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Analytical semiclassical theory for general non-adiabatic transition and tunneling

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Abstract

A semiclassical solution of general two-state non-adiabatic transition and tunneling is found analytically within the Wentzel–Kramers–Brillouin (WKB) semiclassical framework associated with the Stokes phenomenon in mathematics. The non-adiabatic scattering matrix is determined by a complex quantity called the Stokes constant, which can be directly connected to the complex transition points of the WKB solution. An accurate and compact analytical solution is found for this Stokes constant which is a function of three parameters, one of which corresponds to the diabatic-to-adiabatic transformation angle that is interpreted as a type of non-adiabatic transition. Numerical examples demonstrate that the present unified analytical semiclassical theory works very well for both non-adiabatic transition and non-adiabatic tunneling. The present analytical semiclassical method can be a very powerful tool for application to multidimensional non-adiabatic dynamic processes.

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(Some figures in this article are in colour only in the electronic version.)

1. Introduction

The Born–Oppenheimer (BO) approximation [1] that separates the electronic motion from the nuclear motion is an outstanding step toward solving the Schrödinger equation for complicated molecular systems. There are numerous developments and successful applications of electronic structure and molecular dynamics methods for electronically adiabatic motions on the BO potential energy surfaces. Electronically non-adiabatic or non-BO transitions that arise from breakdown of the BO approximation are used in photochemistry, laser-induced chemistry, electronic energy transfer, chemical reaction, electronic transfer, non-radiative transitions and so on. At present and even in the near future, an exact quantum mechanical treatment is impractical for large molecular systems for both BO and non-BO molecular dynamics. Semiclassical methods, mixed quantum-classical methods and mean-field classical methods must be employed for solving the molecular dynamics Schrödinger equation. This review paper is focused on an analytical semiclassical theory for general non-adiabatic transition and non-adiabatic tunneling. As is well known, non-adiabatic transition and non-adiabatic tunneling zones occur at very localized regions

of entire electronic configurations in which molecular dynamics is mostly governed by the BO approximation; it would be especially suitable to apply an analytical semiclassical method to deal with these localized transitions. An analytical semiclassical solution is very useful to understand intermediate dynamics and to analyze associated quantum effects, and it can also be applied as a connection matrix to connect wave functions at various boundary conditions associated with various coordinated systems. It can greatly enhance numerical performance by combining it with various other molecular dynamics methods.

The pioneering works were carried out in 1932 by Landau [2], Zener [3] and Stückelberg [4] for the two-state linear curve crossing case (the LZS model) and by Rosen–Zener [5] for the two-state linear curve non-crossing case (the RZ model). Thereafter, the linear model potentials were extended to nonlinear potentials in which constant coupling is changed to exponential-type coupling by Demkov [6], and both coupling and potentials are changed to exponential-type coupling by Nikitin [7]. Furthermore, the LZS and RZ models were demonstrated to be certain limiting cases of the Nikitin model [8]. Various semiclassical approaches with varying degrees of rigor were developed for

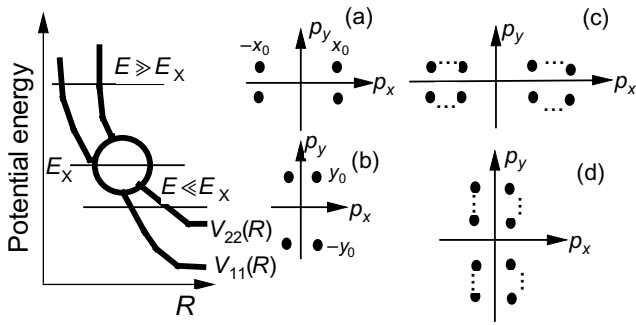


Figure 1. General two-state potential energy surface diagram; $E > E_X$ corresponds to the non-adiabatic transition zone and $E < E_X$ corresponds to the non-adiabatic tunneling zone. The circled area determines the important parameter d in equation (16). Distribution of four transition points in the complex momentum plane for the LZS model: (a) $E \gg E_X$ and (b) $E \ll E_X$. Distribution of infinite transition points in the complex momentum plane for the Nikitin model: (c) $E \gg E_X$ and (d) $E \ll E_X$.

the above model potentials and applied for general-potential systems within both time-dependent representation [8–16] and time-independent representation [17–30]. In general, non-adiabatic processes can be classified into two categories from the semiclassical point of view; one corresponds to a classically allowed transition that is a pure non-adiabatic transition as shown in the collision energy region $E > E_X$ in figure 1, and the other corresponds to a classically forbidden transition that is non-adiabatic tunneling (non-adiabatic transition accompanied by tunneling), as shown in the collision energy region $E < E_X$ in figure 1.

It was found for the first time by Zhu [31] that all kinds of non-adiabatic transitions can be quantitatively described by the adiabatic-to-diabatic transformation angle and then a unified analytical semiclassical theory was established for pure non-adiabatic transition. Ten years later, Zhu and Lin [32] extended the unified analytical semiclassical theory to deal with all kinds of non-adiabatic tunneling.

One of the aims of the present review paper is to reformulate the unified analytical semiclassical theory within the complex Wentzel–Kramers–Brillouin (WKB) method associated with the Stokes phenomenon in mathematics. For general two-state non-adiabatic scattering problems, the coupled Schrödinger equations in the diabatic representation are written as

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \begin{bmatrix} V_{11}(R) & V_{12}(R) \\ V_{21}(R) & V_{22}(R) \end{bmatrix} \right) \begin{pmatrix} \psi_1(R) \\ \psi_2(R) \end{pmatrix} = E \begin{pmatrix} \psi_1(R) \\ \psi_2(R) \end{pmatrix}, \quad (1)$$

where μ is the reduced mass of the system and R is a spatial coordinate that is a general one-dimensional curved coordinate in a multidimensional potential energy surface (along the trajectory for instance). Equation (1) can be transformed into the adiabatic representation by

$$U(\theta(R)) = \begin{bmatrix} \cos \theta(R) & \sin \theta(R) \\ -\sin \theta(R) & \cos \theta(R) \end{bmatrix}, \quad (2)$$

where the diabatic-to-adiabatic transformation angle is given by

$$\tan(2\theta(R)) = \frac{2V_{12}(R)}{V_{22}(R) - V_{11}(R)}. \quad (3)$$

Two adiabatic potential energy surfaces are defined by

$$E_1(R) = \frac{1}{2} (V_{22}(R) + V_{11}(R)) - \frac{1}{2} \sqrt{(V_{22}(R) - V_{11}(R))^2 + 4V_{12}^2(R)} \quad (4)$$

and

$$E_2(R) = \frac{1}{2} (V_{22}(R) + V_{11}(R)) + \frac{1}{2} \sqrt{(V_{22}(R) - V_{11}(R))^2 + 4V_{12}^2(R)}. \quad (5)$$

Thus, the coupled Schrödinger equations in the adiabatic representation can be obtained (not necessarily given here), and the WKB type of wave functions can be obtained as

$$\psi_1(R) = \frac{A_1}{\sqrt{p_1(R)}} \exp\left(i \int_{T_1}^R p_1(R) dR - i \frac{\pi}{4}\right) + \frac{B_1}{\sqrt{p_1(R)}} \exp\left(-i \int_{T_1}^R p_1(R) dR + i \frac{\pi}{4}\right) \quad (6)$$

and

$$\psi_2(R) = \frac{A_2}{\sqrt{p_2(R)}} \exp\left(i \int_{T_2}^R p_2(R) dR - i \frac{\pi}{4}\right) + \frac{B_2}{\sqrt{p_2(R)}} \exp\left(-i \int_{T_2}^R p_2(R) dR + i \frac{\pi}{4}\right), \quad (7)$$

where T_i ($i=1,2$) is the turning point on the adiabatic potential curve $E_i(R)$ with

$$p_i(R) = \frac{\sqrt{2\mu}}{\hbar} \sqrt{E - E_i(R)}. \quad (8)$$

A reduced scattering matrix that includes all necessary information on non-adiabatic dynamics is defined by

$$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} \equiv S^R \begin{pmatrix} B_1 \\ B_2 \end{pmatrix} = \begin{pmatrix} S_{11}^R & S_{12}^R \\ S_{21}^R & S_{22}^R \end{pmatrix} \begin{pmatrix} B_1 \\ B_2 \end{pmatrix}, \quad (9)$$

where A_1 and A_2 (B_1 and B_2) represent amplitudes of the outgoing (incoming) WKB wave functions in equations (6) and (7). This reduced matrix is semiclassically determined by two potential energy surfaces and its coupling in a non-adiabatic transition zone as shown in figure 1. Further analysis can prove that the reduced scattering matrix can be expressed in terms of one complex quantity U_1 ,

$$S^R = \begin{pmatrix} 1 + U_1 U_2 & -U_2 \\ -U_2 & 1 - U_1^* U_2 \end{pmatrix}, \quad (10)$$

where

$$U_2 = \frac{U_1 - U_1^*}{1 + U_1^* U_1}. \quad (11)$$

Equations (10) and (11) are actually proved for the LZS model in [26], and it is assumed here that it holds semiclassically for general two-state non-adiabatic dynamics processes. Therefore, the main goal of the present paper is to find an analytical solution for this complex quantity U_1 that is called the Stokes constant in mathematics. Before starting mathematical derivation, it would be wise

to ask what kind of potential parameter determines the non-adiabatic transition type. The answer actually comes from the diabatic-to-adiabatic transformation angle in equations (2) and (3). Since non-adiabatic transition occurs at a localized region, the most possible region occurs at the complex crossing point R^* defined by

$$0 = E_2(R^*) - E_1(R^*) \\ = \sqrt{(V_{22}(R^*) - V_{11}(R^*))^2 + 4V_{12}^2(R^*)}. \quad (12)$$

For the LZS model of the two-state linear curve crossing problem, inserting a real part of the complex crossing point $\text{Re}(R^*) = R_0$ into equation (3) leads to [31]

$$\tan(2\theta(R_0)) = \infty \Rightarrow \theta(R_0) = \frac{\pi}{4}, \quad \text{for the LZS model.} \quad (13)$$

Then, its diabatic-to-adiabatic transformation matrix in equation (2) shows the maximal mixing of the two representations because the two diagonal elements are equal to the two off-diagonal elements in magnitude: $\cos(\pi/4) = \sin(\pi/4)$. For the RZ model of the two-state linear non-crossing problem, we have [31]

$$\tan(2\theta(R_0)) = 1 \Rightarrow \theta(R_0) = \frac{\pi}{8}, \quad \text{for the RZ model.} \quad (14)$$

Now, the diagonal elements in equation (2) are bigger than the off-diagonal elements in magnitude since $\cos(\pi/8) > \sin(\pi/8)$, so that the RZ model is less mixing of the two representations than the LZS model. This naturally pushes equation (2) into,

$$\tan(2\theta(R_0)) = 0 \Rightarrow \theta(R_0) = 0, \quad (15)$$

which leads to equation (2) being a unity matrix; there is no mixing case and thus there is no non-adiabatic transition at all. From the analysis discussed above, we can conclude that any unified semiclassical theory must include this diabatic-to-adiabatic transformation angle that actually represents a type of non-adiabatic transition. We can use the following parameter to determine a type of non-adiabatic transition [31],

$$d \equiv d(R_0) = 1 + \frac{4V_{12}^2(R_0)}{[V_{22}(R_0) - V_{11}(R_0)]^2}. \quad (16)$$

Unified semiclassical theory now means that the Stokes constant U_1 must be a function of the parameter d in equation (16). The other two parameters that the Stokes constant U_1 should contain are σ and δ , defined by

$$\sigma + i\delta = \int_{T_1}^{R^*} p_1(R) dR - \int_{T_2}^{R^*} p_2(R) dR, \quad (17)$$

where $p_1(R)$ and $p_2(R)$ are defined in equation (8), and the complex crossing point R^* is given in equation (12).

2. The Stokes phenomenon with the WKB solution

From a semiclassical point of view, the non-adiabatic scattering problems can be described by dividing the scattering region into coupled and uncoupled zones. In the

uncoupled zone, the WKB wave functions propagate on two adiabatic potential energy surfaces independently, while in the coupled zone, the WKB wave functions are mixed on two adiabatic potential energy surfaces. This picture exhibits a semiclassical connection problem. The most probable method to discuss this connection is to use the WKB solution with the Stokes phenomenon [33, 34] in mathematics. Let us start with the one-dimensional Schrödinger equation in the complex plane,

$$\frac{d^2\psi(z)}{dz^2} + p^2(z)\psi(z) = 0, \quad (18)$$

where $p(z)$ is the classical momentum defined by

$$p(z) = \frac{\sqrt{2\mu}}{\hbar} \sqrt{E - V(z)}. \quad (19)$$

It is well known that the solution of equation (18) has the following form:

$$\psi(z) = \frac{A}{\sqrt{p(z)}} \exp\left(\pm i \int_a^z p(z) dR\right). \quad (20)$$

All zero points in which $p(z_k) = 0$ (also called transition point z_k , $k = 1, 2, \dots$) are assumed to be in localized regions in the complex plane. The WKB solution in equation (20) is divergent at those transition points, and also becomes a bad approximation nearby. It seems as if we can avoid this divergence by applying the WKB solution to go around those zeros in the complex plane, but it is not so simple. Let us start from the general solution of equation (18):

$$\psi(z) = \frac{A}{\sqrt{p(z)}} \exp\left(i \int_a^z p(z) dR\right) \\ + \frac{B}{\sqrt{p(z)}} \exp\left(-i \int_a^z p(z) dR\right) \\ \equiv A(a, z) + B(z, a), \quad (21)$$

where we use conventional notation for the WKB solution in the second equality. A connection problem from which the scattering matrix can be obtained requires us to find the matrix that connects $\psi(z = \infty)$ with $\psi(z = -\infty)$. In order to avoid all zeros that are singular points of the WKB solution in equation (21), we trace $\psi(z)$ on a pass of $|z| = \infty$ along which the WKB solution in equation (21) is exactly valid all the way. However, there are certain lines, as the Stokes lines known in the complex plane where the WKB solution is discontinuously changed. This is known as the Stokes phenomenon [33]. The Stokes line is defined by

$$\text{Re} \int_a^z p(z) dz = 0, \quad (22)$$

and the anti-Stokes line is defined by

$$\text{Im} \int_a^z p(z) dz = 0. \quad (23)$$

We do not attempt to discuss this Stokes phenomenon in general, and we would rather take two examples to illustrate procedures.

The first example is taken from $V(x) = -Fx$ in equation (19) as shown in figure 2(a), and its transition point

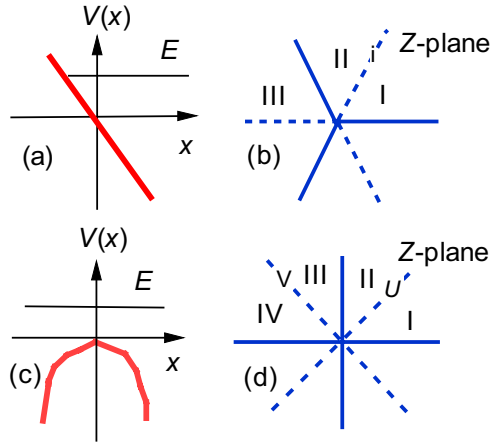


Figure 2. (a) Scattering on linear potential. (b) The Stokes phenomenon for (a): the solid lines stand for the anti-Stokes lines and the dashed lines stand for the Stokes lines. The three Stokes constants are all equal to i . (c) Scattering on parabolic potential. (d) The Stokes phenomenon for (c): the solid lines stand for the anti-Stokes lines and the dashed lines stand for the Stokes lines. U and V stand for the Stokes constants associated with the Stokes lines, respectively.

is at $z = 0$. It is easy to figure out the Stokes and anti-Stokes lines as plotted in figure 2(b), in which the angle between any two of three anti-Stokes lines or three Stokes lines is 120° . Let us trace the WKB solution on the pass of $|z| = \infty$ from region I to region III in figure 2(b); we then have

$$\begin{aligned} \psi(z) &= A(a, z)_s + B(z, a)_d && \text{in region I} \\ &= (A + Bi)(a, z)_s + B(z, a)_d && \text{in region II} \\ &= (A + Bi)(a, z)_d + B(z, a)_s && \text{in region III,} \end{aligned} \quad (24)$$

where suffix s (d) stands for the exponential decay (rise) part of the associated WKB solution, namely subdominant (dominant) part of the WKB solution. Classical turning point a is calculated from $a = -E/F$. By the rules of the Stokes phenomenon, when the WKB solution crosses the Stokes line from region I to II, the coefficient of the subdominant part has to change by adding the coefficient of the dominant part after multiplying the Stokes constant (associated with that of the Stokes line), so that we obtain the second line in equation (24). When the WKB solution crosses the anti-Stokes line from region II to III, the subdominant and dominant parts are interchanged with each other, so that we obtain the third line in equation (24). By physical constraint, the WKB solution at $z = -\infty$ must die out, and this leads the coefficient of the dominant WKB solution in the third line of equation (24) to be zero:

$$A + Bi = 0, \quad (25)$$

which represents a connection between the incoming and the outgoing scattering wave functions in the region of $x = -\infty$ in equation (21), and thus we can derive an elastic scattering phase shift as [21]

$$\delta_{\text{WKB}} = \lim_{x \rightarrow \infty} \left[\frac{1}{\hbar} \left(\int_a^x p(x) dx - p(x)x \right) + \frac{\pi}{4} \right]. \quad (26)$$

It should be pointed out that this WKB phase shift is an exact quantum mechanical solution for the linear potential in figure 2(a).

The second example is taken from $V(x) = -0.5\lambda x^2$ in equation (19) as shown in figure 2(c), and there are two transition points that are either two real zeros for collision energy $E < 0$ or two pure imaginary zeros for $E > 0$. The Stokes and anti-Stokes lines derived from equations (22) and (23) are plotted in figure 2(d). A scattering problem now means to find the connection for the following WKB solutions:

$$\begin{aligned} \psi(x) &\xrightarrow{x \rightarrow \infty} A(0, z) + B(z, 0) && \text{in region I,} \\ \psi(x) &\xrightarrow{x \rightarrow -\infty} C(0, z) + D(z, 0) && \text{in region IV.} \end{aligned} \quad (27)$$

We can carry out the same procedures as in the first example, and thus we trace the WKB solution from region I to IV, as shown in figure 2(d). Finally, we obtain the connection matrix

$$\begin{pmatrix} C \\ D \end{pmatrix} = \mathbf{F} \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}. \quad (28)$$

Through the Stokes constants U and V in figure 2(d), we can find [33]

$$\begin{aligned} \mathbf{F} &= \mathbf{F}(\beta) \\ &= \begin{pmatrix} \frac{\sqrt{2\pi} \exp(\pi\beta/2 - i\beta + i\beta \ln(e^{i\pi}\beta))}{\Gamma(1/2 + i\beta)} & i \exp(\pi\beta) \\ -i \exp(\pi\beta) & \frac{\sqrt{2\pi} \exp(\pi\beta/2 + i\beta - i\beta \ln(e^{i\pi}\beta))}{\Gamma(1/2 - i\beta)} \end{pmatrix} \end{aligned} \quad (29)$$

in which $\beta = -\frac{E}{\hbar\sqrt{\lambda_j/\mu}}$, and from this connection matrix we can easily extract tunneling and reflection probabilities. It should be emphasized that the connection matrix in equation (29) is an exact quantum mechanical solution for a parabolic potential in figure 2(c). However, when we apply equation (29) to the general two-transition problem, it is an approximation in which β in equation (29) can be a complex quantity. This is the case in the next section.

3. An analytical semiclassical solution for the LZS model

A starting point for discussing the LZS model is to assume the diabatic potential matrix in equation (1) as two linear potentials with constant coupling [21]:

$$\begin{aligned} V_{11}(R) &= -F_1(R - R_0) \equiv -F_1x, \\ V_{22}(R) &= -F_2(R - R_0) \equiv -F_2x, \\ V_{12}(R) &= V_{21}(R) = A. \end{aligned} \quad (30)$$

Then, by using the x -coordinate in $-\infty < x < \infty$, we transform equation (1) into momentum space by

$$\psi_j(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ipx} u_j(p) dp. \quad (31)$$

A nice thing about the momentum space is that the coupled equations in equation (1) that are second order are now transformed into first-order coupled equations. These

first-order coupled equations can be further transformed into a single second equation [21],

$$\frac{d^2 B_1(t)}{dt^2} + q^2(t) B_1(t) = 0, \quad (32)$$

where

$$q^2(t) = 0.25 (a^2 t^2 - b^2)^2 - ia^2 t + 0.25, \quad (33)$$

in which

$$a^2 = \frac{\hbar^2 \sqrt{F_1 F_2} (F_1 - F_2)}{2\mu 8A^3} > 0, \quad (34)$$

$$b^2 = (E - E_X) \frac{(F_1 - F_2)}{2\sqrt{F_1 F_2} A},$$

where E_X is the potential energy at a crossing point of two diabatic potentials, and the others are given in equation (30). Two dimensionless parameters a^2 and b^2 in equation (34) represent an effective coupling and an effective collision energy, respectively. If $b^2 = 0$, it means that collision energy is equal to the potential energy at the crossing point. If $b^2 > 1$, it represents classical allowed transition, namely for pure non-adiabatic transition. If $b^2 < -1$, it represents classical forbidden transition, namely for non-adiabatic tunneling. These two cases represent different distributions of the four transition points in $q(t_i) = 0$ of equation (33), where t actually stands for the dimensionless complex momentum p as shown in figures 1(a) and (b). These two cases can be treated on an equal footing in the framework of the WKB solution with the Stokes phenomenon introduced in section 2.

3.1. Non-adiabatic transition case $b^2 > 1$ ($E \gg E_X$ in figure 1)

This is the case when we can separate the four transition points into two pairs along the p_x -axis in figure 1(a) in which one pair is localized at x_0 , and the other pair is localized at $-x_0$ symmetrically with respect to the pair at x_0 . Such a distribution of the four transition points suggests that we should look for the following connection problem for equation (32):

$$B_1(t) \xrightarrow{t \rightarrow \infty} \frac{A}{\sqrt{q(t)}} \exp\left(i \int_{x_0}^t q(t) dt\right) + \frac{B}{\sqrt{p(t)}} \exp\left(-i \int_{x_0}^t q(t) dt\right) \quad (35)$$

and

$$B_1(t) \xrightarrow{t \rightarrow -\infty} \frac{C}{\sqrt{q(t)}} \exp\left(i \int_{-x_0}^t q(t) dt\right) + \frac{D}{\sqrt{p(t)}} \exp\left(-i \int_{-x_0}^t q(t) dt\right), \quad (36)$$

with the connection matrix defined by

$$\begin{pmatrix} C \\ D \end{pmatrix} = \mathbf{L} \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}, \quad (37)$$

where we have an exact solution by treating the four transition points as a whole and all elements of the connection matrix in equation (37) are expressed as functions of the Stokes constant U_1 , i.e. $L_{ij} = L_{ij}(U_1)$, where $i, j = 1, 2$ [27]. This Stokes constant U_1 also appears in equation (10) for the reduced scattering matrix. Now, our task is to find an approximated connection matrix, and thus to obtain an approximated analytical solution for the Stokes constant U_1 . Let us rewrite equation (33) as

$$q^2(t) = \frac{a^4}{4} [(t - x_0)^2 - (\Delta x + iy)^2] [(t + x_0)^2 - (\Delta x - iy)^2], \quad (38)$$

where x_0 , Δx and y can be solved as real functions of the two parameters a^2 and b^2 in equation (34). We have $x_0^2 \gg |\Delta x \pm iy|^2$ with a constraint $E \gg E_X$ and this means we can divide the connection problem into three parts; the first part is the local connection around x_0 , the second one is the local connection around $-x_0$ and the third one is just a simple adiabatic propagation between x_0 and $-x_0$ in figure 1(a). In this way, we simply solve equation (32) as

$$\frac{d^2 B_1(t)}{dt^2} + q^2(t) B_1(t) \approx \frac{d^2 B_1(t)}{dt^2} + a^4 x_0^2 [(t + x_0)^2 - (\Delta x - iy)^2] B_1(t) = 0 \quad \text{around } -x_0 \quad (39)$$

and

$$\frac{d^2 B_1(t)}{dt^2} + q^2(t) B_1(t) \approx \frac{d^2 B_1(t)}{dt^2} + a^4 x_0^2 [(t - x_0)^2 - (\Delta x + iy)^2] B_1(t) = 0 \quad \text{around } x_0. \quad (40)$$

Both equations (39) and (40) can be solved exactly as discussed in the second example of section 2; thus we obtain the connection matrix in equation (37) as

$$\mathbf{L} = \mathbf{F}(\beta_1) \begin{pmatrix} e^{-i\Phi} & 0 \\ 0 & e^{i\Phi} \end{pmatrix} \mathbf{F}(\beta_2), \quad (41)$$

where the \mathbf{F} -matrix is defined in equation (29) and

$$\beta_1 = 0.5a^2 x_0 (\Delta x - iy)^2, \quad (42)$$

$$\beta_2 = 0.5a^2 x_0 (\Delta x + iy)^2$$

and

$$\Phi = \int_{-x_0}^{x_0} q(t) dt. \quad (43)$$

After careful algebraic derivation, we can finally obtain the Stokes constant as [27]

$$U_1 = \sqrt{\frac{1}{p} - 1} \exp(i\phi), \quad (44)$$

where

$$p = e^{-2\delta} \quad (45)$$

and

$$\phi = \sigma - \frac{\delta}{\pi} + \frac{\delta}{\pi} \ln\left(\frac{\delta}{\pi}\right) - \arg \Gamma\left(i \frac{\delta}{\pi}\right) - \frac{\pi}{4} \quad (46)$$

in which the two parameters σ and δ defined in equation (17) can be converted to

$$\delta = \frac{\pi}{8a^2x_0} \left(x_0^2 = \frac{b^2 + \sqrt{b^4 + 1}}{2a^2} \right) \quad (47)$$

and

$$\sigma = \frac{2a^2x_0^3}{3} + \frac{\delta}{\pi} \ln \left(\frac{\pi x_0}{\delta} \right)^2 - \frac{\delta}{\pi}. \quad (48)$$

The two parameters σ and δ defined in equation (17) can be generalized to deal with general two-state non-adiabatic transition and tunneling, while parameters a^2 and b^2 are only useful for the LZS model with the two-state linear curve crossing case. Inserting the Stokes constant in equation (44) into equation (10), we have a complete analytical solution for the reduced scattering matrix.

3.2. Non-adiabatic tunneling case $b^2 < -1$ ($E \ll E_X$ in figure 1)

In this case, the four transition points are separated into two pairs along the p_y -axis and the analysis of their distribution is shown in figure 1(b). It now requires the connection problem that differs from the previous case; we need to look for the connection on the Stokes lines,

$$B_1(t) \xrightarrow{t \rightarrow \infty \exp(i\frac{\pi}{2})} \frac{A}{\sqrt{q(t)}} \exp \left(i \int_{iy_0}^t q(t) dt \right) + \frac{B}{\sqrt{p(t)}} \exp \left(-i \int_{iy_0}^t q(t) dt \right) \quad (49)$$

and

$$B_1(t) \xrightarrow{t \rightarrow \infty \exp(-i\frac{\pi}{2})} \frac{C}{\sqrt{q(t)}} \exp \left(i \int_{-iy_0}^t q(t) dt \right) + \frac{D}{\sqrt{p(t)}} \exp \left(-i \int_{-iy_0}^t q(t) dt \right), \quad (50)$$

in which the WKB wave functions exponentially rise and decay. The connection matrix is defined by

$$\begin{pmatrix} C \\ D \end{pmatrix} = \mathbf{G} \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}, \quad (51)$$

where all matrix elements in \mathbf{G} can also be expressed as functions of the Stokes constant U_1 [27]. The semiclassical method in the present case ($E \ll E_X$) rewrites equation (33) as

$$q^2(t) = \frac{a^4}{4} [(t - iy_0)^2 - x_1^2] [(t + iy_0)^2 - x_2^2], \quad (52)$$

where y_0, x_1 and x_2 can be solved as functions of the two parameters a^2 and b^2 in equation (34) with a constraint of $y_0^2 \gg |x_1^2| + |x_2^2|$. Thus, we solve equation (32) as

$$\frac{d^2 B_1(t)}{dt^2} + q^2(t) B_1(t) \approx \frac{d^2 B_1(t)}{dt^2} - a^4 y_0^2 [(t + iy_0)^2 - x_2^2] B_1(t) = 0 \quad \text{around } -iy_0 \quad (53)$$

and

$$\frac{d^2 B_1(t)}{dt^2} + q^2(t) B_1(t) \approx \frac{d^2 B_1(t)}{dt^2} - a^4 y_0^2 [(t + iy_0)^2 - x_2^2] B_1(t) = 0 \quad \text{around } iy_0. \quad (54)$$

Both equations (53) and (54) can be solved exactly as discussed in section 2 around $-iy_0$ and iy_0 separately, and then we obtain the connection matrix in equation (51) as

$$\mathbf{G} = \mathbf{H}(\alpha_2) \begin{pmatrix} e^{-i\Phi} & 0 \\ 0 & e^{i\Phi} \end{pmatrix} \mathbf{H}(\alpha_1), \quad (55)$$

where

$$\alpha_1 = 0.5a^2 y_0 x_1^2, \quad \alpha_2 = 0.5a^2 y_0 x_2^2 \quad (56)$$

and

$$\Phi = \int_{-iy_0}^{iy_0} q(t) dt. \quad (57)$$

The \mathbf{H} -matrix in equation (55) is the connection along the Stokes lines so that it differs from the \mathbf{F} -matrix in equation (29) that is the connection along the anti-Stokes lines. However, the derivation is similar and we can obtain [27]

$$\mathbf{H}(\alpha) = \begin{pmatrix} \frac{\sqrt{2\pi} \cos(\pi\alpha)}{2\Gamma(0.5-\alpha)} \exp(\alpha - \alpha \ln \alpha) & -\sin(\pi\alpha) \\ \sin(\pi\alpha) & \frac{\sqrt{2\pi}}{2\Gamma(0.5+\alpha)} \exp(-\alpha + \alpha \ln \alpha) \end{pmatrix}. \quad (58)$$

After careful algebraic derivation, we can finally obtain the Stokes constant as [27]

$$U_1 = U_0 \exp(-i\sigma), \quad (59)$$

where

$$U_0 = \exp \left(\delta - \frac{\sigma}{\pi} + \frac{\sigma}{\pi} \ln \left(\frac{\sigma}{\pi} \right) \right) \frac{\sqrt{2\pi}}{\sqrt{\sigma} \Gamma(\sigma/\pi)} \quad (60)$$

in which the two parameters σ and δ can be converted into,

$$\sigma = \frac{\pi}{8a^2 y_0} \left(y_0^2 = \frac{\sqrt{b^4 + 1} - b^2}{2a^2} \right) \quad (61)$$

and

$$\delta = \frac{2a^2 y_0^3}{3} + \frac{\sigma}{\pi} \ln \left(\frac{\pi y_0}{\sigma} \right)^2 - \frac{\sigma}{\pi} \quad (62)$$

in which σ and δ defined in equation (17) can be used for general potentials.

4. An analytical semiclassical solution for the Nikitin model

For the Nikitin model, there are both time-dependent and time-independent approaches. We have followed the time-independent approach by using the diabatic potential

matrix in equation (1) as

$$\begin{aligned} V_{11}(x) &= V_1 e^{-\alpha x}, & V_{22}(x) &= \Delta V + V_2 e^{-\alpha x}, \\ V_{12}(x) &= V_{21}(x) = V_0 e^{-\alpha x}, \end{aligned} \quad (63)$$

where $-\infty < x = R - R_0 < \infty$. All function parts are the same exponential function for both potentials and coupling. Even such a model is not exactly solvable in general. If we transform the Schrödinger equation (1) into the momentum space and then look for complex crossing points, we can have an infinite number of the transition points that can be periodically distributed either along the p_x -axis shown in figure 1(c) in the case of collision energy $E \gg E_X$ (non-adiabatic transition case) or along the p_y -axis shown in figure 1(d) in the case of collision energy $E \ll E_X$. A direct discussion of the Stokes phenomenon for this problem with an infinite number of transition points is not easy. We propose an indirect way to obtain an effective Stokes constant for the model in equation (63).

4.1. Non-adiabatic transition case $E \gg E_X$ (see figure 1)

When $V_1 = V_2 = 0$ in equation (63), Osherov and Voronin [35] applied a certain special function denoted as the G -function [36] to solve equation (1) exactly. Then, a non-adiabatic transition probability was obtained as the RZ type of solution. Following this approach, Zhu [37] could solve equation (1) exactly with $V_1 = \beta V_0$ and $V_2 = V_0/\beta$, where β varies from $(0, \infty)$. Actually, this β corresponds to equation (3) at the real part of the complex crossing point of the two adiabatic potential energy surfaces. This is the reason why this model can lead to a unified semiclassical solution for general non-adiabatic transition. The reduced scattering matrix derived from this model can be utilized to define an effective Stokes constant through equation (10) [31]:

$$U_1 = \sqrt{\frac{1}{p} - 1} \exp(i\phi), \quad (64)$$

where

$$p = \frac{\sinh(d-1)\delta}{\sinh(d\delta)} e^{-\delta} \quad (65)$$

and

$$\begin{aligned} \phi &= \sigma + \arg \Gamma\left(i(d-1)\frac{\delta}{\pi}\right) - \arg \Gamma\left(i\frac{\delta}{\pi}\right) \\ &\quad - (d-1)\frac{\delta}{\pi} \ln(d-1) + (d-2)\frac{\delta}{\pi} \left[1 - \ln\left(\frac{\delta}{\pi}\right)\right], \end{aligned} \quad (66)$$

where d is defined in equation (16), and σ and δ are defined in equation (17). In this way, we established a unified semiclassical theory for general two-state non-adiabatic transition. It is easy to confirm that it agrees with the LZS model when $d = \infty$, and with the RZ model when $d = 2$.

4.2. Non-adiabatic tunneling case $E \ll E_X$ (see figure 1)

In this case, we must consider the general case of equation (63). However, there is no way to solve this general exponential model analytically. Zhu [32] investigated this case

by directly comparing the symmetry relation of the Stokes constant U_1 for the LZS model. If we take the following replacement:

$$\sigma \rightarrow -i\delta \quad \text{and} \quad \delta \rightarrow -i\sigma \quad (67)$$

in equations (45) and (46) for the case of $E \gg E_X$, the Stokes constant in equation (44) exactly coincides with the expression in equation (59) for the case of $E \ll E_X$. This symmetry relation is essentially imbedded in distributions of the four transition points in figures 1(a) and (b), in which the distribution in figure 1(a) for $E \gg E_X$ is interchangeable with the distribution in figure 1(b) for $E \ll E_X$ by rotating the complex plane by 90° . For the exponential model case here, distributions of the four transition points in figures 1(c) and (d) share the same symmetry properties as shown in figures 1(a) and (b); it is reasonably assumed that replacement of equation (67) can be used in equations (65) and (66) to derive an effective Stokes constant for general non-adiabatic tunneling. This leads to equation (64) becoming [32]

$$U_1 = U_0 \exp(-i\sigma), \quad (68)$$

where

$$\begin{aligned} U_0 &= \frac{\Gamma((d-1)\sigma/\pi)}{\Gamma(\sigma/\pi)} \sqrt{d-1} \exp\left(\delta - (d-1)\frac{\sigma}{\pi} \ln(d-1)\right) \\ &\quad + (d-2)\frac{\sigma}{\pi} \left[1 - \ln\left(\frac{\sigma}{\pi}\right)\right]. \end{aligned} \quad (69)$$

In this way, we have established a unified semiclassical theory for general two-state non-adiabatic tunneling. It is easy to confirm that equation (69) goes to equation (60) for the LZS model when $d = \infty$. By matching a more accurate expression for the Stokes constant in the LZS model in the non-adiabatic tunneling case [27], we can propose a final form:

$$\begin{aligned} \text{Re } U_1 &= \cos \sigma (U_0 - \sin^2 \sigma / U_0), \\ \text{Im } U_1 &= -\sin \sigma \sqrt{U_0^2 - \sin^2 \sigma \cos^2 \sigma / U_0^2 + \cos(2\sigma)}, \end{aligned} \quad (70)$$

where U_0 is defined in equation (69), and the two parameters σ and δ are given in equation (17).

5. Numerical results

We illustrate some numerical examples and compare the calculations between exact quantum mechanics and the present unified analytical semiclassical theory for an overall non-adiabatic transition probability defined from the reduced scattering matrix in equation (10):

$$P_{12} = |U_2|^2 = \left| \frac{U_1 - U_1^*}{1 + U_1^* U_1} \right|^2 \quad (71)$$

in which the Stokes constant U_1 is given by equation (64) in the case $E > E_X$ for non-adiabatic transition, and by equation (70) in the case $E < E_X$ for non-adiabatic tunneling. Three parameters d , σ and δ are calculated from equation (16) and (17). Exact calculations are performed with a quantal close-coupling method.

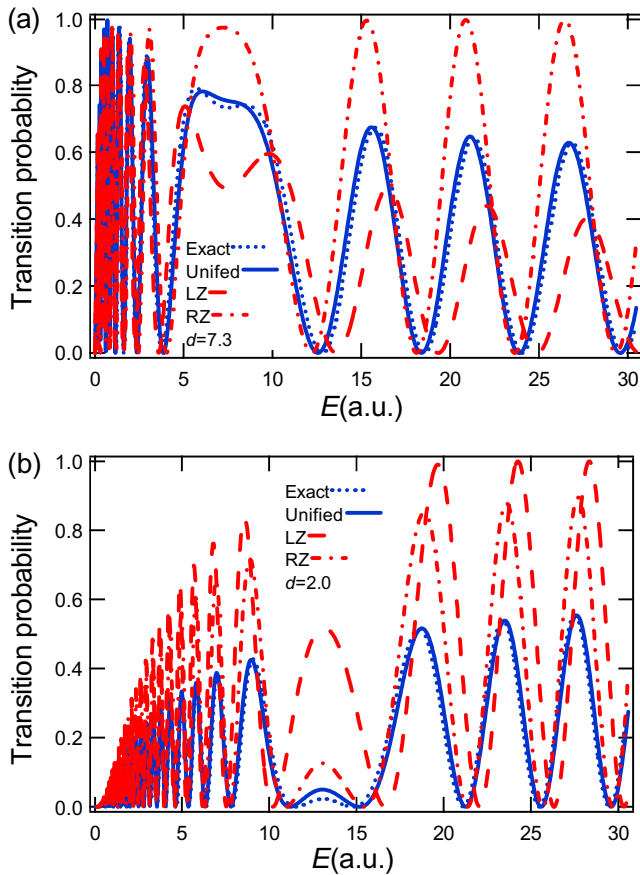


Figure 3. Overall non-adiabatic transition probability P_{12} as a function of the total energy E . Dotted lines are the results of the quantum mechanical close-coupling method, solid lines are the results from the unified analytical semiclassical formula, dashed lines are the results of the LZ formula, and dash-dotted lines are the results of the RZ formula. (a) $d = 7.3$ and (b) $d = 2.0$.

5.1. Non-adiabatic transition case $E > E_X$

The first example is crossing model potentials from the $\text{He}^+ + \text{Ne}$ system [38], and its functional forms in diabatic representation are given in [31, 38]. The most important parameter in equation (16) is calculated as $d = 7.3$, that is, far from the LZS case where $d = \infty$. Figure 3(a) shows very good agreement between exact results and unified analytical semiclassical calculations, and both the LZ and the RZ formulae give relatively good results in a lower energy range and gradually become bad as collision energy increases. The second example is a non-crossing model modified from the first example and its functional forms in diabatic representation are given in [31]. The most important parameter in equation (16) is designed as $d = 2$, that is, exactly the RZ case. Figure 3(b) shows very good agreement between exact results and unified analytical semiclassical calculations, while both the LZ and the RZ formulae give bad results, and the RZ formula seems to present a correct oscillating structure.

5.2. Non-adiabatic tunneling case $E < E_X$

The third example is the general exponential model and its functional forms are given in [32]. The most important parameter in equation (16) is calculated as $d = 2.28$.

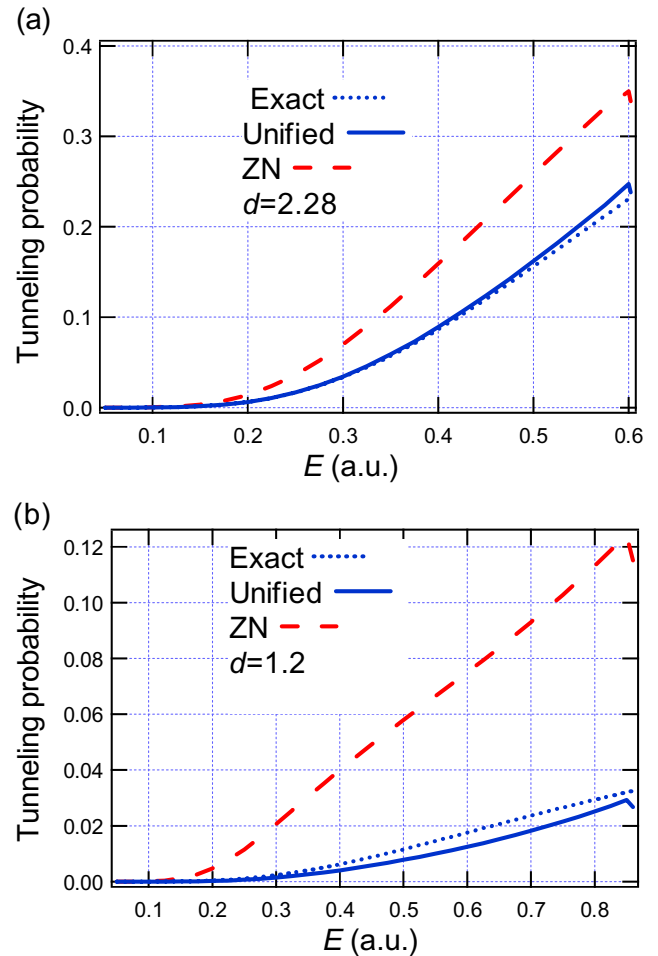


Figure 4. Overall non-adiabatic tunneling probability P_{12} as a function of the total energy E . Dotted lines are the results of the quantum mechanical close-coupling method, solid lines are the results of the unified analytical semiclassical formula, and dashed lines are the results of the ZN formula. (a) $d = 2.28$ and (b) $d = 1.2$.

Figure 4(a) shows very good agreement between the exact results and unified analytical semiclassical calculations, while the ZN formula (equation (70) with $d = \infty$) does not work well. The fourth example is modified from the third example by letting the most important parameter in equation (16) be $d = 1.2$ so that the non-adiabatic tunneling probability should be very small. Figure 4(b) shows very good agreement between the exact results and the unified analytical semiclassical calculations, while the ZN formula becomes a very bad approximation.

6. Concluding remarks

Unified analytical semiclassical theory for general two-state non-adiabatic transition is reviewed within the WKB framework associated with the Stokes phenomenon in mathematics. The reduced scattering matrix is expressed in terms of a single complex quantity that is called the Stokes constant U_1 . Distributions of transition points that are complex crossing points between two adiabatic potential energy surfaces show a certain symmetry and separable pattern in certain limiting cases (see figure 1). This is essential for the WKB method to derive a compact analytical

expression for U_1 . U_1 is a function of three parameters; the most important one is in equation (16) that represents a type of non-adiabatic transition and the other two in equation (17) represent effective magnitude and phase of the non-adiabatic transition.

There are two ways to apply the unified analytical semiclassical theory for multidimensional non-adiabatic dynamics. The first way is to separate multidimensional coordinates into internal coordinates and a reaction coordinate that is curved in one dimension. In this way, one converts the problem into one-dimensional many-state non-adiabatic transitions, and then the so-called two-by-two state method can be applied. The second way is to directly incorporate it with the trajectory surface hopping method and compute hopping probability analytically along the trajectory. The analytical formula here can also be easily applied to various boundary conditions for multidimensional wave functions and trajectories.

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