, and this sequence of the odd and of the even levels is broken, and level displacements are not monotonic almost equidistant one.

The second instructive example treats the one-well and linear diabatic potentials crossing. It leads to the lower adiabatic decay potential and to the upper one-well adiabatic potential. The quantization rules in this case correspond to the vanishing amplitudes for the exponentially increasing solutions when $X \to -\infty$, and besides one has to require that no waves propagating from the region of infinite motion, i.e. at $X > 1/2$. Performing the same as above procedure we find that in the tunneling energy region, the eigenstates are the roots of the following equation

$$\tan(\gamma W^*_n) = -i \frac{4}{\rho^2(\nu)} \exp(2\gamma W^*_B), \quad (7.10)$$

with the same as above notation.

To proceed further it is convenient to introduce the complex action to describe the quasi-stationary states

$$\gamma W^*_L = \pi \left( \frac{E_n}{\Omega} - \frac{i}{2\Omega} \Gamma_n \right), \quad (7.11)$$

where evidently $\Omega = \partial W_L/\partial E$ does depend on $E$. From (7.11) the reel and imaginary parts of the quantized eigenstates are

$$E_n = \Omega \left( n + \frac{1}{2} \right); \quad \Gamma_n = \frac{p^2(\nu)}{2\pi} \Omega \exp(-2\gamma W^*_B). \quad (7.12)$$

This relation (7.12) describes the non-adiabatic tunneling decay of the quasi-stationary states of the lower adiabatic potential. The same as we already got for the two parabolic potentials crossing (7.2), here the tunneling and the adiabatic factors are entering decay rate multiplicatively. Since the decay rate is proportional to the square of the tunneling matrix element, $\Gamma_n \propto p^2(\nu)$ as it should be.

In the over-barrier energy region the quantization rule is

$$(1 - \exp(-2\pi \nu) \exp[-i(\gamma W^*_L + \phi + \phi_0)] \cos(\gamma W^* - \phi + \phi_0) +$$

$$\exp(-2\pi \nu) \exp(-i\gamma W^*/2) \cos \left( \frac{\gamma W^*_L + \gamma W^*_B}{2} \right) = 0; \quad (7.13)$$

and the actions depend on the energy $E$ as

$$\gamma W^*_L = \frac{E}{\Omega}; \quad \gamma W = \pi \left[ -\frac{U^* + U_{12}}{\Omega_1} + \frac{E}{\Omega_1} \right], \quad (7.14)$$

where $\Omega$ and $\Omega_1$ are $E$-dependent frequencies of the diabatic and the upper adiabatic potentials.

In the diabatic limit the decay rate is proportional to the Massey parameter and has a form

$$\Gamma_n \simeq \pi \nu \cos^2(\gamma W - \phi + \phi_0), \quad (7.15)$$

and in the opposite, adiabatic, limit the decay rate is

$$\Gamma_n \simeq \exp(-2\pi \nu)(1 - \sin(2\gamma W^*_B + \phi - \phi_0)). \quad (7.16)$$

In the both limits the decay rate is the oscillating function of $U_{12}$. We illustrate the dependence $\Gamma(U_{12})$ for the crossing diabatic potentials $U_1 = (1 + X)^2/2$ and $U_2 = (1/2) - X$ in the Fig. 13. Note that while the tunneling decay rate of the low-energy states is increased monotonically with the Massey parameter $\nu$, the decay rate of the highly excited states goes to zero in the both (diabatic and adiabatic) limits. Besides there are certain characteristic values of $U_{12}$ when the r.h.s. of (7.15) or (7.16) equal to zero and therefore $\Gamma_n = 0$. 

Last and more general example we consider in this section, describes two non-symmetric potentials crossing at $X = 0$ point:

$$U_1 = \frac{1}{2}(1 + X)^2; \; U_2 = \frac{1}{2b}(X^2 - 2bX + b).$$  (7.17)

In a certain sense it is the generic case, and when the parameter $b$ entering the potential (7.17) is varied from 1 to $\infty$, we recover the two particular examples considered above, and come from two identical parabolic potentials to the case one-well and linear diabatic potentials crossing. This kind of the potential $U_2$ was investigated recently by two of the authors (V.B. and E.K) [64] 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 behavior found in [64] 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 small adiabatic factor. Therefore the coherent - incoherent tunneling crossover region moves to the more dense density of final states, and the larger $U_{12}$ is the smaller will be the region for incoherent tunneling.

Quite different situation occurs for highly 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 these unusual phenomena we show in Fig. 14 time dependence of the survival probability $P$ for the initially prepared localized in the left well state $n = 0$.

VIII. CONCLUSION.

In this paper we have challenged again the very basic subject - LZ problem. Currently there are about 100 publications per year related to LZ problem. Clearly it is impossible to give a complete analysis of what is being achieved in this field. Our aim, therefore, was only to show some recent trends and our new results, to help newcomers and specialists in finding cross-references between the many physical phenomena related to LZ problem. The problem was first addresses a long ago, and many already classical results are known now from the textbooks [1], [37]. Although exact quantum-mechanical calculations are still prohibitively difficult, many important results have been obtained in the framework of the WKB approach [1] - [65]. The accuracy of the modified WKB methods can be improved considerably, note for example [30] where the authors have included into the standard WKB method additionally a special type of trajectories on the complex phase plane, along which the semiclassical motion is described by the Weber functions. This method ascending to Landau [1] is equivalent to the appropriate choice of the integration path around the turning point, and it appears to be quite accurate for the tunneling and over-barrier regions, where the characteristic fourth order polynomial (see (4.16)) can be reduced to the second order one (two pairs of roots are nearly degenerated). However, even in this case there are some non-negligible corrections found in the papers [23]- [25]. In the intermediate energy region, where all 4 roots are noticeably different, the method becomes invalid. Besides the choice of these additional special trajectories (which one has to include to improve the accuracy of the WKB method near the barrier top) depends on the detail form of the potential far from the top, and therefore for each particular case the non-universal procedure should be perform from the very beginning.

We believe we are the first to explicitly addresses the question on the behavior in the intermediate energy region. In all previous publications this region was considered as a very narrow and insignificant one, or in the best case the results were obtained by a simple interpolation from the tunneling (with monotonic decay of the transition probability) to the over-barrier (with oscillating behavior) regions. The fact is that classical trajectories can be separated into two classes: "localized" and "delocalized" in the following sense. If energy is close enough to the minimum or maximum of the potentials, the trajectories could be called confined, since they are determined by the universal features of the potentials in the vicinity of these extremal points. Evidently it is not the case for the intermediate energy region. In the present study we have found that, contrary to the common belief, the instanton trajectory is a rather simple object and can be explicitly computed even for the intermediate energy region.

Within the framework of the instanton approach we present a full and unified description of 1D LZ problem, which is very often can be quite reasonable approximation for real systems. Because different approaches have been proposed to study the LZ problem we develop an uniform and systematic procedure for handling the problem. We reproduced all known results for tunneling and over-barrier regions, and studied as well the intermediate energy region. Specifically we applied our approach to the Born - Oppenheimer scheme, formulated the instanton method in the momentum space, and presented all details of the LZ problem for two electronic states using also the instanton description of
the LZ problem in the coordinate space. Neglecting higher order space derivatives we find asymptotic solutions, and using adiabatic - diabatic transformation we match the solutions in the intermediate region. Based on these results we derived the complete scattering matrix for the LZ problem, the quantization rules for crossing diabatic potentials. Our results can be applied to several models of level crossings which are relevant for the interpretation and description of experimental data on spectroscopy of non-rigid molecules and on other systems undergoing crossing and relaxation phenomena.

Note also, that in spite of the fairly long history of the LZ phenomena, the study is still in an accelerating stage, and a number of questions remain to be clarified (let us mention only few new features of the phenomena attracted attention recently, like LZ interferometry for qubits [74], LZ theory for Bose - Einstein condensates [75], multi-particle and multi-level LZ problems [76], [77], [78], [79]). Much of the excitement arises from the possibility of discovering novel physics beyond say the semiclassical paradigms discussed here. For example, we found in the sections II and III that the wave functions of nuclei moving along the periodic orbits acquire geometrical phases (the effect is analogous to the Aharonov - Bohm effect [38], but in our case it has nothing to do with external magnetic fields and is related to the non-adiabatic interactions). The relation between the both phenomena (the geometrical phases and the periodic orbits) can be established using Lagrangian (instead of Hamiltonian) formulation of the problem, which enables to take into account explicitly, using propagator technique, [34], [35], [36], time dependence of the adiabatic process under consideration (see also, e.g., [4], [43]). However, a proper handling of these aspects is beyond the scope of our work. Further experimental and theoretical investigations are required for revealing the detailed microscopic and macroscopic properties of different LZ systems.

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 (see section II). 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-adiabaticity. The typical examples investigated in the monography [80], are so-called pre-dissociation, singlet-triplet or singlet-singlet conversion, and vibrational relaxation phenomena.

Slow atomic collisions provide other examples of the non-adiabatic transitions between electronic states, where the time dependence of the states is determined by the distance and by the relative velocity of the colliding particles [33]. Some examples of the non-adiabatic transitions relevant for semiconductor physics can be found in [81], for nuclear or elementary particle physics in [82] and for laser or non-linear optic physics in [83] - [86]. The latter topic of course is of interest in its own right but also as an illustration of novel and fundamental quantum effects related to LZ model. The off-diagonal electronic state interactions are arisen for this case from the dipole forces. For relatively short laser pulses, it leads to the time dependent LZ problem for two electronic states, detailed considered in our paper (see also the laser optic formulation in [83] - [85]). The probability to find the system in the upper state after a single resonant passage, can be computed in the frame work of the LZ model. The latter point is related to one important aspect of the LZ problem, namely dissipative and noisy environments. When external actions (say fields) driving LZ transitions are reversed from large negative to large positive values, the dissipation reduces tunneling, that is the system remains in the ground state, or by other words, the thermal excitation from the ground state to the excited one, suppresses such adiabatic transitions. However, in the case of the field swept from the resonance point, the tunneling probability becomes larger in the presence of the dissipation (see e.g., [67]). The increasing precision of experimental tests in the femtosecond laser pulse range enables to excite well defined molecular states and to study their evolution in time using the second probing laser beam [17].

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Figure Captions.

Fig. 1  
Stokes (dashed) and anti-Stokes (solid) lines for a pair of close linear turning points replaced by one second order 
turning point; (a) - classically forbidden region; (b) classically accessible region.

Fig. 2  
Adiabatic (3,4) and diabatic (1,2) potentials for LZ problem.

Fig. 3  
Stokes (dashed) and anti-Stokes (solid) lines in the vicinity of: (a) conjugated bifurcation points \( \pm i \tau_c \); (b) diabatic 
potentials crossing point \( X = 0 \).

Fig. 4  
Stokes (dashed) and anti-Stokes (solid) lines for linear turning points corresponding classically forbidden (a), inter-
mediate (b), and accessible (c) energy regions of LZ problem.

Fig. 5  
Relative placement of the adiabatic levels; (a) \( U_{12} > U^*_{12} \); (b) \( U_{12} < U^*_{12} \), \( U^*_{12} = (3/2)(\hbar^2 F^2/4m)^{1/3} \).

Fig. 6  
\( E, U_{12} \) phase diagram (I - tunneling region, II - over-barrier region, and two intermediate energy regions \( III \) and 
\( III' \) are separated by the line \( \nu^* = 0.325 \).

Fig. 7  
Transition matrix element \( M_{11} \) as a function of \( U_{12}/U^*_{12} \), computed at \( \alpha = 0 \): on the boundary between tunneling 
and intermediate energy regions (a); at \( E = U^\# \) (b); on the boundary between the intermediate and over-barrier 
regions (c);

lines 1,2,3, 1', 2', 3', 1'', 2'', 3'' computed for corresponding energy regions using (5.19), (5.25), and (5.36), respectively.

Fig. 8  
\( T \) versus \( E \) dependence for: (a) \( U_{12} = U^*_{12} \); (b) \( U_{12} = 0.5U^*_{12} \); (c) \( U_{12} = 0.25U^*_{12} \);

stars mark the region \( III' \) boundaries, thin lines show results for the over-barrier and tunneling regions, bold lines 
for the intermediate energy region.

Fig. 9  
Transmitted wave phase as a function of \( E \) in the over-barrier region at \( U_{12} = U^*_{12} \).

Fig. 10  
Amplitudes of the decaying solutions \( \Phi_L^- \) at \( X > 0 \) versus \( E \) for: (1) \( U_{12} = U^*_{12} \); (2) \( U_{12} = 0.5U^*_{12} \); (3) \( U_{12} = 0.25U^*_{12} \).

Fig. 11  
The diabatic level crossing phenomena: (a) crossing region; (b) bound initial and decay final states; (c) bound 
initial and final states.

Fig. 12  
Level displacements versus \( U_{12} \) for two diabatic crossing potentials \( (1 \pm X)^2/2 \). Dashed lines show the intermediate 
energy region; dotted - dashed lines show displacements for the top and for the bottom of the adiabatic potentials. 
\( k, n, and n' \) are quantum numbers for the diabatic, and lower and upper adiabatic potentials.

Fig. 13  
\( \Gamma_n \) versus \( U_{12} \) for the quasi stationary states at the diabatic potentials \( (1 + X)^2/2 \) and \( (1/2) - X \) crossing; (a) 1 - 4 are the level energies 0.042, 0.125, 0.208, and 0.292 for the lower adiabatic potential; (b) 1' - 3' are the level 
energies 0.625; 0.708; 0792 for the upper adiabatic potential.

Fig. 14  
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 \( U_{12} = 0.21 \).
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9
Fig. 10
Fig. 11
Fig. 12
Fig. 13
Fig. 14