

## Semiclassical quantization of bound and quasistationary states beyond the adiabatic approximation

V. A. Benderskii

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

E. V. Vetoshkin

*Institute of Problems of Chemical Physics, RAS, 142432 Moscow Region, Chernogolovka, Russia*

E. I. Kats

*Laue-Langevin Institute, F-38042, Grenoble, France  
and L. D. Landau Institute for Theoretical Physics, RAS, Moscow, Russia*

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We examine one important (and previously overlooked) aspect of well-known crossing diabatic potentials or Landau-Zener (LZ) problem. We derive the semiclassical quantization rules for the crossing diabatic potentials with localized initial and localized or delocalized final states, in the intermediate energy region, when all four adiabatic states are coupled and should be taken into account. We found all needed connection matrices and present the following analytical results: (i) in the tunneling region, the splittings of vibrational levels are represented as a product of the splitting in the lower adiabatic potential and the nontrivial function depending on the Massey parameter; (ii) in the overbarrier region, we find specific resonances between the levels in the lower and in the upper adiabatic potentials and, in that condition, independent quantizations rules are not correct; (iii) for the delocalized final states (decay lower adiabatic potential), we describe quasistationary states and calculate the decay rate as a function of the adiabatic coupling; and (iv) for the intermediate energy regions, we calculate the energy level quantization, which can be brought into a compact form by using either adiabatic or diabatic basis set (in contrast to the previous results found in the Landau diabatic basis). Applications of the results may concern the various systems; e.g., molecules undergoing conversion of electronic states, radiationless transitions, or isomerization reactions.

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### I. INTRODUCTION

There has been great progress in the theory of crossing potentials during the last seven decades (see, e.g., the references in both research and textbook literature [1–9]). Surprisingly, a seemingly simple but basic question as to how well-known semiclassical quantization rules should be modified for this particular situation (crossing diabatic potentials with bound (i.e., localized) initial and localized or delocalized final states) to the best of our knowledge are still unanswered (at least, a complete and unifying description of the quantization for a general case is still not available and a number of other questions remain to be clarified).

Partially, this is related to the fact that, unfortunately, experimental data in this field are still scarce and not very accurate. However, the situation is now changing. Experimental techniques (e.g., the increasing precision of experimental tests in the femtosecond laser pulse range enables us to excite well-defined molecular states and to study their evolution in time using the second probing laser beam [5,10,11]) have progressed to the point where molecular tunneling splitting dependence on energy can be measured in well controlled conditions with a very high accuracy. It would therefore seem appropriate at this time to take a fresh look at the theory, which is the purpose of the present article. Note also that these questions are not only of interest in their

own intellectual right. Recent experimental and theoretical advances [12,13] in particular are beginning to yield a coherent understanding of several phenomena that are far from requiring minor corrections to the standard adiabatic treatment of the problem. Physically, such types of situations can occur as a result of nonadiabatic interactions of different electronic states forming in crossing one-well diabatic vibrational potentials. Adiabatic coupling removes diabatic level crossing, and the diabatic levels are replaced by the adiabatic ones (see Fig. 1 illustrating this phenomenon). In the case of a large adiabatic splitting (see precise criteria below), one can restrict oneself to the only lower adiabatic potential (symmetric or asymmetric double-well, or decay potential for the systems under consideration) and neglect any influence of the upper adiabatic potential (parabolic one-well for our case). However, in a general case of arbitrary adiabatic splittings, intrawell and interwell dynamics depend on both adiabatic potentials (i.e., on tunneling and adiabatic splitting). With respect to applications, the studies of these questions may concern the various molecular systems undergoing so-called conversion of electronic states, isomerization reactions, or radiationless transitions arising from “intersystem” crossings of potential energy surfaces in molecular spectroscopy and chemical dynamics, or inelastic atomic collisions.

It is worth noting that there exists a huge literature devoted to different approaches that have been made by other

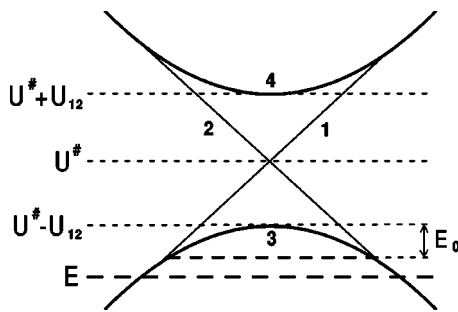


FIG. 1. Potentials in the vicinity of the diabatic potentials crossing point  $U^\#$ : The diabatic potentials (thin lines, 1,2), the adiabatic potentials (bold lines, 3,4), the adiabatic coupling energy  $U_{12}$ , and  $E_0$  is the characteristic zero-point oscillations energy in the parabolic barrier approximated the lower adiabatic potential near its top. The tunneling energy  $E$  region is shown by a broken line.

authors concerning the problem of crossing diabatic potentials (see, e.g., [2,3,6–10,14–20]), but some important differences to our work should be noted. First, suffice it to say, that the problem of how diabatic potentials crossing modifies the adiabatic potentials (occurring as a result of this crossing) quantization rules has not been investigated at all. One of the reasons, is that for many standard rigid molecules with quite large adiabatic splitting of energy levels, one may safely neglect any influence of the upper adiabatic potential (i.e., to use the standard quantization rules). However, nowadays the increasing precision of experimental tests of molecular tunneling splitting and decay (and also investigations and synthesis of more and more new nonrigid molecules), makes the study of this problem relevant and actual. Second is a methodic note. All previous approaches were based on the general semiclassical WKB formalism. The crucial point to treat quantization for crossing diabatic potentials is how to compute the contribution coming from the contour around a complex turning point. The accuracy of the WKB method can be improved considerably [14–17] (more recent references on so-called Laplace contour integration can be found also in [2,13]) by the appropriate choice of the integration path around the turning point. This method, attributed to Landau [1], appears to be quite accurate for the tunneling and overbarrier regions (however, even in this case there are some non-negligible corrections found in the papers [6,18,19]), but in the intermediate energy region (where there are relevant contributions from all four quantum states occurring at the crossing diabatic potentials) the method becomes completely inadequate. Besides the choice of these additional special trajectories (which one has to include to improve the accuracy of the WKB method, and along which the semiclassical motion is described by the Weber functions) depends on the detail form of the potential far from the top, and therefore for each particular case the nonuniversal procedure should be performed from the very beginning.

The essential simplification of the procedure achieved using the standard WKB semiclassical approximation in the momentum space representation was also proposed in the literature [2,6,15–19]. The method works well to compute the Landau-Zener (LZ) transition probability; however, the

application of this approach to the level quantization problem is difficult to realize. Indeed, the problem requires one to know the eigenfunctions in the coordinate space, and one cannot bluntly use the Fourier transform of the functions found in the momentum space, since the WKB method gives us only asymptotics of the eigenfunctions. These drawbacks of the WKB-like methods did not allow the study of the level quantization for crossing diabatic potentials in the previous investigations; here, we 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 overbarrier (with oscillating behavior) regions.

Recently, we have shown [21] that semiclassical solutions of many eigenvalue problems can be simplified by considering second-order turning points. The fact is that one second-order turning point replaces two close linear turning points. Moreover, it turns out (see below) that connection matrices, which link on the complex plane the solutions to the Schrödinger equation in the vicinity of the crossing point with the asymptotic solutions far from this point, can be calculated from the solutions of the Weber equation. Increasing and decreasing solutions in the classically forbidden region around a second-order turning point, are characterized by the action that has a minimum along a certain trajectory, to which we will refer in what follows as the instanton trajectory. The same kind of Weber equation can be formulated to calculate the connection matrices in the vicinity of a saddle point (or a maximum) of the potential, but besides we should also relate increasing and decreasing solutions at the crossing point (see also our recent publications on LZ crossing phenomena [22]).

Our aim is to construct semiclassical wave functions. To do it, we use connection matrix methodology that can be applied to any semiclassical approximation, but details of the method depends on the order of the turning points. For the second-order turning points that are minima of a potential, the whole procedure is equivalent to the traditional instanton approach, and the imaginary time (i.e., after Wick rotation) instanton trajectories correspond to the periodic orbits between the turning points, and the connection matrices in this case (see below and Appendix A) are real-valued ones. It is not the case for the second-order turning point, which is the potential maximum. The complex-valued connection matrix links two regions of infinite motion. Formally, one might refer to the corresponding wave functions also as instanton ones, applying the Wick rotations twice. LZ crossing points are combinations of two second-order turning points with two different Stokes constants [23] corresponding to one minimum and one maximum of the potential. In the tunneling region, there exist periodic orbits for two solutions, while two others correspond to unrestricted (infinite) motions. As above, we will call these wave functions instanton ones since they are Weber functions (as in the traditional instanton method), but with complex-valued arguments occurring as a result of complex coordinate frame rotation.

Thus, our approach in this paper is based on the minimization of the functional of classical action in the upside-down potential, so-called instanton type approach, which represents the most important area of the configurational space where the semiclassical wave functions are localized (see [4,13–22]). The whole analysis can be brought into a more elegant form by introducing connection matrices that link, on the complex plane, the semiclassical solutions to the Schrödinger equation for the model potential of the problem under study and the exact solutions of the so-called comparison equation that is valid near the crossing point, where one can approximate the potential by linear or parabolic ones. The explicit calculations of the connection matrices are rather involved since one should treat the four fundamental solutions to the left and to the right regions with respect to turning or crossing points. Therefore, the connection matrices we are looking for are  $4 \times 4$  matrices. Although the generalization for our case of the already known  $2 \times 2$  connection matrices (see, e.g., [23,24]) is straightforward, it deserves some precaution as it implies quite different procedures for the energy (more accurately for  $E/\gamma$ , where  $\gamma \gg 1$  is the semiclassical parameter, see below) smaller than (the tunneling region), larger than (the overbarrier region), or of the order (the intermediate region) of the potential barrier energy. Within the framework of the connection matrix approach, we present a full and unified description of a one-dimensional (1D) (which very often can be a quite reasonable approximation for real systems) level quantization problem for diabatic potentials crossing.

The remainder of our paper has the following structure. Section II contains basic methodical details and equations necessary for our investigation. Except for a mathematical trick that eliminates a large amount of tedious algebra and allows us to construct a regular method for calculating higher order perturbative corrections, the section contains already known results. Our current physical results are collected in Secs. IV–VI, and partially in Sec. III, where we calculate all needed connection matrices, which provide a very efficient method of finding semiclassical solutions to the Schrödinger equation in potentials having several turning points. The knowledge of the connection matrices is important and significant not only in itself, but also for developing a good analytical approximation and standardized numerical procedures. In Sec. IV, we find the quantization rules for the tunneling and overbarrier energy regions. Section V is devoted to the intermediate energy region, where all four states occurring at the diabatic potentials crossing should be regarded on the same footing. Different particular cases, depending on the ratio of the model parameters, are also examined in this section. In Sec. VI, we investigate the linear coupling of the LZ system to harmonic phonons and find that it renormalizes by the parameters entering the initial diabatic potentials crossing problems considered in the previous Secs. IV and V. The last section VII contains summary and discussion. In two appendices to the paper, we collect some more specialized technical material required for the calculations of the connection matrices in different energy windows (Appendix A), and to reduce the fourth-order Schrödinger equation to two independent second-order Weber equations (Appendix B). Those readers who are not very interested in mathemati-

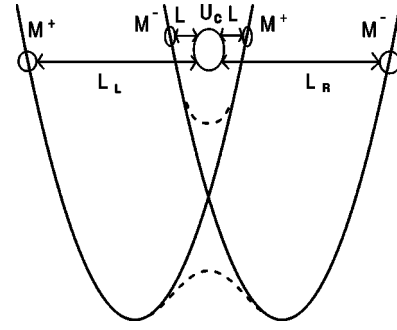


FIG. 2. The diabatic level crossing phenomena: (a) bound initial and final states; (b) bound initial and decay final states.

cal derivations can skip these appendices, finding all essential physical results in the main text of the paper.

## II. FOURTH-ORDER COMPARISON EQUATION FOR THE CROSSING POINT

To move further on smoothly let us first describe our strategy. First, we should define all notations and relevant points of the diabatic potentials crossing problem. We depict the typical situation in the vicinity of the diabatic potentials crossing point in Fig. 1. The diabatic potentials (1,2) are shown by thin solid lines, the adiabatic potentials (3,4) by bold solid lines. In addition, we have introduced in the picture the adiabatic coupling energy  $U_{12}$ , the crossing point energy  $U^\#$ , and  $E_0$  is the characteristic zero-point oscillations energy in the parabolic barrier approximating the lower adiabatic potential near its top.

As a model for diabatic potentials in this paper, we choose two parabolas  $U_L$  and  $U_R$  with a symmetrical crossing at the point  $x=0$ . To be specific, let us consider two types of the diabatic potential crossing depicted in Fig. 2. The corresponding adiabatic potentials are, respectively, the double-well or decay lower potential, and the one-well upper adiabatic potential. At arbitrary values of the parameter  $U_{12}$  to find eigenstates and eigenfunctions for our model potential, we should solve the coupled Schrödinger equations

$$\begin{aligned}
 -\frac{1}{2} \frac{d^2 \Theta_L}{dx^2} + \gamma^2 [U_L(x) - E] \Theta_L &= \gamma^2 U_{12} \Theta_R, \\
 -\frac{1}{2} \frac{d^2 \Theta_R}{dx^2} + \gamma^2 [U_R(x) - E] \Theta_R &= \gamma^2 U_{12} \Theta_L.
 \end{aligned}
 \tag{2.1}$$

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

These equations (2.1) can be written as one fourth-order equation, e.g., for  $\Theta_L$ , as

$$\begin{aligned} & \frac{d^4\Theta_L}{dx^4} - 2\gamma^2[U_L(x) + U_R(x) - 2E]\frac{d^2\Theta_L}{dx^2} - 4\gamma^2\frac{dU_L}{dx}\frac{d\Theta_L}{dx} \\ & + 4\gamma^4\left[(U_L - E)(U_R - E) - U_{12}^2 - \frac{1}{2\gamma^2}\frac{d^2U_L}{dx^2}\right]\Theta_L = 0. \end{aligned} \quad (2.2)$$

In what follows, we use  $\Omega_0$  and  $a_0$  to set corresponding dimensionless scales, e.g., dimensionless energy  $\epsilon = E/\gamma\Omega_0$ ,  $u_{L/R} = U_{L/R}/(\gamma\hbar\Omega_0)$ ,  $u_{12} = 2U_{12}/(\gamma\hbar\Omega_0)$  (we introduce factor 2 in  $u_{12}$  for ease of writing the equations below), coordinate  $X = x/a_0$ , and we put  $\hbar = 1$  (except where explicitly stated to the contrary and where the occurrences of  $\hbar$  are necessary for understanding).

Luckily, Eq. (2.2) admits semiclassical solutions by the Fedoryuk method [25–27] since the coefficients at the  $n$ th-order derivatives proportional to  $\gamma^{-n}$ , and therefore so small that higher order derivatives of the prefactor (in the semiclassical form the wave function can be always presented as the prefactor times the exponent) can be safely neglected in finding of asymptotic solutions. The Fedoryuk method makes possible to find asymptotic solutions to the ordinary differential equations of the form

$$y^{(n)} + \sum_{k=0}^{n-1} \gamma^{n-k} f_k(X) y^{(k)} = 0, \quad (2.3)$$

where we designated  $y^{(k)} \equiv d^k y/dX^k$ , and the coefficients at the derivatives  $f_k(X)$  are arbitrary functions of  $X$ . Note that Eq. (2.2) for  $\Theta$  has this Fedoryuk form. By the standard semiclassical substitution  $y = A \exp[\gamma W(X)]$ , (2.3) can be reduced to the set of equations combining the terms proportional to  $\gamma^n, \gamma^{n-1}, \dots$ , which for  $\gamma \gg 1$  can be represented in the form of generalized so-called Hamilton-Jacobi and transport equations, respectively, as

$$F(\lambda) = \lambda^n + \sum_{k=0}^{n-1} f_k(X) \lambda^k = 0, \quad (2.4)$$

and

$$\frac{dF}{d\lambda} \frac{dA}{dX} + \frac{1}{2} \frac{d^2 F}{d\lambda^2} \frac{d\lambda}{dX} A = 0, \quad (2.5)$$

where  $\lambda = -\gamma dW/dX$ .

Noting that in the vicinity of the crossing point  $X=0$ , the parabolic diabatic potentials can be replaced by the linear ones counted from the barrier top  $U^\#$ , as

$$u_{L/R}(X) = u^\# \pm fX \quad (2.6)$$

[as above,  $u^\# = U^\#/(\gamma\hbar\Omega_0)$ ], and eventually Eq. (2.2) can be presented into a more compact and simple form

$$\frac{d^4\Theta_L}{dX^4} - 2\gamma^2\alpha\frac{d^2\Theta_L}{dX^2} - 2\gamma^2f\frac{d\Theta_L}{dX} + \gamma^4[\alpha^2 - f^2X^2 - u_{12}^2]\Theta_L = 0, \quad (2.7)$$

where in our dimensionless units  $\alpha = 2(u^\# - \epsilon)$ .

The roots of the characteristic polynomial for (2.7)

$$\begin{aligned} F(\lambda, X) &= \lambda^4 - 2\gamma^2(u_L + u_R - 2\epsilon)\lambda^2 - 4\gamma^2\frac{du_L}{dX}\lambda \\ &+ 4\gamma^4\left[(u_L - \epsilon)(u_R - \epsilon) - u_{12}^2 - \frac{1}{2\gamma^2}\frac{d^2u_L}{dX^2}\right] \\ &= 0, \end{aligned} \quad (2.8)$$

or in the equivalent form

$$F(\lambda) = \lambda^4 - 2\alpha\gamma^2\lambda^2 - 2\gamma^2f\lambda + \gamma^4(\alpha^2 - u_{12}^2 - f^2X^2), \quad (2.9)$$

determine independent solutions to (2.7). Solving the equation  $F(\lambda) = 0$  perturbatively over  $\gamma^{-1} \ll 1$ , we find

$$\lambda_j = \lambda_j^0 + \lambda_j^1, \quad (2.10)$$

where

$$\lambda_j^0 = \pm \gamma \left[ \alpha \pm \sqrt{u_{12}^2 + f^2X^2} \right]^{1/2} \quad (2.11)$$

and

$$\lambda_j^1 = \pm \frac{f}{2\sqrt{u_{12}^2 + f^2X^2}}, \quad (2.12)$$

we find finally the four asymptotic solutions of (2.7)

$$\{y_j\} \equiv \{\Theta_+^+, \Theta_-^+, \Theta_+^-, \Theta_-^-\} = \left( \frac{dF}{d\lambda} \right)^{-1/2} \exp \left[ \int_0^X \lambda_j(X') dX' \right]. \quad (2.13)$$

The subscripts in (2.13) correspond to the upper or lower adiabatic levels, and the superscripts refer to the sign of the action.

As was mentioned above, in the vicinity of the crossing point one can replace (2.2) by (2.7), and by the substitution

$$\Theta_L = \exp(\kappa_{1,2}X) \Phi_L^{1,2}, \quad (2.14)$$

we can find the equation for  $\kappa$  as

$$\kappa^4 - \alpha\gamma^2\kappa^2 + \frac{1}{4}\gamma^4u_{12}^2 = -\kappa^4\delta^2(1 + 2\delta) + R(\kappa, \delta), \quad (2.15)$$

where

$$R(\kappa, \delta) = (2\kappa^6)^{-1}(1 - 3\delta)(1 + \delta)^{-3}[1 - Q - \sqrt{1 - 2Q^2}],$$

$$Q = 8\delta^2(1 + \delta),$$

$$\delta = \frac{\gamma^2 f}{4\kappa^3} < \frac{1}{4}, \quad (2.16)$$

and

$$\kappa_{1,2} = \pm \gamma \sqrt{\alpha} \left( 1 - \frac{\delta^2}{2} \right). \quad (2.17)$$

It can be proved that the fourth-order equation (2.7) in variables (2.14) is reduced to the equation with constant coeffi-



cients in front of all derivatives and with the free term in the form of a quadratic over  $X$  function. When the exponent in (2.14) is a solution to Eq. (2.15), the transformed equation is reduced to the Weber equations upon neglecting anharmonic terms like  $X^2 dF/dX$ ,  $X^3 F(X)$ , and  $X^4 F(X)$ . We presented all details of this reduction in Appendix B. Thus, Eq. (2.7) is reduced to two independent Weber equations with the known fundamental solutions [28]

$$\{\Theta_L\} = \left\{ \exp(\pm \gamma \sqrt{\alpha} X) D_{-\nu} \left[ \left( \frac{f^2 \gamma^2}{\alpha} \right)^{1/4} X \right], \right. \\ \left. \exp(\pm \gamma \sqrt{\alpha} X) D_{-1-\nu} \left[ \left( \frac{f^2 \gamma^2}{\alpha} \right)^{1/4} X \right] \right\}, \quad (2.18)$$

where  $\nu = \gamma u_{12}^2 / (4f\sqrt{\alpha})$  is the so-called Massey parameter. The corrections to the indices of the parabolic cylinder functions  $D$  and to the arguments of these functions can be found from (2.15).

Presented above, the leading terms of these solutions corresponding to the tunneling case (here we use a dimensional energy  $E$ ) given by

$$E < (U^\# - U_{12}) \quad (2.19)$$

(in our dimensionless units it is  $\alpha > u_{12}$ ), where the characteristic fourth-order polynomial (2.8) can be reduced to the second-order one (i.e., two pairs of roots are nearly degenerate), are known in the literature (see, e.g., [1–4]) but the Fedoryuk method we used also gives us in the tunneling region the higher order over the parameter  $\delta$  (2.16) corrections.

In the tunneling region (2.19), one can expand the roots of (2.15) in terms of the parameter  $\delta$  (2.16). Using the substitution (2.14) to transform (2.2), we can find easily that at the conditions (2.15), (2.16), the coefficients at the fourth- and at the third-order derivatives in the transformed fourth-order differential equation for  $\Phi$  are small (proportional to  $\delta$  and to  $\sqrt{\delta}$ , respectively), and thus this fourth-order equation can be rewritten as two second-order Weber equations with the solutions

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

where

$$p^{(1)} = -1 + \frac{\delta}{4} - \nu, p^{(2)} = \frac{\delta}{4} - \nu, \beta = \left( \frac{\gamma^2 f^2}{\alpha} \right)^{1/4} \left( 1 + \frac{\delta^2}{4} \right). \quad (2.20)$$

The same manner in the overbarrier energy region, i.e.,

$$E > (U^\# + U_{12}) \quad (2.21)$$

[again as in (2.19) we have used dimensional units, and in dimensionless form (2.21) reads as  $-\alpha > u_{12}$ ] when the energy is larger than the upper adiabatic potential minimum, the roots of Eq. (2.8) are complex conjugated and have the same structure as presented above [see also (B6)] for the tunneling region with the roots  $\kappa$  given as

$$\kappa_{1,2} = \pm i \gamma \sqrt{|\alpha|} \left( 1 - \frac{\tilde{\delta}^2}{2} \right). \quad (2.22)$$

In addition, in (B6),

$$\kappa_0 = i \frac{\gamma}{\sqrt{2}} (|\alpha| + \sqrt{\alpha^2 - u_{12}^2}),$$

and with  $\tilde{\delta}$  playing the role of the small parameter in this region, i.e.,

$$\tilde{\delta} = \frac{f}{4\gamma|\alpha|^{3/2}}. \quad (2.23)$$

Again as above for the tunneling region, the coefficients at the higher order derivatives are small and, therefore, the function  $\Phi$  (2.14) satisfies the Weber equation with the fundamental solutions

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

where

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

$$\tilde{\beta}_1 = \exp(i\pi/4) \left( \frac{\gamma^2 f^2}{|\alpha|} \right)^{1/4} \left( 1 + \frac{\tilde{\delta}^2}{4} \right), \quad (2.24)$$

$$\tilde{\beta}_2 = \exp(-i3\pi/4) \left( \frac{\gamma^2 f^2}{|\alpha|} \right)^{1/4} \left( 1 + \frac{\tilde{\delta}^2}{4} \right)$$

( $\tilde{\nu}$  is defined as the Massey parameter entering (2.18) with  $\alpha \rightarrow |\alpha|$ ; i.e.,  $\tilde{\nu} = [\gamma u_{12}^2 / (4f\sqrt{|\alpha|})]$ ). As it was for the tunneling region (2.20), the leading terms of the expansion (2.24) coincide with the well-known results, but from (2.24) we are able to compute the corrections to the main terms.

The analogous task for the intermediate energy region (in dimensional units), i.e.,

$$(U^\# + U_{12}) \geq E \geq (U^\# - U_{12}), \quad (2.25)$$

is much more tricky. Our results will be presented in Sec. V, but a few comments are necessary here. In the problem we have three dimensionless parameters characterizing the energy ( $\alpha$ ), the level coupling ( $u_{12}$ ), and the potential ( $f$ ), and for the ease of semiclassical estimations, we also keep the semiclassical parameter  $\gamma \gg 1$ . Note also that these parameters are not independent ones, and the relation  $u_{12} = 2f^2$  (which will be useful in our further consideration) should be satisfied. In terms of these parameters within the intermediate energy region (2.25), we have the subregion  $S'$ ,  $|\alpha| \leq 2\gamma^{-1}$  and  $u_{12} \leq 2\gamma^{-1}$ , and the intermediate subregion  $S''$ , where  $\gamma\sqrt{u_{12}/2} \gg 1$ . In Sec. V, we calculate the connection matrices for both subregions; details of the reduction procedures, which are different in  $S'$  (where the comparison equations are reduced to two decoupled Airy equations) and  $S''$  (where these comparisons equations are Weber ones) are described in Appendix B.

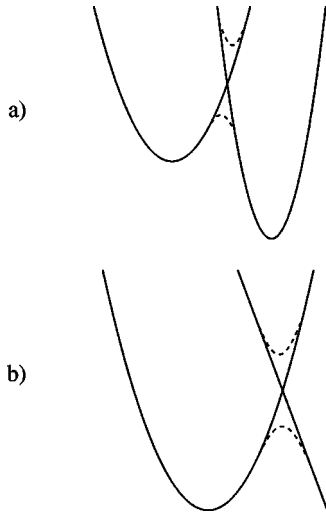


FIG. 3. Connection matrices for the tunneling energy region: (a) in the WKB approach to the lower states, where  $M^\pm$  are the connection matrices for the linear turning points, and  $U_c$  for the crossing point; the shift matrices are depicted as arrows, in the classically accessible regions  $L_L$  and  $L_R$ , and in the classically forbidden region  $F_L$  and  $F_R$  (for the upper states there are no real-valued turning points); (b) in the instanton type method, one has two connection matrices  $M_{L/R}^{(2)}$  for the second-order turning points and shift matrices  $F_L$  and  $F_R$  in the classically forbidden region.

III. CONNECTION MATRICES

The purpose of this section is to briefly indicate the main steps in the derivation of the connection matrices. The matching points we must find to quantize the energy levels depend essentially on the energy window under consideration [(2.19), (2.21), and (2.25)]. The tunneling region is placed in the lower adiabatic potential. In the WKB method, in this case starting from the crossing point ( $X=0$ ), one has to investigate the classically forbidden region in the lower adiabatic potential barrier [see Fig. 3(a) and the corresponding figure caption for all notations]. The solutions can be found easily in the vicinity of the crossing point, but to derive the quantization rules, one should also know the solutions quite far from the crossing point. To do it explicitly in the WKB method, we should match the two exponentially decreasing and two exponentially increasing solutions in the

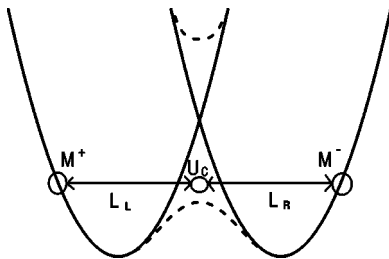


FIG. 4. Connection matrices for the overbarrier energy region. The shift matrices from the crossing point to the inner turning points are designated by  $L$  (all other notations are the same as in Fig. 3).

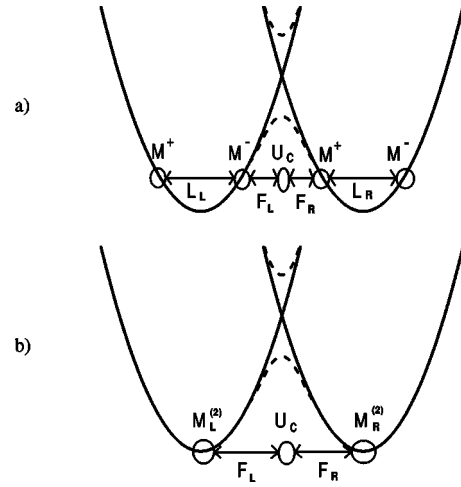


FIG. 5. Connection matrices for the intermediate energy region (as in the tunneling region, there are no real valued turning points for the upper states).

barrier with the oscillation solutions in the wells. Technically, the matching should be performed asymptotically; i.e., at small  $|X|$  but for large enough  $\sqrt{\gamma}|X|$ . To do it one has to calculate all needed connection matrices (namely, at the crossing point, and at the linear and second-order turning points, and the shift matrices from the crossing point to the turning points in the classically forbidden region and between the turning points in the classically accessible region). Within the instanton type method, the trajectory goes through only the classically forbidden region [see Fig. 3(b)], and matching should be performed only at two second-order turning points. In the overbarrier energy region (see Fig. 4), the matching is performed by using the crossing point con-

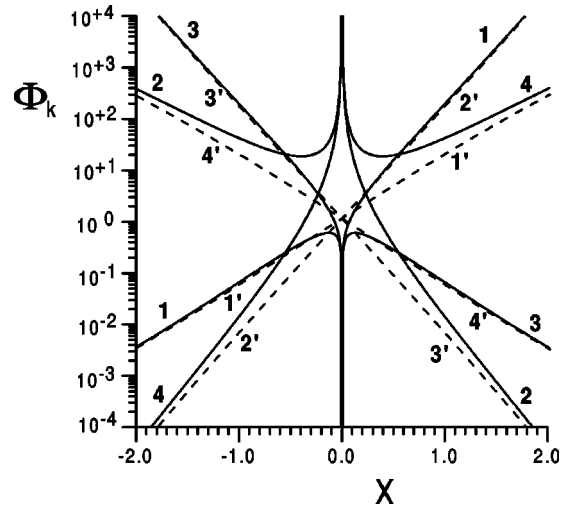


FIG. 6. The matching of the asymptotic solutions in the tunneling region for the diabatic levels crossing shown in Fig. 1(a): 1 - the function  $\Phi_L^+(X)\sqrt{2\pi}/\Gamma(1+\nu)$ ; 2 - the function  $\Phi_L^-(X)$ ; 3 - the function  $\Phi_R^+(X)\sqrt{2\pi}/\Gamma(1+\nu)$ ; 4 - the function  $\Phi_R^-(X)$ ; 1' - the function  $\exp(k_0X)D_{-1-\nu}(\beta X)$ ; 2' - the function  $\exp(k_0X)D_{-1-\nu}(-\beta X)$ ; 3' - the function  $\exp(-k_0X)D_{-1-\nu}(\beta X)$ ; 4' - the function  $\exp(-k_0X)D_{-1-\nu}(-\beta X)$ .

nection matrix  $\hat{U}'_c$ , the shift matrix  $\hat{L}$  connecting the crossing point and the linear turning points at the upper adiabatic potential, and the shift matrices  $\hat{L}_{L/R}$  belonging to the diabatic potentials. In this case, all matching solutions are oscillating ones. Finally, for the intermediate energy region, there are no real-valued turning points for the upper states (see Fig. 5), and the matching between two oscillating and two exponentially varying solutions is determined by the connection matrix (see Fig. 5) linking the linear imaginary turning points of the adiabatic potentials.

To recast the analysis into a compact form, it is convenient to formulate the general procedure for calculating the connection matrices for arbitrary combinations of the first- and second-order turning points. After that, the procedure can be applied to any particular problem under investigation. To do it, one has to extend the linear turning points procedure which is already known [23]. For a generic semiclassical equation

$$\frac{d^2\Psi}{dz^2} + \gamma^2 q(z)\Psi(z) = 0, \quad (3.1)$$

in the limit  $\gamma \gg 1$ , the Stokes and anti-Stokes lines are determined by the respective conditions

$$\text{Re } W(z) = 0 \quad (3.2)$$

and

$$\text{Im } W(z) = 0, \quad (3.3)$$

where the action

$$W(z) = \int^z \sqrt{q(z)} dz. \quad (3.4)$$

The lower integration limit in (3.4) is not relevant because we are interested in semiclassical solutions for large  $|z|$ . These Stokes and anti-Stokes lines separate the complex plane  $z$  into the sectors. On the anti-Stokes lines, the increasing and decreasing solutions become equal, and the type of the solution is interchanged upon crossing the anti-Stokes lines. The Stokes lines are bisectors between neighboring anti-Stokes lines. After the crossing with the Stokes line, one should add to the coefficient at the decreasing solution the coefficient at the increasing solution times so-called Stokes constant. The latter one occurs as a result of going around the turning point and depends on the turning point type.

To find the connection matrices for the tunneling region, we have to establish the correspondence between the solutions of the fourth-order differential equation (2.2) 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  $L$ ), as

$$\gamma W_L^* \simeq \gamma W_{0L}^* + k_0 X + \frac{\beta^2}{4} X^2, \quad (3.5)$$

$$\gamma W_R^* \simeq \gamma W_{0R}^* - k_0 X + \frac{\beta^2}{4} X^2,$$

where  $k_0 = \gamma\sqrt{\alpha}$  is imaginary momentum ( $U^\#$  sets the energy corresponding to the diabatic potentials crossing point), and  $W_{0L,R}^*$  are the actions computed from an arbitrary distant point in the  $L$  or in the  $R$  wells, respectively, to the point  $X=0$ . On the other hand, in the adiabatic potentials  $u^\pm = u^\# \pm \sqrt{u_{12}^2 + f^2 X^2}$ , the corresponding actions can be represented as

$$\gamma W^\pm - \gamma W_0^\pm = k_0 X \pm \frac{\beta^2}{4} X^2 \text{sgn}(X). \quad (3.6)$$

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 nonzero amplitudes of the following transitions:

$$\langle \Phi_L^+ | \Phi_R^- \rangle, \langle \Phi_L^- | \Phi_R^+ \rangle, \langle \Phi_R^+ | \Phi_L^- \rangle, \langle \Phi_R^- | \Phi_L^+ \rangle. \quad (3.7)$$

Recalling that

$$\gamma W^\pm = \gamma \int (\alpha \pm \sqrt{u_{12}^2 + f^2 X^2})^{1/2} \simeq k_0 X \pm \frac{\beta^2}{4} X^2 \pm \frac{\nu}{2} (1 - \ln \nu), \quad (3.8)$$

we come to the conclusion that the quantum solutions (2.20), valid in the vicinity of the level crossing point asymptotically, match increasing and decreasing solutions smoothly, leading to the Landau description [1] of the level crossing transitions. To illustrate the analytical results presented above, we show schematically in Fig. 6 the matching of the asymptotic (Fedoryuk) solutions (2.13) for the crossing diabatic potentials with localized initial and final states via the Weber functions in the tunneling region. We use the symmetric basis constructed from the functions (2.13) (see detailed description in the Fig. 6 caption).

In the tunneling region (2.19) for every well ( $L$  or  $R$ ), there exist exponentially increasing and decaying real-valued solutions to the Schrödinger equation. The solutions are matched at the crossing point; therefore, they are linked by the real-valued  $4 \times 4$  connection matrix, which should have two  $2 \times 2$  blocks linking the increasing (decreasing) diabatic solution in the  $L$ -well with the decreasing (increasing) diabatic solution in the  $R$ -well, in the agreement with the standard Landau scheme of the tunneling transitions [1]. Omitting a large amount of tedious algebra, we can represent the connection matrix linking the ‘‘asymptotic’’ [i.e., in the left/right ( $L, R$ ) wells and for the upper/lower (+, -) adiabatic potentials] solutions in the tunneling energy region in the following form:

$$\begin{pmatrix} \Phi_R^- \\ \Phi_R^+ \\ \Phi_L^+ \\ \Phi_L^- \end{pmatrix} = \begin{pmatrix} \hat{M}_c^{(+)} \hat{L}_R^{(c)} \hat{M}_c^{(-)} \hat{F}_c & 0 \\ & \hat{1} \end{pmatrix} \times \hat{U}_c \begin{pmatrix} \hat{F}_c \hat{M}_c^{(+)} \hat{L}_L^{(c)} \hat{M}_c^{(-)} & 0 \\ & \hat{1} \end{pmatrix} \begin{pmatrix} \Phi_L^+ \\ \Phi_L^- \\ \Phi_R^- \\ \Phi_R^+ \end{pmatrix}. \quad (3.9)$$

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

$$\hat{U}_c = \begin{bmatrix} p & 0 & 0 & -\cos(\pi\nu) \\ 0 & [\sin^2(\pi\nu)]/p & -\cos(\pi\nu) & 0 \\ 0 & \cos(\pi\nu) & p & 0 \\ \cos(\pi\nu) & 0 & 0 & [\sin^2(\pi\nu)]/p \end{bmatrix}, \quad (3.10)$$

where we designated

$$p = \frac{\sqrt{2\pi} \exp(-2\chi)}{\Gamma(\nu)}, \quad (3.11)$$

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

$$\hat{M}_c^{(-)} = \begin{pmatrix} 1 & -i \\ -(i/2) & (1/2) \end{pmatrix}, \quad (3.12)$$

and  $\hat{M}_c^{(+)}$  is the matrix Hermitian conjugated to (3.12). The  $\hat{L}_{L/R}^{(c)}$  and  $\hat{F}_c$  matrices are called shift matrices, and those are related to the variations of the coefficients of increasing and decaying semiclassical solutions in the regions between the turning points ( $\hat{F}_c$  is the shift matrix when one moves from the crossing to the turning point in classically forbidden region, and  $\hat{L}_{L/R}^{(c)}$  are the shift matrices in the classically accessible regions). Explicitly, we get

$$\hat{F}_c = \begin{pmatrix} \exp(-\gamma W_B^*/2) & 0 \\ 0 & \exp(\gamma W_B^*/2) \end{pmatrix}. \quad (3.13)$$

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

$$\hat{L}_{L/R}^{(c)} = \begin{pmatrix} \exp(i\gamma W_{L/R}^*) & 0 \\ 0 & \exp(-i\gamma W_{L/R}^*) \end{pmatrix}, \quad (3.14)$$

where  $W_{L/R}^*$  is the action calculated by the integration between the turning points. We present explicit expressions for the total connection matrix in Appendix A.

The overbarrier region (2.21) can be treated in the same manner. In this case, the crossing point is in the classically accessible region for the both potentials. The fundamental diabatic solutions can be represented as the waves propagating in the opposite directions, and the complex-valued connection matrix has as it was for the tunneling region  $2 \times 2$  block structure, where the blocks link the waves in the  $L$  and  $R$  wells propagating in the same direction. Specifically, the corresponding connection matrix at the crossing point  $\hat{U}'_c$ ,

$$\hat{U}'_c = \begin{bmatrix} s \exp(-i\phi) & 0 & 0 & -\exp(-\pi\nu) \\ 0 & s \exp(i\phi) & -\exp(-\pi\nu) & 0 \\ 0 & \exp(-\pi\nu) & s \exp(-i\phi) & 0 \\ \exp(-\pi\nu) & 0 & 0 & s \exp(i\phi) \end{bmatrix}, \quad (3.15)$$

where we denoted  $s = \sqrt{1 - \exp(-2\pi\nu)}$ ,  $\phi = \arg \Gamma(-i\nu) + \text{Im}(2\tilde{\chi})$ , and

$$\tilde{\chi} = -(i/2)[(\pi/4) + \nu(1 - \ln \nu)] + (1/4)(\pi\nu + \ln \nu), \quad (3.16)$$

should be multiplied by two blocks: the block from the left gives the contribution at the turning point and includes the shift matrix to the crossing point in  $L$  and in  $R$  wells of the lower adiabatic potential, and the right block is related to the turning point and to the shift matrix to the crossing point in

the upper one-well adiabatic potential. Thus, finally, in the overbarrier region, we get

$$\begin{pmatrix} \Phi_R^- \\ \Phi_R^+ \\ \Phi_L^+ \\ \Phi_L^- \end{pmatrix} = \begin{pmatrix} \hat{M}_c^{(+)} \hat{L}_R^{(c)} & 0 \\ 0 & \hat{M}_c^{(+)} \hat{L}_L^{(c)} \end{pmatrix} \hat{U}'_c \begin{pmatrix} \hat{L}_L^{(c)} \hat{M}_c^{(-)} & 0 \\ 0 & \hat{L}_R^{(c)} \hat{M}_c^{(-)} \end{pmatrix} \begin{pmatrix} \Phi_L^+ \\ \Phi_L^- \\ \Phi_R^- \\ \Phi_R^+ \end{pmatrix}. \quad (3.17)$$

Here, we used the same notations as above for the tunneling region, the matrices  $\hat{M}_c^{(\pm)}$  are transposed with respect to the matrices  $\hat{M}_c^{(\pm)}$  given in (3.12), and the new shift matrix  $\hat{L}$  is



$$\begin{pmatrix} \exp(-i\gamma W^*/2) & 0 \\ 0 & \exp(i\gamma W^*/2) \end{pmatrix} \quad (3.18)$$

(recall that  $W^*$  is the action in the upper adiabatic potential). Combining (3.12)–(3.18), one can trivially find the full connection matrix for the overbarrier energy region (2.21). We present the explicit form of the matrix in Appendix A.

A more tricky task is to calculate the connection matrix in the intermediate energy region (2.25). Following the same line as above, we first present the general structure of the connection matrix in the intermediate energy region as

$$\begin{pmatrix} \Phi_R^- \\ \Phi_R^+ \\ \Phi_L^+ \\ \Phi_L^- \end{pmatrix} = \begin{pmatrix} \hat{M}_c^{(+)} \hat{L}_R^{(c)} \hat{M}_-^{(+)} & 0 \\ 0 & \hat{M}_+^{(-)} \end{pmatrix} \times \hat{U}_c'' \begin{pmatrix} \hat{M}_-^{(-)} \hat{L}_L^{(c)} \hat{M}_c^{(-)} & 0 \\ 0 & \hat{M}_+^{(+)} \end{pmatrix} \begin{pmatrix} \Phi_L^+ \\ \Phi_L^- \\ \Phi_R^- \\ \Phi_R^+ \end{pmatrix}. \quad (3.19)$$

These matrices  $\hat{M}_\pm^{(\pm)}$  have been introduced in our paper [21] for the imaginary turning points characterizing the both adiabatic potentials in the region  $|\alpha| < u_{12}$ , and they read

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

where  $W_i^\pm$  are so-called Euclidian actions in the reversed upper and lower adiabatic potentials, which can be estimated as

$$W_i^\pm \simeq \frac{\pi q_{1,2}}{\gamma},$$

where

$$q_{1,2} = \frac{\gamma u_{12} \sqrt{u_{12} \pm \alpha}}{4f},$$

and all other matrices entering (3.19) are already defined. Since  $M_\pm^{(\pm)}$  turn into the unit matrices at  $\alpha > u_{12}$  and  $\alpha < -u_{12}$ , the connection matrix (3.19) matches continuously into the corresponding matrices (3.9) and (3.17) for the tunneling and overbarrier regions, respectively.

The connection matrix in the intermediate energy subregion  $S''$  can be calculated using Weber function asymptotic expansion for large complex indices (B15), which are the solutions to the comparison equations (2.15) in the intermediate energy subregion  $S''$ . These four roots are arranged clockwise and counterclockwise on the radius  $\gamma\sqrt{u_{12}/2}$  circle around the crossing point. The following combinations of the comparison equations match the semiclassical solutions (2.13):

$$\Theta_1^+ + \Theta_4^+ \leftrightarrow \Theta_2^+ \quad \Theta_2^- + \Theta_3^- \leftrightarrow \Theta_1^- \quad \Theta_1^- + \Theta_3^+ \leftrightarrow \Theta_2^- \quad \Theta_2^+ + \Theta_4^- \leftrightarrow \Theta_3^-.$$

Combining the asymptotic expansions for these combinations, we find, at the crossing point, the matrix  $\hat{U}_c''$  is

$$\hat{U}_c'' = \begin{bmatrix} [\sqrt{2\pi}/\Gamma(q^*)]\exp[-2\chi(q^*)] & 0 & & & & & \\ 0 & [\Gamma(q)/\sqrt{2\pi}] \exp[2\chi(q)][1 - \exp(-2\pi q_2)\cos^2(\pi q_1)] & & & & & \\ 0 & \exp(-2\pi q_2)\cos(\pi q_1) & & & & & \\ \exp(-2\pi q_2)\cos(\pi q_1) & 0 & & & & & \\ 0 & \exp(-2\pi q_2)\cos(\pi q_1) & & & & & \\ -\exp(-2\pi q_2)\cos(\pi q_1) & 0 & & & & & \\ [\sqrt{2\pi}/\Gamma(q)]\exp[2\chi(q)] & 0 & & & & & \\ 0 & [\Gamma(q^*)/\sqrt{2\pi}]\exp[2\chi(q^*)][1 - \exp(-2\pi q_2)\cos^2(\pi q_1)] & & & & & \end{bmatrix}, \quad (3.20)$$

where, as above,

$$q = q_1 + iq_2, \quad q_{1,2} = \frac{\gamma u_{12} \sqrt{u_{12} \pm \alpha}}{4f}, \quad q^* = q_1 - iq_2, \quad (3.21)$$

and we then introduce the abridged notations

and analogously

$$\chi = \chi_1 + i\chi_2, \quad 2\chi_1 = q_1 - \left(q_1 - \frac{1}{2}\right)\ln|q| + \varphi q_2, \quad (3.22)$$

$$2\chi_2 = q_2 - q_2 \ln|q| - \varphi \left( q_1 - \frac{1}{2} \right), \quad (3.23)$$

where  $\varphi$  is defined by (B10). Now, the full connection matrix in the both intermediate energy subregions can be found easily by simply collecting the expressions given above, and the explicit form for the connection matrix is presented in Appendix A. Note that the intermediate energy region connection matrix (3.20) has the same block structure as the connection matrices in the tunneling and overbarrier regions. This is a consequence of the fact that in the neighborhood of the diabatic potential crossing point, only the Weber functions with equal indices can be hybridized. At  $|\alpha|=u_{12}$ , the connection matrix (3.20) turns into the connection matrices (3.10) for the tunneling region and into (3.15) for the overbarrier energy region, enabling us to construct semiclassical solutions for any arbitrary energy window. Note, however, that in the intermediate energy region, the Massey parameter is replaced by the complex index  $q$ . In Sec. V, we will present another derivation of the connection matrix (3.20), and will discuss specific relations between the adiabatic and diabatic states in the intermediate energy region.

#### IV. QUANTIZATION RULES

In the tunneling energy region, one has only real-valued eigenfunctions, since in both wells there are only localized states. In this energy window, the connection matrix linking the ‘‘asymptotic’’ (i.e., in the left/right ( $L,R$ ) wells and for the upper/lower ( $+, -$ ) adiabatic potentials) solutions is represented in the form (3.9) and is given by (A1)–(A7). Within the WKB method, we should match the two exponentially decreasing and two exponentially increasing solutions in the barrier with the oscillation solutions in the wells; thus requiring the knowledge of the connection matrices at the crossing point and at the linear turning points, and the shift matrices from the crossing point to the turning points in the classically forbidden region and as well between the turning points in the classically accessible region [Fig. 3(a)]. Within the instanton type method, the trajectory goes through only the classically forbidden region [see Fig. 3(b)], and to perform the matching one should know also the connection matrices for the second-order turning points.

The overbarrier region can be treated in the same manner, with the corresponding connection matrix (3.17) and (A9). Evident modifications of the expressions given above for the tunneling and overbarrier regions should be performed to treat the intermediate energy windows. Indeed, in this case one has also to take into account the contributions from the imaginary turning points. The procedure is reduced to replacement of oscillating factors by exponentially decaying ones (see details in the next section). Finally, for the intermediate energy region, there are no real-valued turning points for the upper states (see Fig. 5), and the matching between two oscillating and two exponentially varying solutions is determined by the connection matrix (3.19) linking the linear turning points of the adiabatic potentials (see Fig. 5).

#### A. Two diabatic parabolic potentials crossing

Now (collecting the explicit expressions for all needed connection matrices from Appendix A), we are in the position to derive the quantization rules, which can be formulated as a condition that the amplitudes of solutions  $\Phi_L^+$ ,  $\Phi_R^+$ , exponentially increasing at  $X>0$  and  $X<0$ , respectively, must vanish. Taking into account that  $W_L^* = W_R^*$  (the actions in the corresponding wells of the lower adiabatic potential) and using the connection matrix relating the fundamental solutions of the Weber equation, we can formulate the corresponding quantization rule for the tunneling region in terms of the matrix elements defined by (3.9), as

$$m_{22}m_{33} - m_{23}m_{32} = 0, \quad (4.1)$$

where  $m_{ij}$  are corresponding matrix elements from (3.9).

Putting all together, we can find from (3.9), (3.10), and (4.1) the quantization rule for this case

$$\tan(\gamma W_L^*) = \pm \frac{2}{p} \exp(\gamma W_B^*), \quad (4.2)$$

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 (3.10).

Only the factor  $1/p$  varying from 0 to 1 in the diabatic and adiabatic limits, respectively, makes this quantization condition (4.2) different from the well-known [1] quantization rule for the symmetric double-well potential. Correspondingly, the tunneling splitting at finite values of the so-called Massey parameter  $\nu$  can be represented as a product

$$\Delta_n = \Delta_n^0 p(\nu) \quad (4.3)$$

of the tunneling splitting  $\Delta_n^0$  in the adiabatic potential and the factor

$$p(\nu) = \frac{\sqrt{2\pi}}{\Gamma(\nu)} \gamma^{\nu-(1/2)} \exp(-\nu), \quad (4.4)$$

associated with the transition amplitudes between the diabatic potentials in the crossing region.

It is particularly instructive to consider (4.2) as the standard [1] Bohr-Sommerfeld quantization rule, where in the right-hand side (r.h.s.) both the geometrical  $\varphi_n$  and the tunneling  $\chi_n$  phases are included additively. In the adiabatic limit when  $p(\nu) \rightarrow 1$ , we find that  $\varphi_n \rightarrow 0$ , and (4.2) 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 overbarrier energy region. Closely following the consideration performed above for the tunneling region, and replacing the connection matrix (3.10) by the corresponding matrix for the

overbarrier region (see Sec. II) (and making some other self-evident replacements), we end up after some algebra with the quantization rule

$$[1 - \exp(-2\pi\nu)]\cos[2\gamma W_L^* - \phi]\cos(\gamma W^* + \phi) + \exp(-2\pi\nu)\cos^2\left(\gamma W_L^* + \frac{\gamma W^*}{2}\right) = 0, \quad (4.5)$$

where  $W^*$  is the action in the well formed by the upper adiabatic potential, and  $\phi = \arg \Gamma(-i\nu) + \text{Im}(2\tilde{\chi})$  is determined according to (3.16). From Eq. (4.5), it follows that the eigenstates are determined by the parameter

$$B = \frac{\exp(-2\pi\nu)}{1 - \exp(-2\pi\nu)}. \quad (4.6)$$

In the diabatic limit  $\nu \rightarrow 0$ , and, therefore,  $B \rightarrow 1/(2\pi\nu)$ , in (4.5) the main contribution is due to the second term, and it leads to a splitting of degenerate levels in the diabatic potentials. Moreover, since

$$\gamma\left(W_L^* + \frac{W^*}{2}\right) = \pi\left\{n + \frac{1}{2} \pm 2\nu \sin\left[\gamma\left(W_L^* + \frac{W^*}{2}\right) + \phi\right]\right\}, \quad (4.7)$$

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  $\nu \rightarrow \infty$ ,  $\phi \rightarrow 0$ , and, therefore, from (4.6)  $B \approx \exp(-2\pi\nu)$ , the main contribution to (4.5) 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 overbarrier energy region; 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 (4.5) two sets of quantization rules leading to two sets of independent energy levels

$$\gamma W^* = \pi\left(n_1 + \frac{1}{2}\right); \quad 2\gamma W_L^* = \pi\left(n_2 + \frac{1}{2}\right). \quad (4.8)$$

Since the eigenstate energy level displacements depend on the adiabatic coupling  $U_{12}$  the resonances can occur at certain values of this parameter, where the independent quantization rules (4.8) are no longer correct. 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.

### B. Bound initial and decay final states: the diabatic potentials $(1+X)^2/2$ and $(1/2)-X$ crossing

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 po-

tential. The quantization rules in this case correspond to the vanishing amplitudes for the exponentially increasing solutions when  $X \rightarrow -\infty$ , and one also has to require that no waves propagating from the region of infinite motion; i.e., at  $X > 1/2$ . Performing the same procedure as above, we find that in the tunneling energy region, the eigenstates are the roots of the equation

$$\tan(\gamma W_L^*) = -i \frac{4}{p^2(\nu)} \exp(2\gamma W_B^*), \quad (4.9)$$

with the same notation as above. To proceed further, it is convenient to introduce the complex action to describe the quasistationary states, given by

$$\gamma W_L^* = \pi\left(\frac{E_n}{\Omega} - i \frac{\Gamma_n}{2\Omega}\right), \quad (4.10)$$

where evidently  $\Omega = \partial W_L / \partial E$  does depend on  $E$ . From (4.10), the real and imaginary parts of the quantized eigenstates are

$$E_n = \Omega\left(n + \frac{1}{2}\right), \quad \Gamma_n = p^2(\nu) \frac{\Omega}{2\pi} \exp(-2\gamma W_B^*). \quad (4.11)$$

This relation (4.11) describes the nonadiabatic tunneling decay of the quasistationary states of the lower adiabatic potential. Similar to what we obtained for the two parabolic potentials crossing (4.3), here, the tunneling and the adiabatic factors are entering the 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 overbarrier energy region, the quantization rule is

$$1 - \exp(-2\pi\nu)\exp[-i(\gamma W_L^* - \phi)]\cos(\gamma W^* + \phi) + \exp(-2\pi\nu)\exp(-i\gamma W^*/2)\cos(\gamma W_L^* + \gamma W^*/2) = 0, \quad (4.12)$$

and the actions depend on the energy  $E$  as

$$\gamma W_L^* = \pi \frac{E}{\Omega}, \quad \gamma W^* = \pi \left[ -\gamma \frac{\Omega_0(u^\# + u_{12})}{\Omega_1} + \frac{E}{\Omega_1} \right], \quad (4.13)$$

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

In the diabatic limit, the decay rate is proportional to the Massey parameter  $\nu$  and has a form

$$\Gamma_n \approx \frac{\Omega_0}{2} \nu \cos^2(\gamma W^* + \phi), \quad (4.14)$$

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

$$\Gamma_n \approx \Omega_0 \exp(-2\pi\nu)[1 - \sin(2\gamma W_L^* - \phi)]. \quad (4.15)$$

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 Fig. 7. Note that while the tunneling decay rate of the low-energy

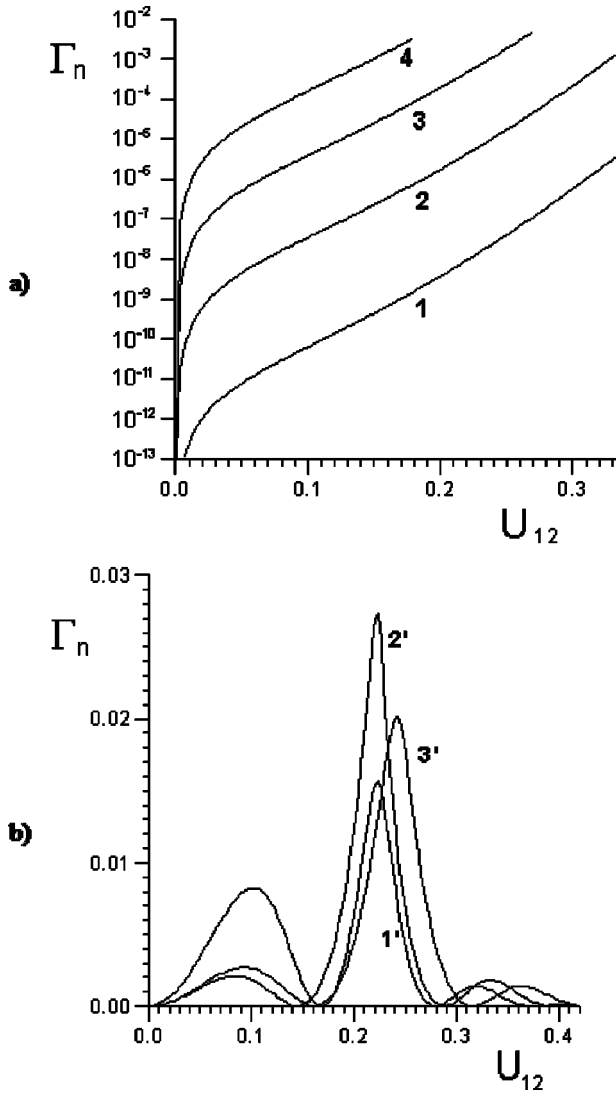


FIG. 7.  $\Gamma_n$  versus  $U_{12}$  for the quasistationary states at the diabatic potentials  $(1+X)^2/2$  and  $(1/2)-X$  crossing; (a) 1–4 are the level energies 0.042, 0.125, 0.208, and 0.292, respectively, for the lower adiabatic potential; (b) 1'–3' are the level energies 0.625, 0.708, and 0.792 respectively, for the upper adiabatic potential.

states is increased monotonically with the Massey parameter  $\nu$ , the decay rate of the highly excited states goes to zero in both (diabatic and adiabatic) limits. Besides there are certain characteristic values of  $U_{12}$  when the r.h.s. of (4.14) and (4.15) equal to zero and therefore  $\Gamma_n=0$ . This result, seemingly paradoxical and contradictory to conventional wisdom, can be rationalized as follows. For the case under consideration (one-well upper adiabatic and decay lower adiabatic potentials), there are always energy levels blocked by the upper adiabatic potential. This resonance phenomenon manifests wavelike particle properties omnipresent in quantum mechanics. For the system under consideration, the upper adiabatic potential is equivalent to a resonator with a set of well-defined modes (resonances) with high quality factors. An important feature (in distinction to a conventional resonators where these modes occupy more or less homogeneously the whole phase space) is that the resonance modes

are localized in its own effective cavity whose position is given by the conditions  $\Gamma_n=0$  (4.14) or (4.15).

Similarly, one can study the more general example, describing two nonsymmetric diabatic potentials crossing at  $X=0$  point:

$$u_1 = \frac{1}{2}(1+X)^2, \quad u_2 = \frac{1}{2b}(X^2 - 2bX + b). \quad (4.16)$$

In a certain sense it is the generic case, and when the parameter  $b$  entering the potential (4.16) is varied from 1 to  $\infty$ , we recover the two particular examples considered above, and come from two identical parabolic potentials to the case of one-well and linear diabatic potentials crossing. This kind of the potential was investigated recently by two of the authors (V.B. and E.K.) [29] aiming to study crossover behavior from coherent to incoherent tunneling upon increase of the parameter  $b$ ; the larger this parameter  $b$ , the larger will be the density of final states. The criterion for coherent-incoherent crossover behavior found in [30] is based on comparison of the transition matrix elements and the interlevel spacings in the final state. The analogous criterion should hold for the level crossing problem; however, in the latter case, the tunneling transition matrix elements have to be multiplied by the small adiabatic factor. Therefore, the coherent-incoherent tunneling crossover region moves to the larger density of final states, and the larger  $U_{12}$  is the smaller will be the region for incoherent tunneling. Quite a 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 interwell 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 nonmonotonically varying functions.

## V. INTERMEDIATE ENERGY REGION

A more difficult task is to derive the quantization rule in the intermediate energy region, where all four roots of the characteristic equation contribute into the solutions. One has to use the connection matrix (3.19) computed for this region (see details in Sec. III and Appendix A). It has two  $2 \times 2$  blocks structure, the same as the connection matrices for the tunneling and overbarrier regions. Here, we present another derivation of the same connection matrix using the adiabatic representation. It offers a deeper insight into the mathematical structure of the problem, and also provides physically relevant relations between the adiabatic and diabatic states in the intermediate energy region. The very possibility to use both the representation is stipulated by the fact (already mentioned in Sec. III) that the semiclassical eigenfunctions in the intermediate energy region can be represented as linear combinations either diabatic or adiabatic functions (this adiabatic-diabatic transformation has been discussed for quantum coherence phenomena in [30], see also [2]).



Since the adiabatic potentials have two second-order turning points (the minimum of the upper, and the maximum of the lower adiabatic potentials) the blocks of the connection matrix in the intermediate energy region (where now, unlike the matrices (3.9) and (3.17) describing the transitions between the diabatic states, the connection matrix corresponds to the transitions between the adiabatic states, and nonadiabatic perturbations induce the transitions [21]), are characterized by the parameters  $\tilde{q}_{1,2}$  analogous to  $q_{1,2}$  from (3.21) entering (3.20). For the real-valued blocks,

$$\tilde{q}_1 = \frac{\gamma\sqrt{2u_{12}}}{4f}(u_{12} + \alpha), \quad (5.1)$$

and for the complex-valued blocks (associated with the maximum of the lower adiabatic potential),

$$\tilde{q}_2 = \frac{\gamma\sqrt{2u_{12}}}{4f}(u_{12} - \alpha). \quad (5.2)$$

We can now reap the fruits of the previous subsection efforts. First, let us note that from the relations (2.20) and (2.24), 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, are 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  $\delta \rightarrow 0$ , these  $|X|$  values are located deep in the classically forbidden region, where the potentials are close to the diabatic potentials, while for  $\delta \geq 1/4$ , these coordinates  $|X|$  are of the order of the quantum zero-point oscillation amplitudes. Therefore, to find the solution in this region, we have to use the adiabatic representation.

Although, as it is shown in Appendix B, the intermediate region for the both subregions  $S''$  at  $\delta < 1/4$ , and  $S'$  at  $\delta > 1/4$  can be investigated on equal footing in the framework of the comparison equations (i.e., at the diabatic basis), it is instructive to study the problem in the adiabatic representation as well, which is the purpose of this section. As a subproduct of this consideration, we also get the justification of the comparison equation approach. In the adiabatic basis, the intermediate subregions  $S'$  and  $S''$  should be studied separately. Two simple observations give us a conjecture as to how to treat the problem in the intermediate energy region. First of all, the energetical ‘‘window’’ for the intermediate subregion  $S''$ , where  $\delta \leq 1/4$ , and  $|\alpha| \leq u_{12}$ , in terms of the dimensional energy scale is determined by the rectangle around the crossing point, as

$$U_{12} \leq 2U_{12}^*, \quad |U^\# - E| \leq U_{12}^*, \quad (5.3)$$

where we define  $U_{12}^* \equiv (1/2)(\hbar^2 F^2/m)^{1/3}$ . In other words, the characteristic interaction energy at the intermediate region boundaries does not depend on  $U_{12}$ . Analogously, the intermediate subregion  $S'$  is restricted by the lines

$$U_{12} \geq 2U_{12}^*, \quad |U^\# - E| \leq U_{12}. \quad (5.4)$$

The positions of the linear turning points  $|X^*|$  corresponding to the energies  $U^\# \pm U_{12}^*$  do depend on the ratio  $U_{12}/U_{12}^*$ . These points are located inside or outside of the interval  $[-\gamma^{-1/2}; +\gamma^{-1/2}]$  at  $U_{12}/U_{12}^* < 1$  and at  $U_{12}/U_{12}^* > 1$ , respectively. Accordingly, for 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. For the latter case, the matchings are performed in the region where the potentials are linear ones; thus the equations are reduced to the Airy ones.

Let us discuss first the intermediate energy subregion  $S''$ , where  $\tilde{q}_1$  and  $\tilde{q}_2$  are large, and therefore the Massey parameter, i.e., the indices of the Weber functions, are also large. The arguments of the Weber functions are  $\propto X\sqrt{\gamma}$ , and their asymptotic expansions determine the interval where the matching should be done (5.4). In what follows, we will closely follow the method we borrowed from Olver [31] (for the asymptotic expansions of the Weber functions with large indices, see also his monograph [32]), which is in fact an expansion over small parameters  $1/|\tilde{q}_i|$  [where  $|\tilde{q}_i|$  are the exponents (5.1) and (5.2)] of the fundamental Weber solutions, and it leads to an asymptotic solution at  $X > 0$

$$\Psi_+(X) \approx Y_+^{-1/2}(X + Y_+)^{-\tilde{q}_1} \exp(-\gamma XY_+),$$

$$\Psi_-(X) \approx Y_-^{-1/2}(X + Y_-)^{i\tilde{q}_2} \exp(i\gamma XY_-), \quad (5.5)$$

where  $Y_\pm = \sqrt{u_{12}^2 \pm \alpha^2 + f^2 X^2}$ . Using the known relation between the fundamental solutions of the Weber equation [28]

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

we can find two other [complementary to (5.5)] solutions

$$\Psi_+(X) = Y_+^{-1/2} \left[ -\sin(\pi\tilde{q}_1)(X + Y_+)^{-\tilde{q}_1} \exp(-\gamma XY_+) + \exp(-2\chi_1) \frac{\sqrt{2\pi}}{\Gamma((1/2) + \tilde{q}_1)} (X + Y_+)^{\tilde{q}_1} \exp(\gamma XY_+) \right], \quad (5.6)$$

and

$$\Psi_-(X) = Y_+^{-1/2} \left[ -i \exp(-\pi\tilde{q}_2)(X + Y_-)^{i\tilde{q}_2} \exp(i\gamma XY_-) + \exp(-2\chi_2) \frac{\sqrt{2\pi}}{\Gamma((1/2) - i\tilde{q}_2)} (X + Y_-)^{i\tilde{q}_2} \times \exp(-i\gamma XY_-) \right]. \quad (5.7)$$

In the case of weak level coupling, (i.e., for the intermediate energy subregion  $S''$ ), the adiabatic potentials everywhere

(except in a small neighborhood of the level crossing point) can be linearized (i.e., represented as  $\alpha \pm f|X|$ ), and the asymptotic solutions are reduced to a linear combination of the functions

$$\begin{aligned}\Phi_+^\pm &\propto (f|X|)^{-1/2} \exp(\pm \xi_\pm + \text{sgn } X), \\ \Phi_-^\pm &\propto (f|X|)^{-1/2} \exp(\pm \xi_\pm - \text{sgn } X),\end{aligned}\quad (5.8)$$

$$\xi_\pm = \frac{2}{3f} (f|X| \pm \alpha)^{3/2},$$

and these functions are smoothly matched with semiclassical solutions (see details in Appendix B). As a result, we can calculate, finally, the connection matrix  $U_c''$  in the intermediate energy region in the adiabatic basis, as

$$\hat{U}_n^c = \begin{bmatrix} [\sqrt{2\pi}/\Gamma(-i\tilde{q}_2)] \exp[-2\chi(i\tilde{q}_2)] & 0 \\ 0 & [\Gamma(\tilde{q}_1)/\sqrt{2\pi}] \exp[2\chi(\tilde{q}_1)] \sin^2(\pi\tilde{q}_1) \\ 0 & \cos(\pi\tilde{q}_1) \\ i \exp(-\pi\tilde{q}_2) & 0 \\ 0 & -i \exp(-\pi\tilde{q}_2) \\ -\cos(-\tilde{q}_1) & 0 \\ [\sqrt{2\pi}/\Gamma(\tilde{q}_1)] \exp[2\chi(\tilde{q}_1)] & 0 \\ 0 & 2[\Gamma(-i\tilde{q}_2)/\sqrt{2\pi}] \exp[-2i\chi(\tilde{q}_2)] \exp(-\pi\tilde{q}_2) \cosh^2(\pi\tilde{q}_2) \end{bmatrix},$$

where the function  $\chi$  is defined in (3.22) and (3.23). We see that the connection matrix in the adiabatic basis, unlike (3.20) defined in the diabatic basis, does not provide continuous transformation into the connection matrices for the tunneling and overbarrier energy regions [(3.10) and (3.15), correspondingly]. This apparent inconsistency is due to disregarding of adiabatic level interactions, which become relevant in the intermediate energy region. However, there is a simple remedy to ensure the continuous over all energy windows matching of the connection matrices. One has to rotate the complex plane  $q$  over the angle  $\varphi$  (B10). Thus, luckily (as is often the case in semiclassical approaches), we can safely reduce the problem quite accurately to the Weber or Airy equations in the both intermediate energy subregions, using, respectively, the perturbation theory with respect to the diabatic or adiabatic states. The adiabatic connection matrix found above could be used on the same footing as the diabatic connection matrix (3.20), e.g., to derive the quantization rule, which for the intermediate energy window can be written in the simple and compact form as

$$\cos(2\gamma W_I^*) = -\exp(-\pi\tilde{q}_2). \quad (5.9)$$

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

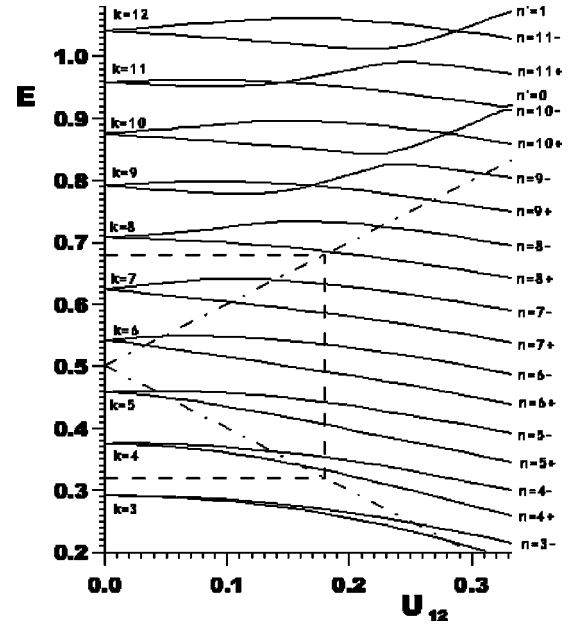


FIG. 8. Level displacements versus  $U_{12}$  for two diabatic crossing potentials  $(1 \pm X)^2/2$ . Dashed lines show the intermediate energy region (the subregion  $S''$  is between the dashed and dotted-dashed lines); dotted-dashed lines also show displacements for the top and for the bottom of the adiabatic potentials.  $k$ ,  $n$ , and  $n'$  are quantum numbers for the diabatic, and lower and upper adiabatic potentials, respectively. Note that the figure level displacements shown coincide with the error not exceeding 10%, with the results of the numerical diagonalization in the basis of harmonic oscillator functions.

$$\Psi^\pm = \frac{1}{\sqrt{2}}(\Phi_L \pm \Phi_R). \quad (5.10)$$

The functions are orthogonal, and two sets of the functions  $(\Psi_e^+, \Psi_0^-)$  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. 8, we depict schematically the dependence of the level positions on the coupling  $U_{12}$ . In the energy region  $E \leq U^* + U_{12}$ , where there only exist the discrete levels of the lower adiabatic potentials, there are pairs of alternating parity levels  $(\Psi_e^+, \Psi_0^-)$  and  $(\Psi_0^+, \Psi_e^-)$ . 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 remain correct for the energy region above the barrier of the lower adiabatic potential, where the spectrum becomes an almost equidistant one. However, in the overbarrier region, the resonances occur between the levels of the same parity, this sequence of the odd and even levels is broken, and level displacements are not monotonic functions of  $U_{12}$ . Some of the levels of different parities can be mutually crossed. For the upper adiabatic potential, the level sequence is opposite to that for the lower adiabatic potential. The intermediate subregion  $S''$  limits are shown by two dashed lines. The boundaries between the intermediate subregion  $S'$  and the tunneling and the overbarrier regions are shown by the dotted-dashed lines outgoing from the corners of the subregion  $S''$  rectangle; these lines coincide with energetic displacements of the top and of the bottom of the adiabatic potentials. Note also that we checked the results of our semiclassical approach and found remarkably good agreement with the numerical quantum diagonalization. As shown in Fig. 8, level displacements versus  $U_{12}$  coincide (with the error not exceeding 10% for the full range of variation of  $U_{12}$ , including the both intermediate energy subregions) with the results of the numerical diagonalization in the basis of harmonic oscillator functions of the initial Hamiltonian (2.1) for two diabatic crossing potentials  $(1 \pm X)^2/2$ .

## VI. COUPLING TO A THERMAL RESERVOIR

We have considered semiclassical quantization of bound and quasistationary states beyond the adiabatic approximation, but for the 1D case only. 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, regarding all other degrees of freedom as a bath of harmonic oscillators. In this section, we investigate the simplest multidimensional Hamiltonian describing the nonadiabatic transitions, namely, the  $2 \times 2$  matrix potential for the  $X$  variable (or what are the same two 1D diabatic potentials crossing considered in the previous sections) and the set of "transverse" harmonic oscillators  $\{Y_k\}$  coupled with the reaction coordinate  $X$ , given by

$$V(X, \{Y_k\}) = V_1(X) + \sum_k \frac{\omega_k^2}{2} Y_k^2 + F(X) \sum_k C_k Y_k. \quad (6.1)$$

Here,  $V_1(X)$  is the bare (in a general case anharmonic) 1D potential,  $\omega_k$  is the eigenfrequency of the transverse oscillator  $k$ , the function  $F(X)$  describes how the only strongly fluctuating coordinate  $X$  is coupled to thermal bath of transverse oscillators, and  $C_k$  are corresponding coupling constants. This kind (6.1) of multidimensional potential has been studied in the literature (see, e.g., [4]), and some efforts were made to find a feasible approximation to treat the potential within the semiclassical approach. In this section, we legitimate the method proposed in [4] focusing on the LZ problem in the tunneling region. Similar considerations can be easily generalized for the overbarrier and intermediate regions.

The equation of classical motion (in imaginary time) for the longitudinal coordinate has the form

$$\ddot{X} = \frac{dV_1}{dX} - \sum_k \frac{C_k^2}{\omega_k^2} \frac{dF(X)}{dX} I(\omega_k, [F(X)]), \quad (6.2)$$

where  $I$  is the integral transformation

$$I(\omega_k, [F(X)]) = \frac{\omega_k}{2} \int_{-\infty}^{\infty} \exp[-\omega_k |t - t'|] F(X(t')) dt'. \quad (6.3)$$

It can be expanded in the following high- and low-frequency limits, as

$$I(\omega, [F]) = \begin{cases} F + \omega^{-2} \ddot{F} + \omega^{-4} \ddot{\ddot{F}} + \dots, & \omega \rightarrow \infty \\ -\omega^2 R_2 - \omega^4 R_4 - \dots, & \omega \rightarrow 0, \end{cases} \quad (6.4)$$

where

$$R_n = \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \dots \int_{-\infty}^{t_{n-1}} F(t_n) dt_n. \quad (6.5)$$

At the high-frequency limit, (6.4) is reduced to the trajectory equation, but with the renormalized potential corresponding to the  $X$ -dependent effective mass

$$\sqrt{m^*} \frac{d}{dt} [\sqrt{m^*} \dot{X}] = \frac{d\tilde{V}}{dX} + O(\rho_6), \quad (6.6)$$

where

$$m^*(X) = 1 + \rho_4 \left( \frac{dF}{dX} \right)^2, \quad \tilde{V}(X) = V_1(X) - \frac{1}{2} \rho_2 \frac{dF^2}{dX},$$

$$\rho_n \equiv \sum_k \frac{C_k^2}{\omega_k^n} \quad (6.7)$$

(recall that we put unity for the bare mass  $m$  in our dimensionless units).

In the low-frequency limit, the trajectory equation reads

$$\ddot{X} = \frac{dV_1}{dX} - \rho_0 R_2(t). \quad (6.8)$$

In the  $\rho_4$  approximation for the spectral density of oscillators, the terms proportional to  $\rho_6$ , neglected in (6.7) [and the last term in (6.8)] are small. The physical message of the calculation performed in this section is that the renormalization of the effective mass leads to slowing down of the motion, and it is equivalent to saying that the Massey parameter is renormalized as

$$\nu \rightarrow \nu^* = \nu \sqrt{m^*(X_c)}, \quad (6.9)$$

where  $X_c$  is the crossing point. Of course, the coupling will also change the action along the extremal action trajectory (this effect has been discussed in the literature, see, e.g., [4]). The phenomenon specific to the LZ problem is the renormalization of the Massey parameter (6.9), which controls the main features of the behavior for any system undergoing level crossing.

## VII. CONCLUSION

In conclusion, we stress again the main point of our methodology. We have shown that the comparison equations for the fourth-order differential Landau-Zener equations in the coordinate space can be represented as two decoupled Weber equations. The indices and the arguments of the corresponding Weber functions defined by the roots of the characteristic equation (2.15) for the complex wave vector  $\kappa$ , and  $|\kappa| \gg 1$  in the semiclassical approximation. In the framework of our method, the diabatic potential crossing points are treated as two second-order turning points characterized by different Stokes constants [23]. The accuracy of the method depends on anharmonic terms, which are not taken into account in the comparison equations, but which are small in the semiclassical approach over small parameters  $\delta$ ,  $\tilde{\delta}$ , or  $\delta_{int}$  respectively, in the tunneling, overbarrier, and intermediate subregion  $S''$  energy windows. In the subregion  $S'$ ,  $\delta_{int}$  is not a small parameter. However, since the asymptotically smooth matching is performed at small  $|X| < \gamma^{-1/2}$ , anharmonic corrections to the comparison equations can be safely neglected for this subregion as well.

We have presented detailed semiclassical analysis of the crossing diabatic potentials problem. We examine one important (and previously overlooked) aspect of well-known energy level quantization problem for crossing diabatic potentials. We derive the semiclassical quantization rules for the particular situation of crossing diabatic potentials with localized initial and localized or delocalized final states, in the intermediate energy region, when all four diabatic states are coupled and should be taken into account. In fact, it exhausts all cases practically relevant for spectroscopy of nonrigid molecules (i.e., with more than one stable configuration).

We use the connection matrix methodology, which presents a simple and standardized description of any semiclassical approximation, and which offers therefore a deeper insight into the mathematical and physical structure of the approximation. We found that in the tunneling region, the tunneling splitting is represented as a product of the splitting

in the adiabatic potential and the nontrivial function  $p(\nu)$  (we calculated analytically) depending on the Massey parameter; i.e., on the energy and the slopes of the diabatic potentials in the crossing region. In the overbarrier region, we found specific resonances between the levels in the lower and in the upper adiabatic potentials; in that condition, one may not use independent quantization rules. Interesting results have emanated from our consideration of the intermediate energy region. For this energy region we calculated the energy level quantization, using adiabatic basis.

We have presented in this paper all details of the LZ problem for two electronic states using the connection matrix approach for the LZ problem in the coordinate space, the approach that turned out to be very efficient for this class of problems, and which is important in many areas of pure and applied sciences. Even though only model potentials are investigated here, our approach is quite general and has potential applicability for various systems in physics and chemistry, and the results can be tested by their experimental consequences for many examples of molecular systems undergoing conversion of electronic states, nonradiative transitions, and isomerization reactions, among others. The results of the LZ problem investigations are very relevant for slow atomic or molecular collisions [2,33], where the interaction of diabatic potentials induces transitions between initial and final electronic states. However, since the interaction is essential only near the crossing point, one can compute the transition probability, linearizing both diabatic potentials (see our consideration in Sec. II). The same approximation works quite well for the so-called predissociation phenomena.

However (in contrast to the atomic and molecular collision problems), there are fundamental problems of chemical physics and molecular spectroscopy where one may not restrict oneself only to the transition probability calculations, but should know the complete eigenvalues/eigenfunctions solution. This is the case, for example, if we are interested in the calculation of vibrational-tunneling spectra of nonrigid molecules, or reactive complexes with more than one stable configuration. The lowest multi-well potential of such systems is formed from one-well diabatic potentials crossing, corresponding to each stable configuration. Apart from the lowest potential, the upper adiabatic potential with its minimum above the maximum of the lowest potential should be also taken into account for these situations (see Fig. 1). In the most of the calculations of tunneling splittings in the ground and low excited vibrational states, the coupling to the upper potential is neglected, which is certainly correct only for strong enough adiabatic coupling. Evidently, it is not the case for the levels close to the adiabatic barrier top, and especially in the upper potential well. The quantization of these levels is noticeable in the spectroscopy of nonrigid molecules, and the same situation takes place for systems undergoing the Jahn-Teller effect, where the interference of the diabatic states occurs in this energy region [3].

One more example for the application of our results are molecular radiationless transitions within excited electronic states. Typically for this situation, the decay potential is formed owing to crossing of bound and unbound diabatic potentials. Since the radiationless transitions are followed by luminescence and chemical reaction phenomena (see, e.g.,



[34–37]) one should know the complex eigenvalues of the quasistationary states prepared by optical pumping.

Let us also stress that in real systems, the characteristic values of the coupling between the diabatic states can vary within the very wide range from several eV for the electronic states of the same symmetry to zero (for the states with different spins). To treat all these cases, one should know the solution of the diabatic potentials crossing problem described in our paper for the corresponding wide range of the Massey parameter from  $\nu=0$  to  $\nu \gg 1$ .

### ACKNOWLEDGMENTS

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### APPENDIX A

Putting all the Sec. II expressions (3.9)–(3.14) together, we can recapitulate the matrix elements  $m_{ij}$  of the full connection matrix in the tunneling region:

$$m_{11} = \frac{p}{4} \exp(-\gamma W_B^*) \cos(\gamma W_L^*) \cos(\gamma W_R^*) - \frac{\sin^2(\pi\nu)}{p} \exp(\gamma W_B^*) \sin(\gamma W_L^*) \sin(\gamma W_R^*), \quad (\text{A1})$$

$$m_{12} = \frac{p}{2} \exp(-\gamma W_B^*) \sin(\gamma W_L^*) \cos(\gamma W_R^*) + 2 \frac{\sin^2(\pi\nu)}{p} \exp(\gamma W_B^*) \cos(\gamma W_L^*) \sin(\gamma W_R^*), \quad (\text{A2})$$

$$m_{21} = -\frac{p}{2} \exp(-\gamma W_B^*) \cos(\gamma W_L^*) \sin(\gamma W_R^*) - 2 \frac{\sin^2(\pi\nu)}{p} \exp(\gamma W_B^*) \sin(\gamma W_L^*) \cos(\gamma W_R^*), \quad (\text{A3})$$

$$m_{22} = -p \exp(-\gamma W_B^*) \sin(\gamma W_L^*) \sin(\gamma W_R^*) + 4 \frac{\sin^2(\pi\nu)}{p} \exp(\gamma W_B^*) \cos(\gamma W_L^*) \cos(\gamma W_R^*), \quad (\text{A4})$$

$$m_{13/24} = \pm \cos(\pi\nu) \exp(\pm \gamma W_B^*/2) \sin(\gamma W_R^*),$$

$$m_{14} = -\frac{1}{2} \cos(\pi\nu) \exp(-\gamma W_B^*/2) \cos(\gamma W_R^*), \quad (\text{A5})$$

$$m_{23} = -2 \cos(\pi\nu) \exp(\gamma W_B^*/2) \cos(\gamma W_R^*),$$

$$m_{31/42} = \pm \cos(\pi\nu) \exp(\pm \gamma W_B^*/2) \sin(\gamma W_L^*), \quad (\text{A6})$$

$$m_{41} = \frac{1}{2} \cos(\pi\nu) \exp(-\gamma W_B^*/2) \cos(\gamma W_L^*),$$

$$m_{32} = 2 \cos(\pi\nu) \exp(\gamma W_B^*/2) \cos(\gamma W_L^*), \quad (\text{A7})$$

$$m_{33} = p; m_{44} = \frac{\sin^2(\pi\nu)}{p}; m_{34} = m_{43} = 0. \quad (\text{A8})$$

For the overbarrier region, the full connection matrix could be given in a more compact form. Using (3.17), (3.15), (3.18), and (3.12) from the main body of the paper, we get the following matrix:

$$\begin{bmatrix} (s/2) \cos(\gamma W_{LR} - \phi) & s \sin(\gamma W_{LR} - \phi) & -\exp(-\pi\nu) \sin(\gamma W_{R^*}) & -\exp(-\pi\nu)/2 \cos(\gamma W_{R^*}) \\ -s \sin(\gamma W_{LR} - \phi) & 2s \cos(\gamma W_{LR} - \phi) & -2 \exp(-\pi\nu) \cos(\gamma W_{R^*}) & \exp(-\pi\nu) \sin(\gamma W_{R^*}) \\ -\exp(-\pi\nu) \sin(\gamma W_{L^*}) & 2 \exp(-\pi\nu) \cos(\gamma W_{L^*}) & 2s \cos(\gamma W^* + \phi) & -s \sin(\gamma W^* + \phi) \\ \exp(-\pi\nu)/2 \cos(\gamma W_{L^*}) & \exp(-\pi\nu) \sin(\gamma W_{L^*}) & s \sin(\gamma W^* + \phi) & (s/2) \cos(\gamma W^* + \phi) \end{bmatrix}, \quad (\text{A9})$$

where  $W_{LR} \equiv W_L^* + W_R^*$ , and  $W_{L/R,*} \equiv W_{L/R}^* + W^*/2$ .

### APPENDIX B

The efficiency of the standard instanton approach [38,39] (see also [4,22]) is based on a successful choice of the comparison equation near second-order turning points, where asymptotically smooth matching of semiclassical solutions to the solutions of this equation should be performed. It is known, for example [21], that for anharmonic potentials, the Weber equation provides such a very successful choice since

in the matching region anharmonic corrections are still small. The aim of this appendix is to show that the analogous situation holds for crossing diabatic potentials points, where two Weber equations can be successfully used as the comparison equations to the fourth-order Landau-Zener equation (2.2). The arguments and the indices of the fundamental solutions to these Weber comparison equations are determined by the roots of the corresponding characteristic equations (see below and the main body of the paper).

To prove the statement, let us first substitute (2.14) into Eq. (2.7). We get

$$D^4\Phi + 4\kappa D^3\Phi + (6\kappa^2 - 2\alpha\gamma^2)D^2\Phi + 4\left(\kappa^3 - \alpha\gamma^2\kappa - \frac{1}{2}\gamma^2f\right)D\Phi + [\kappa^4 - 2\alpha\gamma^2\kappa^2 - 2\gamma^2f\kappa + \gamma^4(\alpha^2 - u_{12}^2 - f^2X^2)]\Phi = 0, \quad (\text{B1})$$

where  $D^n \equiv d^n/dX^n$ . Equation (B1) can be formally derived by simple manipulations (two sequential differentiations and summations) from the second-order equation

$$D^2\Phi + (a_0 + a_1X + a_2X^2)\Phi = 0, \quad (\text{B2})$$

where the coefficients are

$$a_0 = \kappa^2 - \alpha\gamma^2 - \frac{\gamma^2f}{2\kappa}(1 + \delta), \quad a_1 = \gamma^2f\delta, \quad a_2 = -\gamma^2f\kappa\delta, \quad (\text{B3})$$

where  $\kappa$  should be found from the characteristic equation (2.15), and  $\delta$  is given by (2.16).

The fundamental solutions to (B2) read as

$$D_p \left[ \pm \left( \frac{\gamma^4 f^2}{\kappa^2} \right)^{1/4} \left( X - \frac{1}{2\kappa} \right) \right], \quad (\text{B4})$$

where

$$p = -\frac{1}{2} + \left( \frac{\gamma^4 f^2}{\kappa^2} \right)^{-1/2} \left( a_0 - \frac{a_1^2}{4a_2} \right). \quad (\text{B5})$$

In the tunneling (2.19) and overbarrier (2.21) regions of energies, these four solutions [two solutions of (B4) for two largest modulus roots of the characteristic equation (2.15)] can be separated into two independent pairs. In the tunneling region, the two largest modulus roots of (2.15) are (two other roots are small and do not satisfy semiclassical approach)

$$\kappa = \kappa_0 \left( 1 \pm \frac{\delta^2}{2} \frac{\kappa_0^2}{2\kappa_0^2 - \alpha\gamma^2} \right), \quad \kappa_0 = \frac{\gamma}{\sqrt{2}} (\alpha + \sqrt{\alpha^2 - u_{12}^2})^{1/2}. \quad (\text{B6})$$

Putting (B6) into (B5), we find (neglecting  $\delta^2$  terms, i.e., for  $\kappa = \kappa_0$ ) four fundamental solutions to the comparison equation in the form (2.18). Thus, from the expressions given above and (2.16) and (2.17) from the main text, we conclude that the solutions  $\Theta_{L/R}$  (2.18) can be expanded over our small parameter  $\delta$ , and due to the condition (2.16) anharmonic corrections to the Weber functions (B4) are small (in other words, the parameter  $\delta$  determines the accuracy of our approximation). Indeed, the anharmonic terms neglected in the Weber comparison equations are of the order of  $\delta$  (it is an upper estimation at  $X = \alpha/f$ , i.e., at the boundaries of the intermediate energy region); thus the corrections are small according to (2.16). The same kind of analysis can be performed in the overbarrier region (2.21), where one finds two imaginary largest modulus roots of the characteristic equation. The roots are given by (B6) with  $\kappa_0$  and the small parameter  $\tilde{\delta}$  defined according to (2.22) and (2.23).

One simple observation helps to perform the same analysis for the intermediate energy region (2.25). Indeed, since the differences between the solutions to the characteristic

equations for  $\lambda$  (2.9) and for  $\kappa$  (2.15) determine the accuracy of our approach, let us compare the solutions. The roots of (2.9) at  $X=0$ ,

$$\lambda_{1,2} \approx \pm \gamma \sqrt{\alpha + u_{12}}, \quad \lambda_{3,4} \approx \pm \gamma \sqrt{\alpha - u_{12}}, \quad (\text{B7})$$

are moved upon the variation of  $\alpha$  in the intermediate energy region from the real to imaginary coordinate axis. Analogously, the roots of (2.15),

$$\kappa_{1,2} \approx \pm \frac{\gamma}{\sqrt{2}} (\alpha + \sqrt{\alpha^2 - u_{12}^2})^{1/2},$$

$$\kappa_{3,4} \approx \pm \frac{\gamma}{\sqrt{2}} (\alpha - \sqrt{\alpha^2 - u_{12}^2})^{1/2}, \quad (\text{B8})$$

are moved along the real and imaginary axes in the tunneling and overbarrier regions, respectively.

We conclude from (B7) and (B8) that in the tunneling and overbarrier energy regions, there is one-to-one correspondence between the roots  $\lambda$  of (2.9) and  $\kappa$  of (2.15). Just this correspondence allows us to match smoothly the semiclassical solutions to the Schrödinger equation and the Weber functions found as the solutions to the comparison equations. It is not the case in the intermediate energy region, where two roots of (2.9) are real and two are imaginary ones having the same modulus; i.e., moving upon  $\alpha$  variation along a circle with the radius  $\gamma\sqrt{u_{12}}/2$ . In this case, the semiclassical solutions can be presented as certain linear combinations of the comparison equation solutions. We have found these combinations in the adiabatic basis in Sec. V. In this appendix, we show how to solve the same problem in the diabatic basis, and it reveals more clearly and explicitly an estimate of the omitted terms in the equation and the areas where the solutions become wrong and where the matching procedure is carried out. Indeed, the roots of (2.15) in the intermediate energy region (2.25) are

$$\kappa_{1,2} \approx \pm \gamma \sqrt{\frac{u_{12}}{2}} \exp(i\varphi), \quad \kappa_{3,4} \approx \pm i\gamma \sqrt{\frac{u_{12}}{2}} \exp(-i\varphi), \quad (\text{B9})$$

where

$$\tan \varphi = \sqrt{\frac{u_{12} - \alpha}{u_{12} + \alpha}}. \quad (\text{B10})$$

Correspondingly to these roots (B10), the arguments and the indices of the Weber functions (B4) and (B5) read as

$$z_1 = z_2 = 2\kappa_{int} \sqrt{\delta_{int}} \exp(-i\varphi/2) [X + (2\kappa_{int})^{-1} \exp(-i\varphi)], \quad (\text{B11})$$

$$z_3 = z_4 = 2\kappa_{int} \sqrt{\delta_{int}} \exp(i\varphi/2) [X + (2\kappa_{int})^{-1} \exp(i\varphi)],$$

and

$$p_1 = p_2 - 1 = -1 - \frac{1}{4\delta_{int}} \exp(-i\varphi) [1 + \delta_{int}^2 \exp(-2i\varphi)];$$

$$p_4 = p_3 - 1 = -1 - \frac{1}{4\delta_{int}} \exp(i\varphi) [1 + \delta_{int}^2 \exp(2i\varphi)], \quad (\text{B12})$$

where  $\kappa_{int} = \gamma(u_{12}/2)^{1/2}$ , and  $\delta_{int} = (\gamma^2 f)/(4\kappa_{int}^3)$ .

Using known asymptotics of the Weber functions due to Olver ([31,32]), we are in the position to compare the semiclassical functions with the solutions to the comparison equations. The former functions are determined by the exponential factor

$$F_0^\pm(X) = \gamma \sqrt{u_{12} \pm \alpha} X + \frac{\gamma f^2}{12u_{12} \sqrt{u_{12} \pm \alpha}} X^3, \quad (\text{B13})$$

while the exponential factors entering corresponding asymptotics of the Weber functions are

$$F_{1,2}(X) = \gamma \sqrt{u_{12} \pm \alpha} (1 + \delta_{int}) X \pm \kappa_{int}^2 \delta_{int}^2 \exp(-2i\varphi) X^2 + \frac{\gamma f^2}{12u_{12} \sqrt{u_{12} \pm \alpha}} \left[ 1 \pm \frac{\alpha}{u_{12}} - \delta_{int} \right] X^3. \quad (\text{B14})$$

Let us consider now the intermediate subregion  $S'$ ,  $|\alpha| \leq (f/\gamma)^{2/3}$ , and  $u_{12} \leq 2/\gamma$ , [see (5.3)], where (2.16) does not hold. Luckily, however, the asymptotically smooth matching is performed at small  $|X| < \gamma^{-1/2}$ , where the comparison equation (B2), and, therefore, the characteristic equation (2.15) are valid (although  $\delta$  is not a small parameter). In this subregion, we have to take into consideration the term  $R(\kappa, \delta)$  in (2.15). At  $\alpha=0$  and  $u_{12}=0$ , the characteristic equation has one double degenerate root  $\kappa=0$ , or correspondingly in (B2),  $a_2=0$ . Thus, the comparison equations are reduced to two decoupled Airy equations. Using known Olver asymptotics

for the Weber functions with large arguments and indices [31,32],

$$D_p(z) \propto \exp \left\{ -\frac{1}{2} \int \left[ z^2 - 4 \left( p + \frac{1}{2} \right) \right]^{1/2} dz \right\}, \quad (\text{B15})$$

we can find asymptotics to the solutions of (B2) and

$$\Phi_0 \propto \exp \left( -i \int \sqrt{a_0 + a_1 X + a_2 X^2} dx \right), \quad (\text{B16})$$

valid at arbitrary values of the parameters  $a_i$  ( $a_2=0$  including). This relation (B16) provides asymptotically smooth matching of the semiclassical solutions with the Weber functions in the intermediate subregion  $S''$  (where  $\kappa$  is of the order of  $\gamma \gg 1$ ), and with the Airy solutions in the subregion  $S'$ , when  $\kappa \approx \sqrt{\gamma}$ .

This consideration provides the justification of our approach described in the main body of the paper. As is seen from (B13), and from (B14) at small  $\alpha$ , the accuracy of the asymptotically smooth matching of the semiclassical solutions with the Weber functions is of the order of  $\delta_{int}$ , and, close to the energetic boundaries (2.25) of the intermediate region, anharmonic corrections ( $X^3$ ) are increased. Thus, we conclude that the matching for this case (2.25) can be performed either in the adiabatic basis (as has been done in Sec. V) or in the diabatic basis as we have shown in this appendix. The simplest way to prove the equivalence of the both representation is to transform into exponential forms the factors like  $(X+Y_+)^{q_1}$  etc., entering the solutions (5.6) and (5.7), found in Sec. V. In both methods, the accuracy is of the order of  $\delta_{int}$ , and the connection matrices presented in Appendix A do not depend on the basis.

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