# STOKES PHENOMENON
# AND
# TWO-STATE LINEAR CURVE CROSSING PROBLEMS

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# Abstract

The Stokes phenomena of the standard second-order ordinary differential equations with the coefficient functions of the certain n-th order polynomials are investigated. Four cases of the coefficient function $q(z)$ are solved to find analytical solutions of the Stokes constants: (i) $q(z) = a_{2N}z^{2N} + \sum_{j=-\infty}^{N-1} a_j z^j$; (ii) $q(z) = a_{2N-1}z^{2N-1} + \sum_{j=-\infty}^{N-2} a_j z^j$; (iii) $q(z) = \sum_{j=0}^{4} a_j z^j$; and (iv) $q(z) = \sum_{j=0}^{3} a_j z^j$. The case (iii) can be immediately applied to the two-state linear curve crossing problems which represent the most basic models for non-adiabatic transition processes in atomic and molecular physics. The two-state linear curve crossing problems are generally classified into the following two cases: (1) the same sign of slopes of two diabatic potential curves(Landau-Zener case), and (2) the opposite sign of slopes(nonadiabatic tunneling case). The reduced scattering matrix for each case has been found to be expressed in terms of only one Stokes constant $U_1$, which is solved exactly and analytically in a form of convergent infinite series. This means that exact quantal solutions of the reduced scattering matrices for both cases are analytically found for the first time. Furthermore, new semiclassical solutions of the reduced scattering matrices for both cases are derived in simple compact forms. Especially, the case that the collision energy is lower than the crossing point is correctly dealt with for the first time. Both quantal and semiclassical solutions for the reduced scattering matrix are made possible by expressing the connection matrix, which is a crucial bridge to link physics and mathematics, in terms of Stokes constants. Among the fruitful results obtained, one of the most notable ones is about a derivation of a new formula to replace the widely used Landau-Zener formula for nonadiabatic transition probability. The new one is as simple as the Landau-Zener, but works much better than the latter. On the the other hand, by fully analyzing the distributions of the four transition points and the Stokes lines in complex plane for the basic equations of the two-state linear curve crossing problems, the validity conditions are made clear for the present and the other available semiclassical formulas of the reduced scattering matrices.

## Chapter 1

This thesis begins with the asymptotic solutions of the second-order differential equations for the four cases mentioned above. The asymptotic solutions are found exactly in the form of infinite series, in which the recurrence relations among the coefficients are given explicitly. This is made possible by transforming the original differential equations from the complex-$z$ plane to a new complex-$\xi$ plane in which all the Stokes lines coincide with the real axis. At the same time, the standard asymptotic WKB solutions are introduced for convenience as reference functions to define Stokes constants. The Stokes phenomenon is reviewed and explained briefly so that physicists and chemists can get quickly an insight on the topics discussed in this thesis.

## Chapter 2

A central task in the subject of Stokes phenomenon is to find analytical solutions of Stokes constants. The standard asymptotic WKB solutions are proved to be quite useful for the present type of analysis, especially for deriving the relations among Stokes constants. Actually, three independent relations for all Stokes constants $U_i$ defined in the complex-$z$ plane are easily established. They are very useful for many physical problems although they are not enough to have a complete. A further deduction is made by transforming the asymptotic solutions from complex-$z$ plane to the complex-$\xi$ plane where the Stokes constants $T_i$ are defined. One-to-one simple correspondence is obtained between $U_i$ and $T_i$. What is fascinating about the complex-$\xi$ plane is that all Stokes constants $T_i$ can be simply related to only one, for instance, $T_1$, by using a particular transformation under which the differential equation in the complex-$\xi$ plane is invariant. The conclusions obtained up to now hold not only for the four cases mentioned above but generally. The remaining most difficult problem is how to find an analytical solution for $T_1$ for each case. By generalizing the coupled-wave-integral- equations method devised by Hinton, Stokes constant $T_1$ is finally shown to be expressed in the analytical form of a convergent infinite series as a function of the coefficients $q(z)$ for all four cases.

## Chapter 3

A connection matrix presented in this chapter represents an important physical quantity i.e., scattering matrix, and bridge between the Stokes phenomenon in mathematics and the two-state linear curve crossing problems in physics. If the standard WKB solutions are used in the asymptotic region $|z| \to \infty$ of the complex plane, the connection matrix is exactly expressed in terms of the Stokes constants. This matrix can connect solutions in one asymptotic region in complex plane to solutions in another asymptotic region, such as physical important connections between two anti-Stokes lines, two Stokes lines, and one anti-Stokes and Stokes lines. What is fascinating about expressing the connection matrix in terms of Stokes constants is as follows: A physically required connection matrix sometimes can not be well-approximated by following traditional semiclassical path. It is much more flexible and versatile to try to find Stokes constants. Based on the knowledge of the distributions of transition points and Stokes lines, such a path which may not correspond to the physical connection matrix can be designed to derive the best semiclassical solution from Stokes constants. Excellent examples will be given in chapters 5 , 6 and 7 for semiclassical solutions of the reduced scattering matrices for the cases of energy lower than the crossing points. The connection problems for one transition point and two transition points are briefly reviewed, and those for three transition points and four transition points are presented in detail. The last case is mainly concerned with the curve crossing problems discussed in the subsequent chapters.

## Chapter 4

The classic problems of the two-state linear curve crossing were initially discussed by Landau, Zener and Stueckelberg. As mentioned before, there are the following two cases: (1) the same sign of slopes of two diabatic potentials(Landau- Zener case), and (2) the opposite sign of slopes(nonadiabatic tunneling case). It is well known that the reduced scattering matrices for these two problems can be described in terms of the two parameters $a^2$(effective coupling strength) and $b^2$(effective collision energy). Finding the exact analytical quantal solutions for the reduced scattering matrices is very challenging and very difficult question. The answer to this question is given in this chapter. The starting point is the basic differential equation of the case (iii) mentioned before. By using the connection matrix obtained in chapter 3, the reduced scattering matrix for each case is first expressed in terms of three Stokes constants. Then by taking into account two extra conditions in addition to the unitarity of reduced scattering matrix, it is shown to be expressed finally in terms of only one Stokes constant $U_1$. Finally, this one Stokes constant is given exactly and analytically by a convergent infinite series which is a direct result from chapter 2. Another work reported in this chapter is a new numerical method to solve reduced scattering matrix for the nonadiabatic tunneling case. The original coupled equations suffer from very rapid oscillation asymptotically and can not give stable and reliable numerical results. New coupled equations are presented which involve ordinary sine and cosine solutions asymptotically. Numerical results of reduced scattering matrix can be obtained with any desirable accuracy.

## Chapter 5

The distributions of the four transition points and the Stokes lines are fully analyzed for both Landau-Zener and nonadiabatic tunneling cases in the whole plane of the two parameters $a^2$ and $b^2$. This analysis is, of course, important in itself, but what is more significant about this is that the structure of the distributions essentially determines which path in complex plane is the best for obtaining good semiclassical solutions of the reduced scattering matrices. The semiclassical method used here and in the following chapters should be potentially useful for other problems in physics and chemistry.

## Chapter 6

The semiclassical solution of the reduced scattering matrix for the Landau-Zener case is obtained in this chapter. Since the reduced scattering matrix is expressed in terms of one Stokes constant $U_1$ in chapter 4, question now is how to find an approximate solution for $U_1$. The distributions of transition points and Stokes lines analyzed in chapter 5 clearly show that there are two best choices of path to get good approximate solutions of $U_1$. One path corresponds to the connection on the anti-Stokes lines along which the four transition points are separated in two paris. Another path corresponds to the connection on the Stokes lines along which the four transition points are again separated in two pairs. The former(latter) corresponds to high(low) energy limit. In each limiting case, the exact connection matrix can be approximately decomposed into a product of the two matrices, each of which represents the connection matrix based on two transition points as is given in chapter 3. Finally, two new compact analytical formulas for the reduced scattering matrix are derived and compared with available ones. The $a^2 - b^2$ plane is now divided into five regions, in each one of which the best recommended formulas are proposed. The new formulas proposed are simple and explicit functions of the two parameters $a^2$ and $b^2$. Especially, a simple formula which works much better than the conventional Landau-Zener formula is obtained for nonadiabatic transition probability for one passage of crossing point.

## Chapter 7

The semiclassical solution of the reduced scattering matrix for the nonadiabatic tunneling case is obtained in this chapter. The reduced scattering matrix is, of course, given in chapter 4 in terms of one Stokes constant $U_1$. The distributions of transition points and Stokes lines in this case are more complicated than the previous case. There are two limiting cases, $b^2 \gg 1$ and $b^2 \ll -1$, which are similar to the Landau-Zener case. Therefore, the two new formulas for reduced scattering matrix are obtained in these two limiting cases again by simple functions of the two parameters $a^2$ and $b^2$. Especially formula for $b^2 < -1$ is the first one ever obtained. The distributions of transition points and Stokes lines in the region $|b^2| \leq 1$ are very different from and have no correspondence to the former Landau-Zener case. Based on the solvable special differential equation given in chapter 3, an approximate expression for Stokes constant $U_1$ is found with use of a fitting procedure. Again, the $a^2 - b^2$ plane is divided into five regions and the best recommended formula for reduced scattering matrix is proposed for each region. Thus, a complete picture of the nonadiabatic tunneling case is attained.

# Notations

Throughout this thesis, solid line represents Anti-Stokes line, dashed line Stokes line, and wavy line branch cut.

Anti-Stokes line

Stokes line

Branch cut

It should be noted that the definitions of Stokes and anti-Stokes lines used here are those in physics, and that they are interchanged in mathematics.

# Contents

# PART 1. STOKES PHENOMENON

The Stokes phenomenon[3] is the phenomenon that asymptotic solutions of ordinary differential equations exhibit discontinuous change across certain lines(Stokes lines) in the complex plane. Certain constant called Stokes constant is assigned to each Stokes line to ensure the single-valuedness of the solution. In general, it is very difficult to determine the Stokes constants; and therefore it is very usual to treat particular differential equations for which the Stokes constants can be calculated either exactly or approximately[2 – 7 , 14 – 22]. A few efforts have been made so far to develop methods that calculate the Stokes constants for as general differential equations as possible[2, 4, 7, 22].

Part 1 in this thesis is actually a new work toward this aim. The Stokes phenomena for the certain four general cases of second-order differential equations are discussed. Analytical solutions of the Stokes constants are obtained exactly in a form of convergent infinite series for all four cases. On the other hand, the connection matrices which connect solutions from one asymptotic region to another in complex plane are exactly expressed in terms of the Stokes constants. The connection matrices for the cases of two and four transition points discussed in this Part 1 are applied to the two-state linear curve crossing problems in Part 2.

# Chapter 1

# Asymptotic solutions

Asymptotic solutions of a standard second-order differential equation constitute the basis to analyze Stokes phenomenon and to define Stokes constant. In this chapter four kinds of the differential equations defined in the complex-$z$ plane can not be directly solved. By transforming the differential equations from the complex-$z$ plane to a new complex-$\xi$ plane, exact asymptotic solutions for all these four cases are solved in the form of convergent infinite series. A brief introduction about Stokes phenomenon is presented for those people who do not know well about this subject, and it is also an aim to make a smooth connection to the contents of this thesis.

## 1.1 WKB solutions

A standard second-order differential equation

$$\frac{d^2\phi}{dx^2} + q(x)\phi(x) = 0, \quad \text{for} \quad -\infty < x < \infty, \tag{1.1}$$

represents numerous physical problems. As we know, exact solutions can be obtained analytically only for a very limited number of functions $q(x)$. The use of approximations are quite necessary; and the Wentzel-Kramers-Brillouin (WKB)[1] solution constitutes one of the most powerful techniques among these approximations.

Task of many typical physical problems, in which physicists are only concerned with physical quantities such as eigenvalues and scattering matrices, is aimed to find a connection of wave function $\phi(x)$ between two asymptotic regions $x \to +\infty$ and $x \to -\infty$, where the WKB solutions coincide with original exact solutions. This connection can hardly be obtained by using WKB solutions only on real axis. So, for this purpose, a real independent variable $x$ may often be replaced by the complex variable $z$. The two independent WKB solutions are given by

$$\phi_{\pm}(z) = q(z)^{-\frac{1}{4}} e^{\pm i \int_{z_0}^{z} q^{\frac{1}{2}}(z) dz}, \tag{1.2}$$

where $z_0$ is called reference point. A zero of q(z) in the complex plane is called transition point; evidently the Eq (1.2) ceases to be valid near a transition point due to the singularity caused by the factor $q(z)^{-\frac{1}{4}}$, while the exact solutions of Eq (1.1) must obviously remain finite at such a point. The farther from all transition points the WKB solutions are, the more accurate they become. There is a method which allows us to trace the WKB solutions in the asymptotic region $|z| \longrightarrow \infty$ where WKB solutions always remain exact; evidently the solutions of certain physical quantities obtained by this way are also exact. But it is not always possible and necessary to use WKB solutions only in the region of $|z| \rightarrow \infty$. In many physical problems we can still construct quite good approximation by using the WKB solutions in the certain region , in which the solutions should be far from all transition points.

Our investigation about Stokes phenomenon in part 1 of this thesis focuses attention on the certain n-th order polynomial coefficient function of Eq (1.1),

$$q(z) = \sum_{j=-\infty}^{n} a_j z^j, \qquad (n > 0); \tag{1.3}$$

and more precisely speaking, a complete analysis is presented for the following four cases:

**Case** (i ) $q(z) = a_{2N} z^{2N} + \sum_{j=-\infty}^{N-1} a_j z^j$,

**Case** (ii ) $q(z) = a_{2N-1} z^{2N-1} + \sum_{j=-\infty}^{N-2} a_j z^j$,

**Case** (iii) $q(z) = a_4 z^4 + a_2 z^2 + a_1 z + a_0$,

and

**Case** (iv ) $q(z) = a_3 z^3 + a_1 z + a_0$,

with N being positive integer.

## 1.2 Asymptotic solutions

A starting point to find asymptotic solutions of four cases mentioned above is to introduce the following transformation[2]

$$\phi(z) = z^{-\frac{n}{4}}\psi(\xi), \tag{1.4}$$

and

$$\xi = \frac{4}{n+2}(-a_n)^{\frac{1}{2}} z^{(n+2)/2}. \tag{1.5}$$

Simple calculation leads $\psi(\xi)$ to

$$\frac{d^2\psi}{d\xi^2} + Q(\xi)\psi(\xi) = 0, \tag{1.6}$$

where

$$Q(\xi) = -\frac{1}{4} - \frac{q(z) - a_n z^n}{4a_n z^n} - \frac{(n+2)^2 - 4}{64a_n} z^{-(n+2)}. \tag{1.7}$$

For general case of Eq (1.3), we can assume that $Q(\xi)$ is given in the form,

$$Q(\xi) = -\frac{1}{4} + \sum_{K}^{\infty} Q_K \xi^{-K}, \tag{1.8}$$

Hinton[2] discussed the case in which K are positive integers, here we will deal with the case K are positive fractions.

In order to analyze Stokes phenomenon in a unified way, we shall first introduce standard WKB solutions as asymptotic WKB solutions, in which we consider the leading terms(omit all constant terms) in the phase integrals and the first leading term of $q(z)^{\frac{1}{4}}$ in Eq (1.2). Then, relations between exact asymptotic solutions in the complex-$\xi$ plane and the standard WKB solutions will be made clear in the following.

**A. Case** (i)

First, let us write the following asymptotic WKB solutions which we call standard WKB solutions:

$$(\bullet, z) = (z^{2N})^{-1/4} \exp[i\frac{\sqrt{a_{2N}}}{N+1} z^{N+1} + i\frac{a_{N-1}}{2\sqrt{a_{2N}}} \ln(z)], \tag{1.9}$$

$$(\bullet, z) = (z^{2N})^{-1/4} \exp[-i\frac{\sqrt{a_{2N}}}{N+1} z^{N+1} - i\frac{a_{N-1}}{2\sqrt{a_{2N}}} \ln(z)], \tag{1.10}$$

where

$$\int q^{1/2}(z)dz \sim \frac{\sqrt{a_{2N}}}{N+1}z^{N+1} + \frac{a_{N-1}}{2\sqrt{a_{2N}}}\ln(z), \quad \text{for } |z| \to \infty \tag{1.11}$$

and the notation • simply means that the lower limit of integration i.e. the reference point is not specified. As is seen from Eq (1.8), $Q(\xi)$ can be expanded as

$$Q(\xi) = -\frac{1}{4} + \sum_{n=1}^{\infty} Q_n \xi^{-\frac{N+n}{N+1}}, \tag{1.12}$$

where the fractional powers of $\xi$ are expicitly introduced. We can assume a solution of the form

$$\psi(\xi) = \xi^{-\rho} e^{\sigma(\xi/2)} \sum_{n=0}^{\infty} c_n \xi^{-\frac{n}{N+1}}. \tag{1.13}$$

If this is substituted into Eq. (1.6) with Eq. (1.12), we can find

$$\rho = \frac{Q_1}{\sigma}, \quad \sigma = \pm 1, \tag{1.14}$$

$$c_m(\sigma\frac{m}{N+1}) = \sum_{n=0}^{m-1} c_n Q_{m+1-n} \quad \text{for } 1 \leq m \leq N, \tag{1.15}$$

and

$$c_m(\sigma\frac{m}{N+1}) = (\rho + \frac{m}{N+1} - 1)(\rho + \frac{m}{N+1})c_{m-N-1} + \sum_{n=0}^{\infty} c_n Q_{m-n+1} \tag{1.16}$$

for $m \geq N+1$,

where $c_0$ is an arbitrary constant. This formal solution is an asymptotic expansion of a solution in a certain region of $\xi$, if we assume that the infinite series in Eq. (1.13) converges for sufficiently large $|\xi|$. Corresponding to the choices of $\sigma = \pm 1$, the two independent solutions in the complex $\xi$-plane are defined as

$$u(\xi; Q_1, Q_2, \ldots) = (\bullet, \xi) \sum_{n=0}^{\infty} c_n^{(1)} \xi^{-\frac{n}{N+1}} \quad \text{for } \sigma = 1, \tag{1.17}$$

and

$$v(\xi; Q_1, Q_2, \ldots) = (\xi, \bullet) \sum_{n=0}^{\infty} c_n^{(2)} \xi^{-\frac{n}{N+1}} \quad \text{for } \sigma = -1, \tag{1.18}$$

where

$$(\bullet, \xi) = \xi^{-Q_1} e^{\xi/2} \tag{1.19}$$

and

$$(\xi, \bullet) = \xi^{Q_1} e^{-\xi/2}, \tag{1.20}$$

which correspond to the standard WKB solutions in complex-$z$ plane, as shown in Eqs. (1.9) and (1.10). We can easily see that exact asymptotic solutions in Eqs. (1.17) and (1.18) are made up of two parts, one include all divergent terms which are the standard WKB solutions, others are convergent terms in the power series expansion. This fact is also true for other three cases.

**B.** Case (ii)

The same procedure as in case(i) can be utilized. The standard WKB solutions are

$$(\bullet, z) = (z^{2N-1})^{-1/4} \exp[i\frac{2\sqrt{a_{2N-1}}}{2N+1} z^{\frac{2N+1}{2}}], \tag{1.21}$$

and

$$(z, \bullet) = (z^{2N-1})^{-1/4} \exp[-i\frac{2\sqrt{a_{2N-1}}}{2N+1} z^{\frac{2N+1}{2}}]. \tag{1.22}$$

The coefficient $Q(\xi)$ is equal to

$$Q(\xi) = -\frac{1}{4} + \sum_{n=1}^{\infty} Q_n \xi^{-2\frac{N+n}{2N+1}}, \tag{1.23}$$

and a formal solution is given by

$$\psi(\xi) = e^{\sigma(\xi/2)} \sum_{n=0}^{\infty} c_n \xi^{-\frac{n}{2N+1}} \tag{1.24}$$

with

$$\sigma = \pm 1. \tag{1.25}$$

The recurrence relations for $c_n$ are

$$c_{2n-1}(\sigma\frac{2n-1}{2N+1}) = \sum_{m=0}^{n-1} c_{2m} Q_{n-m} \quad \text{for } 1 \leq n \leq N, \tag{1.26}$$

$$c_{2n}(\sigma\frac{2n}{2N+1}) = \sum_{m=0}^{n-1} c_{2m+1} Q_{n-m} \quad \text{for } 1 \leq n \leq N, \tag{1.27}$$

$$c_{2n-1}(\sigma\frac{2n-1}{2N+1}) = \frac{2(n-N-1)}{2N+1}[\frac{2(n-N-1)}{2N+1} + 1]c_{2(n-N-1)} + \sum_{m=0}^{n-1} c_{2m} Q_{n-m}, \tag{1.28}$$

for $n \geq N+1$,

$$c_{2n}(\sigma\frac{2n}{2N+1}) = \frac{2(n-N-1)+1}{2N+1}[\frac{2(n-N-1)+1}{2N+1} + 1]c_{2(n-N-1)+1}$$

$$+\sum_{m=0}^{n-1} c_{2m+1}Q_{n-m} \quad \text{for } n \geq N+1. \tag{1.29}$$

It should be noted that we have used exactly the same notation for $c_n$ and $Q_n$ as in case (i), but they have naturally different definitions in each case.

**C. Case** (iii)

In this case, we have

$$\int q^{1/2}(z)dz \sim \frac{\sqrt{a_4}}{3}z^3 + \frac{a_2}{2\sqrt{a_4}}z + \frac{a_1}{2\sqrt{a_4}}\ln(z) \quad \text{for } |z| \to \infty, \tag{1.30}$$

in which the second term is new, missing in the case(i) and will give an additional complexity in the procedure to obtain Stokes constants, as is seen next chapter. The standard WKB solutions are thus explicitly obtained as

$$(\bullet, z) = z^{-1}\exp[i\frac{\sqrt{a_4}}{3}z^3 + i\frac{a_2}{2\sqrt{a_4}}z + i\frac{a_1}{2\sqrt{a_4}}\ln(z)], \tag{1.31}$$

and

$$(z, \bullet) = z^{-1}\exp[-i\frac{\sqrt{a_4}}{3}z^3 - i\frac{a_2}{2\sqrt{a_4}}z - i\frac{a_1}{2\sqrt{a_4}}\ln(z)]. \tag{1.32}$$

The coefficient $Q(\xi)$ and a formal solution $\psi(\xi)$ are given by

$$Q(\xi) = -\frac{1}{4} + \frac{Q_0}{\xi^{2/3}} + \frac{Q_1}{\xi} + \frac{Q_2}{\xi^{4/3}} + \frac{Q_4}{\xi^2} \tag{1.33}$$

and

$$\psi(\xi) = \xi^{-\rho}e^{(\sigma/2)(\xi - \alpha\xi^{1/3})}\sum_{n=0}^{\infty} c_n\xi^{-\frac{n}{3}}, \tag{1.34}$$

where

$$\rho = \frac{Q_1}{\sigma}, \sigma = \pm 1, \alpha = 6Q_0, \text{ and } Q_4 = 2/9. \tag{1.35}$$

The recurrence relations for $c_n$ are

$$c_1 = 3\frac{Q_0^2 + Q_2}{\sigma}c_0, \tag{1.36}$$

$$c_2 = [(\frac{3}{\sigma}Q_1 + 1)Q_0 + \frac{9}{2}(Q_0^2 + Q_2)^2]c_0, \tag{1.37}$$

and

$$(\sigma\frac{n}{3})c_n = [(\rho + \frac{n-3}{3})(\rho + \frac{n}{3}) + \frac{2}{9}]c_{n-3} +$$

$$[2Q_0Q_1 + \frac{2}{3}\sigma Q_0(n-1)]c_{n-2} + [Q_0^2 + Q_2]c_{n-1}, \quad \text{for } n \geq 3. \tag{1.38}$$

Two independent solutions in the complex $\xi$-plane are thus denoted as

$$u(\xi; Q_0, Q_1, Q_2) = (\bullet, \xi) \sum_{n=0}^{\infty} c_n^{(1)} \xi^{-\frac{n}{3}}, \quad \text{for } \sigma = +1 \tag{1.39}$$

and

$$v(\xi; Q_0, Q_1, Q_2) = (\xi, \bullet) \sum_{n=0}^{\infty} c_n^{(2)} \xi^{-\frac{n}{3}}, \quad \text{for } \sigma = -1, \tag{1.40}$$

where

$$(\bullet, \xi) = \xi^{-Q_1} e^{(\xi - 6Q_0\xi^{1/3})/2} \tag{1.41}$$

and

$$(\xi, \bullet) = \xi^{Q_1} e^{-(\xi - 6Q_0\xi^{1/3})/2}, \tag{1.42}$$

in which the second terms in the exponentials are new, missing in the case (i).

**D. Case** (iv)

The same procedure as in case(iii) can be used, and the following results are obtained:

$$(\bullet, z) = z^{-3/4} \exp[i\frac{2\sqrt{a_3}}{5} z^{5/2} + i\frac{a_1}{\sqrt{a_3}} z^{1/2}], \tag{1.43}$$

$$(z, \bullet) = z^{-3/4} \exp[-i\frac{2\sqrt{a_3}}{5} z^{5/2} - i\frac{a_1}{\sqrt{a_3}} z^{1/2}], \tag{1.44}$$

$$Q(\xi) = -\frac{1}{4} + \frac{Q_0}{\xi^{4/5}} + \frac{Q_2}{\xi^{6/5}} + \frac{Q_3}{\xi^2}, \tag{1.45}$$

and

$$\psi(\xi) = e^{\sigma(\xi - \alpha\xi^{1/5})/2} \sum_{n=0}^{\infty} c_n \xi^{-\frac{n}{5}}, \tag{1.46}$$

where

$$\sigma = \pm 1, \alpha = 10Q_0, \text{and } Q_3 = 21/100. \tag{1.47}$$

The recurrence relations for $c_n$ are

$$c_1(\frac{\sigma}{5}) = c_0 Q_2,$$

$$c_2(\frac{2\sigma}{5}) = c_1 Q_2,$$

$$c_3(\frac{3\sigma}{5}) = c_0 Q_0^2 + c_2 Q_2,$$

$$c_4(\frac{4\sigma}{5}) = 2c_0\sigma\alpha/25 + c_1 Q_0 + c_3 Q_2,$$

and

$$c_n(n\sigma/5) = c_{n-5}[n(n-5)/25 + 21/100]$$
$$+ c_{n-4}[(n-2)\sigma\alpha/25] + c_{n-3}Q_0^2 + c_{n-1}Q_2, \quad \text{for } n \geq 5. \tag{1.48}$$

Two independent solutions in the complex $\xi$-plane are given by

$$u(\xi; Q_0, Q_2, Q_3) = (\bullet, \xi) \sum_{n=0}^{\infty} c_n^{(1)} \xi^{-\frac{n}{5}}, \quad \text{for } \sigma = +1 \tag{1.49}$$

and

$$v(\xi; Q_0, Q_2, Q_3) = (\xi, \bullet) \sum_{n=0}^{\infty} c_n^{(2)} \xi^{-\frac{n}{5}}, \quad \text{for } \sigma = -1, \tag{1.50}$$

where

$$(\bullet, \xi) = e^{(\xi - 10Q_0\xi^{1/5})/2}, \tag{1.51}$$

and

$$(\xi, \bullet) = e^{-(\xi - 10Q_0\xi^{1/5})/2}. \tag{1.52}$$

For the above four cases, the explicit recurrence relations for the coefficients $c_n$ in the asymptotic solutions have been made possible due to transforming the differential equations from complex-$z$ plane to $\xi$ plane. But, it should be pointed out that explicit recurrence relations are not always possible for general form of Eq. (1.3). However, for given $q(z)$ in Eq. (1.3) explicit expressions of standard WKB solutions can be derived in principal.

## 1.3 Stokes phenomenon

A general solution for the differential equation (1.1) in the whole complex plane can be given by a certain linear combination of two independent solutions; this fact should hold also in any asymptotic region of complex plane . But , what Stokes[3] discovered is that if in a certain region of arg $z$ a general solution is given by a certain combination of two asymptotic solutions, in the neighbouring region of arg $z$ it is no longer necessary to maintain the same linear combination as before. The constant coefficients of the linear combination changed discontinuously as certain lines are crossed in the complex plane. This phenomenon is called Stokes phenomenon.

In order to deal with this phenomenon quantitatively, we first need to introduce our basic terminology used in this subject. Let us start with the following convenient notations[4] to rewrite the WKB solutions in Eq. (1.2):

$$(z_0, z) = q(z)^{-\frac{1}{4}} e^{i \int_{z_0}^{z} q^{\frac{1}{2}}(z) dz} \tag{1.53}$$

and

$$(z, z_0) = q(z)^{-\frac{1}{4}} e^{-i \int_{z_0}^{z} q^{\frac{1}{2}}(z) dz}, \tag{1.54}$$

in which $q^{\frac{1}{2}}$ and $q^{-\frac{1}{4}}$ can be specified by means of certain branch cut in the complex plane , and the path of integration should not cross the branch cut. If for given $z$ the exponential in Eq. (1.53) is dominant, a suffix $d$ is inserted, namely $(z_0, z)_d$; then solution in Eq. (1.54) is subdominant, a suffix $s$ is used, namely $(z, z_0)_s$.

In the complex $z$-plane, there are certain lines that are called anti-Stokes lines on which we have

$$\mathrm{Im} \int_{z_0}^{z} q^{\frac{1}{2}}(z) dz = 0. \tag{1.55}$$

Interchange between the subdominancy and the dominancy of solutions takes place if the solutions cross the anti-Stokes lines, on which the solutions are neither dominant nor subdominant. On the other hand, we define Stokes lines by

$$\mathrm{Re} \int_{z_0}^{z} q^{\frac{1}{2}}(z) dz = 0. \tag{1.56}$$

On the Stokes lines, one of the two independent solutions reaches its position of maximum subdominancy, while the other attains its maximum dominancy.

Now, we can turn to quantitatively describe discontinuous change of asymptotic solution in the complex plane. Assume that for certain $q(z)$ in Eq. (1.1) a asymptotic solution in the region 1 of Fig.1.1 is given by the linear combination of two solutions of Eqs. (1.53) and (1.54),

$$\phi(z) = A(z_0, z)_d + B(z, z_0)_s, \tag{1.57}$$

where $A$ and $B$ are arbitrary constants. In the neighbouring of the region 1, region 2 , this solution becomes

$$\phi(z) = A(z_0, z)_d + (B + AU)(z, z_0)_s, \tag{1.58}$$

where a discontinuous change occurs in the coefficient of the subdominant solution, and $U$ is called Stokes constant which is associated with a particular Stokes line in Fig.1.1.

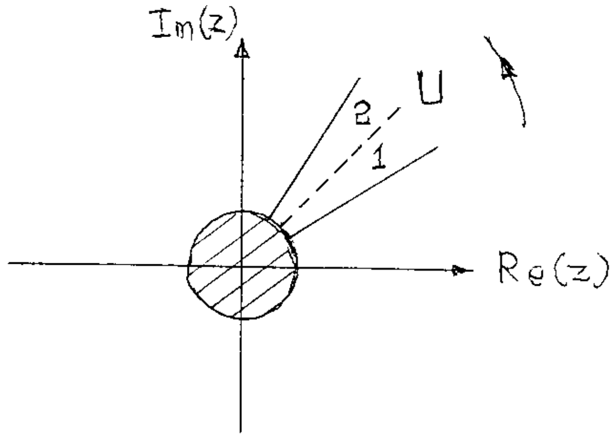



Figure 1.1.

Taking the Airy equation as an example , we shall demonstrate the procedure how to find Stokes constant. Assuming that $q(z) = z$ in Eqs. (1.53) and (1.54) with the reference point $z_0 = 0$, we have WKB solutions given by

$$(0, z) = z^{\frac{-1}{4}} e^{i\frac{2}{3}z^{3/2}} \tag{1.59}$$

and

$$(z, 0) = z^{\frac{-1}{4}} e^{-i\frac{2}{3}z^{3/2}}. \tag{1.60}$$

A branch cut is shown in Fig.1.2, where three Stokes constants are assigned to three Stokes lines. Considering now a given solution $\phi(z) = A(0, z) + B(z, 0)$ on the anti-Stokes line arg $= 0$, and tracing the solution round positively in the complex plane, we have

$$\begin{aligned}
&1. \quad A(0,z)_s + B(z,0)_d, \\
&2. \quad (A + BU_1)(0,z)_s + B(z,0)_d, \\
&3. \quad (A + BU_1)(0,z)_d + B(z,0)_s, \\
&4. \quad (A + BU_1)(0,z)_d + [B + U_2(A + BU_1)](z,0)_s,
\end{aligned} \tag{1.61}$$

and then negatively,

$$\begin{aligned}
&7. \quad A(0,z)_d + B(z,0)_s, \\
&6. \quad iA(0,z)_d + iB(z,0)_s, \\
&5. \quad iA(0,z)_d + i(B - U_3A)(z,0)_s, \\
&4. \quad iA(0,z)_s + i(B - U_3A)(z,0)_d,
\end{aligned} \tag{1.62}$$

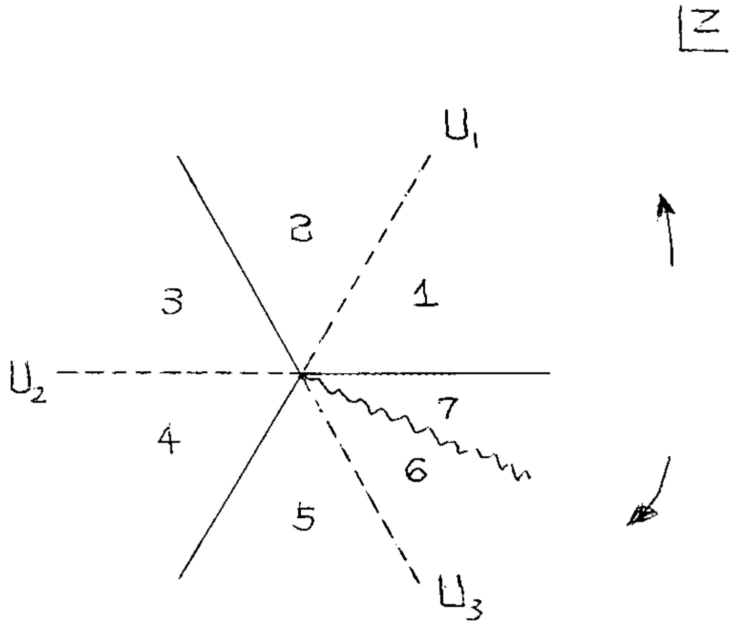



Figure 1.2.

where we have used a rule for the solutions $(0, z)$ and $(z, 0)$ crossing branch cut in negative sense:

$$
\begin{aligned}
(0, z) &\longrightarrow i(0, z), \\
(z, 0) &\longrightarrow i(z, 0).
\end{aligned}
\tag{1.63}
$$

This is because the continuity of the solutions must remain when they cross the branch cut. A another rule is $U_i \to -U_i$ when the solutions cross Stokes lines in negative sense. Comparison of Eq. (1.61) with Eq. (1.62) leads to

$$A + BU_1 = (B - U_3 A)i \tag{1.64}$$

and

$$B + U_2(A + BU_1) = iA. \tag{1.65}$$

Thus, we obtain $U_1 = U_2 = U_3 = i$. The method used above for finding Stokes constants is not possible for general case of $q(z)$ in Eq. (1.3), nevertheless, the procedure can always provide three independent equations for all Stokes constants. This is quite useful for many physical problems, an example of which will be seen in part 2.

A numerical method based on the definition of Stokes constant from Eqs. (1.57) and (1.58) may be designed for the computation of Stokes constant, but it is a question whether the method can produce results with an acceptable accuracy due to the fact that a dominant solution is asymptotically divergent. For the certain simple cases of $q(z)$ some numerical tests were actually tried by Emamzadeh[5]. On the other hand, there are several analytical method used for finding Stokes constants. Heading[4, 6] investigated the cases that for certain polynomials of $q(z)$ the differential equations can solved analytically .But , his method can not be extended to deal with the case when differential equation can not be solved analytically. In this case, Sibuya[7] developed a procedure to obtain connection matrices that connect subdominant solutions in different regions of complex plane. Some formal solutions for Stokes constants were obtained by this method, but not convenient for many physical problems. Hinton[3] introduced a method that transforms differential equations from the complex-$z$ plane to the complex-$\xi$ plane. With help of coupled wave equations method an explicit expression for Stokes constant was obtained. But the method can deal with quite limited cases of $q(z)$. For instance , it can not solve the case of $q(z)$ we encounter in the two-state linear curve crossing problems. A great extension from his method is done in the present thesis, so that the present method can now deal with more general cases of $q(z)$ which frequently appear in many interesting physical problems.

Finally, let us make a further discussion about why discontinuity is allowed in the asymptotic solutions that is originally continuous. Actually, subtracting Eq. (1.57) from Eq. (1.58) gives

$$\epsilon = AU(z, z_0)_s, \tag{1.66}$$

in which $(z, z_0)_s$ obviously approaches to zero for $|z| \to +\infty$ due to its subdominancy. According to the precise definition of asymptotic expansion in mathematics[8], this discontinuity is acceptable. This is because $\epsilon$ can be arbitrarily small by taking $|z|$ sufficiently large. This fact also shows that an exact solution of Stokes constant $U$ can be obtained only by requiring $|z| \to +\infty$ .

# Chapter 2

# Stokes constants

In this chapter we shall derive analytical solutions of the Stokes constants for the four cases discussed in the previous chapter. First, three independent relations for all Stokes constants $U_i$ defined in the complex-$z$ plane are established. these relations are quite useful for obtaining the connection matrix discussed in the next chapter. Second, we shall transform the asymptotic solutions from complex-$z$ plane to the complex-$\xi$ plane where the Stokes constants $T_i$ are defined. One-to-one correspondence between $U_i$ and $T_i$ is simply obtained. Furthermore, the transformation "-" introduced in this chapter shows a link between two asymptotic solutions $u(\xi)$ and $v(\xi)$. This link essentially concludes that all Stokes constants $T_i$ can be simply related to only one of them, for instance, $T_1$. By generalizing the coupled-wave-integral-method devised by Hinton, Stokes constant $T_1$ is finally shown to be expressed in the analytical form of a convergent infinite series as a function of the coefficients $q(z)$ for all four cases.

## 2.1 Relations among the Stokes constants

In this section , we derive relations among the Stokes constants and prove that they can be expressed in terms of one Stokes constant. First, by tracing the standard WKB solutions across the Stokes lines, the anti-Stokes lines, and a branch cut, three independent equations are found among the Stokes constants in the complex-$z$ plane. Next, we establish inter-relations between the two ($z$- and $\xi$-) complex planes. Finally, we shall prove that all the Stokes constants in each case can be given in terms of only one. Since the procedure is easily demonstrated in the cases (iii) and (iv), we start with them.

**A. Case** (iii)

First of all, we need to determine the Stokes lines and anti-Stokes lines in the complex plane. Our focus is in asymptotic region where Stokes constants are exactly defined, so that the anti-Stokes lines are defined by the phase integration of Eq. (1.30), and given as

$$\mathrm{Im}[\frac{\sqrt{a_4}}{3}z^3 + \frac{a_2}{2\sqrt{a_4}}z + \frac{a_1}{2\sqrt{a_4}}\ln(z)] \overset{|z|\to\infty}{\Longrightarrow} \mathrm{Im}[\frac{\sqrt{a_4}}{3}z^3]$$

$$= \mathrm{Im}[\frac{\sqrt{a_4}}{3}r^3(\cos 3\theta + i\sin 3\theta)] = \frac{\sqrt{a_4}}{3}r^3 \sin 3\theta = 0, \tag{2.1}$$

where $z = re^{i\theta}$ is used and $a_4$ is assumed to be positive. Thus, anti-Stokes lines are

$$\theta = \frac{1}{3}k\pi, \quad k = 0, 1, 2, 3, 4, 5. \tag{2.2}$$

And Stokes lines can be found in the same way ,

$$\theta' = \frac{1}{3}k\pi + \frac{1}{6}\pi, \quad k = 0, 1, 2, 3, 4, 5. \tag{2.3}$$

As are shown in Fig.2.1(a).

Next, let us determine a rule for governing WKB solutions across the branch cut. Assume that the branch cut is inserted at $\arg z = \delta$, and if $z = re^{i\delta}$ just before the cut, then

$$(\bullet, z) = (\bullet, z)|_{z=re^{i\delta}}, \tag{2.4}$$

but just after the cut we must have $z = re^{i\delta - 2\pi i}$, so that we have

$$(\bullet, z) = (\bullet, z)|_{z=re^{i\delta-2\pi i}}$$

$$= e^{\frac{a_1}{\sqrt{a_4}}\pi}(\bullet, z)|_{z=re^{i\delta}}. \tag{2.5}$$

In order to maintain the continuity of the standard WKB solutions on crossing the branch cut , we have

$$(\bullet, z) \longrightarrow e^{-6\pi i Q_1}(\bullet, z), \tag{2.6}$$

and the similar discussion gives

$$(z, \bullet) \longrightarrow e^{6\pi i Q_1}(z, \bullet), \tag{2.7}$$

where we have $Q_1 = -\frac{ia_1}{6\sqrt{a_4}}$. The rule given above is for positive (anti-clockwise) crossing. For negative (i.e. clockwise) crossing, it can be easily proved that the sign of the exponents should be changed.

Now, we start with a given solution $A(\bullet, z) + B(z, \bullet)$ on the anti-Stokes line $\arg z = 0$ in region of Fig.2.1(a), here $A$ and $B$ are arbitrary constants. if we trace this solution in a positive sense, then we obtain

1. $A(\bullet, z)_s + B(z, \bullet)_d,$

2. $(A + BU_1)(\bullet, z)_s + B(z, \bullet)_d,$

3. $(A + BU_1)(\bullet, z)_d + B(z, \bullet)_s,$

4. $(A + BU_1)(\bullet, z)_d + [B + (A + BU_1)U_2](z, \bullet)_s,$

5. $(A + BU_1)(\bullet, z)_s + [B + (A + BU_1)U_2](z, \bullet)_d,$

6. $\{(A + BU_1) + [B + (A + BU_1)U_2]U_3\}(\bullet, z)_s$

$$+ [B + (A + BU_1)U_2](z, \bullet)_d, \qquad (2.8)$$

and if we go round negatively we have

13. $A(\bullet, z)_d + B(z, \bullet)_s,$

12. $Ae^{6\pi i Q_1}(\bullet, z)_d + Be^{-6\pi i Q_1}(z, \bullet)_s,$

11. $Ae^{6\pi i Q_1}(\bullet, z)_d + (Be^{-6\pi i Q_1} - U_6 A e^{6\pi i Q_1})(z, \bullet)_s,$

10. $Ae^{6\pi i Q_1}(\bullet, z)_s + (Be^{-6\pi i Q_1} - U_6 A e^{6\pi i Q_1})(z, \bullet)_d,$

9. $[Ae^{6\pi i Q_1} - (Be^{-6\pi i Q_1} - U_6 A e^{6\pi i Q_1})\, U_5](\bullet, z)_s + (Be^{-6\pi i Q_1} - U_6 A e^{6\pi i Q_1})(z, \bullet)_d,$

8. $[Ae^{6\pi i Q_1} - (Be^{-6\pi i Q_1} - U_6 A e^{6\pi i Q_1})\, U_5](\bullet, z)_d + (Be^{-6\pi i Q_1} - U_6 A e^{6\pi i Q_1})(z, \bullet)_s,$

7. $[Ae^{6\pi i Q_1} - (Be^{-6\pi i Q_1} - U_6 A e^{6\pi i Q_1})\, U_5](\bullet, z)_d + \{(Be^{-6\pi i Q_1} - U_6 A e^{6\pi i Q_1})$

$$- U_4[Ae^{6\pi i Q_1} - (Be^{-6\pi i Q_1} - U_6 A e^{6\pi i Q_1})U_5]\}(z, \bullet)_s. \qquad (2.9)$$

One-valuedness of the solution, as was discussed in the section 1.3, leads to the following equations:

$$(1 + U_2U_3) = (1 + U_5U_6)e^{6\pi i Q_1},$$

$$(1+U_1U_2) = (1+U_4U_5)e^{-6\pi i Q_1},$$
$$U_1+U_3+U_1U_2U_3 = -U_5e^{-6\pi i Q_1},$$
$$U_4+U_6+U_4U_5U_6 = -U_2e^{-6\pi i Q_1}, \tag{2.10}$$

among which three of them are independent.

Now let us consider the Stokes constants denoted as $T_j (j = 1-6)$ in the complex $\xi$-plane based on solutions $u(\xi; Q_0, Q_1, Q_2)$ and $v(\xi; Q_0, Q_1, Q_2)$ of Eqs. (1.39) and (1.40). If we start with the function $v(\xi; Q_0, Q_1, Q_2)$ of Eq. (1.40) in region 1 of Fig.2.1(b), which corresponds to $A = 0$ in Eq. (2.8), then $\psi(\xi)$ in the region $\pi/2 < \arg\xi < 2\pi$ can be easily found to be given by

$$\psi(\xi) \sim v(\xi; Q_0, Q_1, Q_2) + T_1\Theta_1(\xi)u(\xi; Q_0, Q_1, Q_2), \quad \text{for } \pi/2 < \arg\xi < 2\pi, \tag{2.11}$$

where $\Theta_1(\xi)$ is a step function defined as

$$\Theta_n(\xi) = \begin{cases} 0, & \arg\xi \le n\pi, \\ 1, & \arg\xi \ge n\pi, \quad \text{for } n = 1, 2, \cdots. \end{cases} \tag{2.12}$$

Here $c_0^{(1)} = c_0^{(2)}$ is assumed in Eqs. (1.39) and (1.40). Repeating this procedure, we obtain

$$\psi(\xi) \sim (1 + T_1T_2\Theta_2(\xi))v + T_1\Theta_1(\xi)u, \quad \text{for } \pi/2 < \arg\xi < 3\pi, \tag{2.13}$$

and, finally,

$$\begin{aligned} \psi(\xi) \sim \{1 + T_1T_2\Theta_2 + [T_1 + (1+T_1T_2)T_3]T_4\Theta_4 + \{T_1 + (1+T_1T_2)T_3 + \\ [1 + T_1T_2 + (T_1 + (1+T_1T_2)T_3)T_4]T_5\}\Theta_6T_6\}v + \\ \{T_1\Theta_1 + (1+T_1T_2)\Theta_3T_3 + \\ [1 + T_1T_2 + (T_1 + (1+T_1T_2)T_3)T_4]\Theta_5T_5\}u, \quad \text{for } \pi/2 < \arg\xi < 7\pi. \end{aligned} \tag{2.14}$$

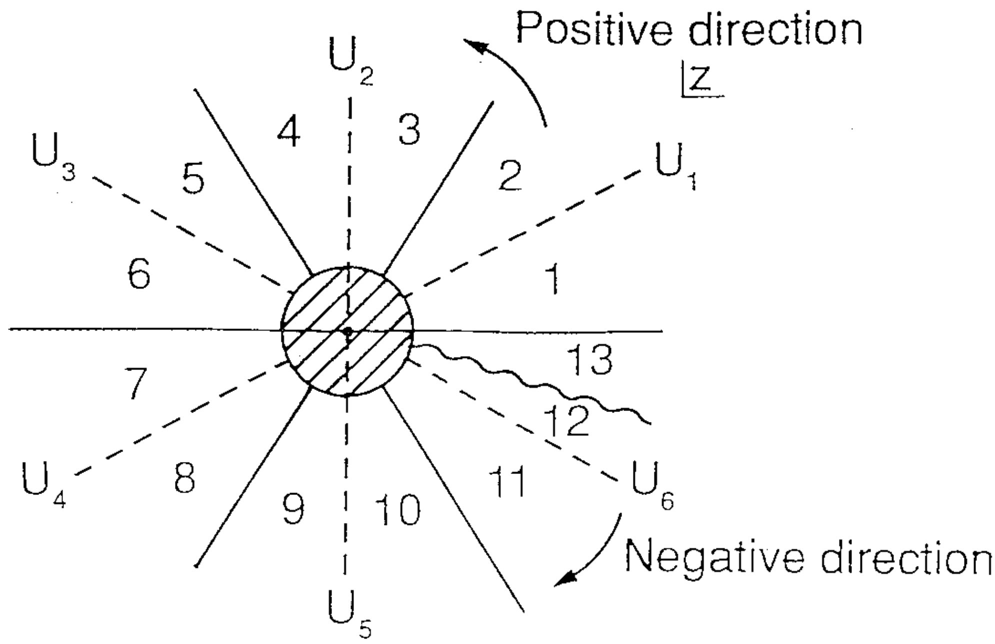
From Eqs. (1.31),(1.32),(1.41), and (1.42) we can easily prove

$$(\bullet, \xi) = [2i\sqrt{a_4}/3]^{-Q_1} z(\bullet, z) \tag{2.15}$$

and

$$(\xi, \bullet) = [2i\sqrt{a_4}/3]^{-Q_1} z(z, \bullet). \tag{2.16}$$

a)




b)

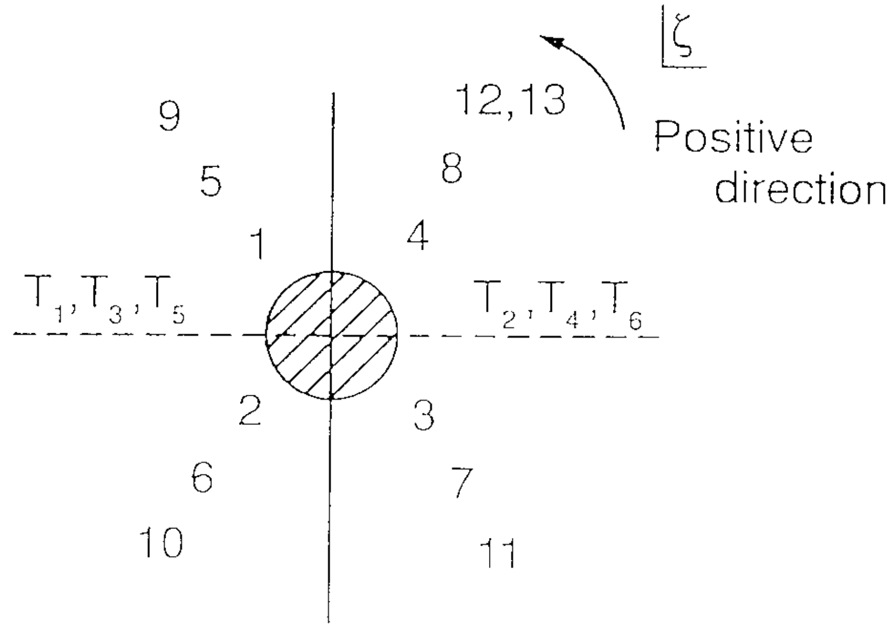



Figure 2.1: Stokes lines and anti-Stokes lines in the asymptotic region in the case (iii), in which $\arg \xi = 3 \arg z + \pi/2$.

Substitution of this equation into Eqs. (2.11) and (2.13) leads to

$$\phi(z) = z^{-1}\psi(\xi) \sim [2i\sqrt{a_4}/3]^{Q_1}\{(z,\bullet) + T_1(2i\sqrt{a_4}/3)^{-2Q_1}\Theta_1(\xi)(\bullet, z)\},$$

$$\text{for} \quad 0 < \arg z < \pi/2 \tag{2.17}$$

and

$$\phi(z) = z^{-1}\psi(\xi) \sim [2i\sqrt{a_4}/3]^{Q_1}\{(1 + T_1T_2\Theta_2(\xi))(z,\bullet)+$$

$$T_1(2i\sqrt{a_4}/3)^{-2Q_1}\Theta_1(\xi)(\bullet, z)\}, \quad \text{for } 0 < \arg z < 5\pi/6, \tag{2.18}$$

where the power series with respect to $\xi^{-1}$ in Eqs. (1.39) and (1.40) are neglected for simplicity. Comparing Eqs.(2.17) and (2.18) with Eq. (2.8) for $A = 0$ and $B = [2i\sqrt{a_4}/3]^{Q_1}$, we find

$$U_1 = T_1[2i\sqrt{a_4}/3]^{-2Q_1} \tag{2.19}$$

and

$$U_2 = T_2[2i\sqrt{a_4}/3]^{2Q_1}. \tag{2.20}$$

Similarly, we obtain

$$U_3 = T_3[2i\sqrt{a_4}/3]^{-2Q_1}, U_5 = T_5[2i\sqrt{a_4}/3]^{-2Q_1},$$

$$U_4 = T_4[2i\sqrt{a_4}/3]^{2Q_1}, \text{ and, } U_6 = T_6[2i\sqrt{a_4}/3]^{2Q_1}. \tag{2.21}$$

Simple one-to-one relations between Stokes constants $U_i$ in the $z$-plane and $T_i$ in the $\xi$-plane have been set up.

Finally, we drive inter-relations among the Stokes constants $T_i$ which enable us to express all Stokes constants in terms of one . First of all, we define a symbol "-" to indicate a transformation,

$$\begin{aligned} \xi &\longrightarrow \xi e^{-i\pi}, \\ Q_0 &\longrightarrow \omega^2 Q_0, \\ Q_1 &\longrightarrow \omega^3 Q_1, \\ Q_2 &\longrightarrow \omega^4 Q_2, \end{aligned} \tag{2.22}$$

with $\omega = e^{-i\pi/3}$. It is easily seen that $Q(\xi)$ in Eq. (1.33) is unchanged under this transformation, so that the differential equation (1.6) is invariant. Actually, this invariance ultimately leads to the inter-relations among six Stokes constants. Next, let us employ this transformation to the two independent solutions in Eqs. (1.39) and (1.40), and take $u$ as an example, we have

$$\begin{aligned}\overline{u} &\equiv u(\xi e^{-i\pi}; Q_0\omega^2, Q_1\omega^3, Q_2\omega^4) \\ &= \overline{(\bullet, \xi)} \sum_{n=0}^{\infty} \overline{c}_n^{(1)} e^{in\pi/3} \xi^{-n/3},\end{aligned} \tag{2.23}$$

where

$$\overline{(\bullet, \xi)} = e^{-i\pi Q_1} (\bullet, \xi). \tag{2.24}$$

With further effort by using the recurrence relations for the $c_n^{(1)}$ and $c_n^{(2)}$, we can prove

$$\overline{c}_n^{(1)} = c_n^2 \omega^n, \tag{2.25}$$

hence we obtain

$$\begin{aligned}\overline{u} &= e^{-i\pi Q_1} v(\xi; Q_0, Q_1, Q_2) \\ &= e^{-i\pi Q_1} v,\end{aligned} \tag{2.26}$$

and in the same way we have

$$\begin{aligned}\overline{v} &\equiv v(\xi e^{-i\pi}; Q_0\omega^2, Q_1\omega^3, Q_2\omega^4) \\ &= e^{i\pi Q_1} u(\xi; Q_0, Q_1, Q_2).\end{aligned} \tag{2.27}$$

Now, we start to trace the solution $v$ from region 1 to region 5 in Fig.2.1(b) by using two interchangeable ways as explained below. One way is that we first trace $v$ to region 5 where we obtain Eq. (2.13), and then take the transformation of Eq. (2.22) to Eq. (2.13), we have

$$\begin{aligned}\overline{\psi}(\xi) &\sim (1 + \overline{T}_1 \overline{T}_2 \Theta_2(\xi e^{-i\pi}))\overline{v} + \overline{T}_1 \Theta_1(\xi e^{-i\pi})\overline{u} \\ &= \overline{T}_1 \Theta_2(\xi) e^{-i\pi Q_1} v + e^{i\pi Q_1} u, \quad \text{for } \pi/2 < \arg\xi < 3\pi,\end{aligned} \tag{2.28}$$

where $\overline{T}_j \equiv T_j(Q_0\omega^2,\ Q_1\omega^3, Q_2\omega^4)$. It should be noted here that $\Theta_2(\xi e^{-i\pi}) = 0$ and $\Theta_1(\xi e^{-i\pi}) = \Theta_2(\xi)$, because $\pi/2 < \arg\xi < 3\pi$. Another way is that we first take the transformation of Eq. (2.22) to v, then we have

$$\overline{\psi}(\xi) \sim e^{i\pi Q_1} u(\xi; Q_0, Q_1, Q_2), \quad \text{for } \pi/2 < \arg\xi < \pi, \tag{2.29}$$

and now we trace this solution to region 5 , we obtain

$$\overline{\psi}(\xi) \sim e^{i\pi Q_1}(u + T_2\Theta_2(\xi)v), \quad \text{for } \pi/2 < \arg\xi < 3\pi. \tag{2.30}$$

Comparing this with Eq. (2.28), we find

$$T_2 = \overline{T}_1 e^{-2i\pi Q_1}. \tag{2.31}$$

Repeating the same procedure, we can prove

$$T_3 = \overline{T}_2 e^{2i\pi Q_1}, T_4 = \overline{T}_3 e^{-2i\pi Q_1},$$

$$T_5 = \overline{T}_4 e^{2i\pi Q_1}, \text{ and } T_6 = \overline{T}_5 e^{-2i\pi Q_1}. \tag{2.32}$$

**B. Case** (iv)

In this case, there are five Stokes constants associated with five Stokes lines in the asymptotic region of $z$, as is shown in Fig.2.2. The coefficient $a_3$ is again assumed to be positive. Since we follow the same procedure as in the previous case (iii), only the results are given below.

First, three independent equations for the five Stokes constants in the complex $z$-plane are

$$1 + U_3U_4 = iU_1, \quad 1 + U_4U_5 = iU_2, \quad \text{and} \quad 1 + U_1U_2 = iU_4. \tag{2.33}$$

Secondly, the relations between $U_i$ and $T_i$ are

$$U_i = T_i, \qquad i = 1 \sim 5. \tag{2.34}$$

But, the rule for the solutions to cross branch cut now becomes

$$\begin{aligned} (\bullet, z) &\longrightarrow e^{-i3\pi/2}(z, \bullet), \\ (z, \bullet) &\longrightarrow e^{-i3\pi/2}(\bullet, z), \end{aligned} \tag{2.35}$$

in the positive sense, this is because $Q_1 = 0$ in this case.

The "-" transformation in this case is given by

$$\begin{aligned} \xi &\longrightarrow \xi e^{-i\pi}, \\ Q_0 &\longrightarrow \omega^4 Q_0, \\ Q_2 &\longrightarrow \omega^6 Q_2, \end{aligned} \tag{2.36}$$

with $\omega = e^{-i\pi/5}$. We can prove that under this transformation the solutions in Eqs. (1.49) and (1.50) satisfy

$$\overline{u} \equiv u(\xi e^{-i\pi}; Q_0\omega^4, Q_2\omega^6)$$

$$= v(\xi; Q_0, Q_2) \tag{2.37}$$

and

$$\overline{v} = u(\xi; Q_0, Q_2). \tag{2.38}$$

Thus, we finally obtain

$$\overline{T}_i = T_{i+1}(Q_0, Q_2), \quad i = 1 \sim 4, \tag{2.39}$$

where $\overline{T}_i = T_i\ (\omega^4 Q_0, \omega^6 Q_2)$.

**C. Case** (i)

There are $2N+2$ Stokes constants associated with $2N+2$ Stokes lines, as is shown in Fig.2.3. Three independent equations among the $2N+2$ Stokes constants can always be derived from the one-valuedness of asymptotic solution. Explicit expressions can be obtained when $N$ is specified. Again, we can employ the same procedure as in the case(iii). As a result, relations between $U_i$ and $T_i$ are

$$U_1 = T_1[2i\sqrt{a_{2N}}/3]^{-2Q_1}, U_2 = T_2[2i\sqrt{a_{2N}}/3]^{2Q_1},$$

$$U_3 = T_3[2i\sqrt{a_{2N}}/3]^{-2Q_1}, U_4 = T_4[2i\sqrt{a_{2N}}/3]^{2Q_1},$$

$$\vdots$$

$$U_{2N+1} = T_{2N+1}[2i\sqrt{a_{2N}}/3]^{-2Q_1}, U_{2N+2} = T_{2N+2}[2i\sqrt{a_{2N}}/3]^{2Q_1}. \tag{2.40}$$

The transformation "-" is

$$\begin{aligned} \xi &\longrightarrow \xi e^{-i\pi}, \\ Q_1 &\longrightarrow \omega^{N+1} Q_1, \\ Q_2 &\longrightarrow \omega^{N+2} Q_2, \\ &\vdots \end{aligned} \tag{2.41}$$

with $\omega = e^{-i\pi/(N+1)}$. The final relations among the $2N+2$ Stokes constants $T_j$ are obtained as

$$T_2 = \overline{T}_1 e^{-2i\pi Q_1},$$

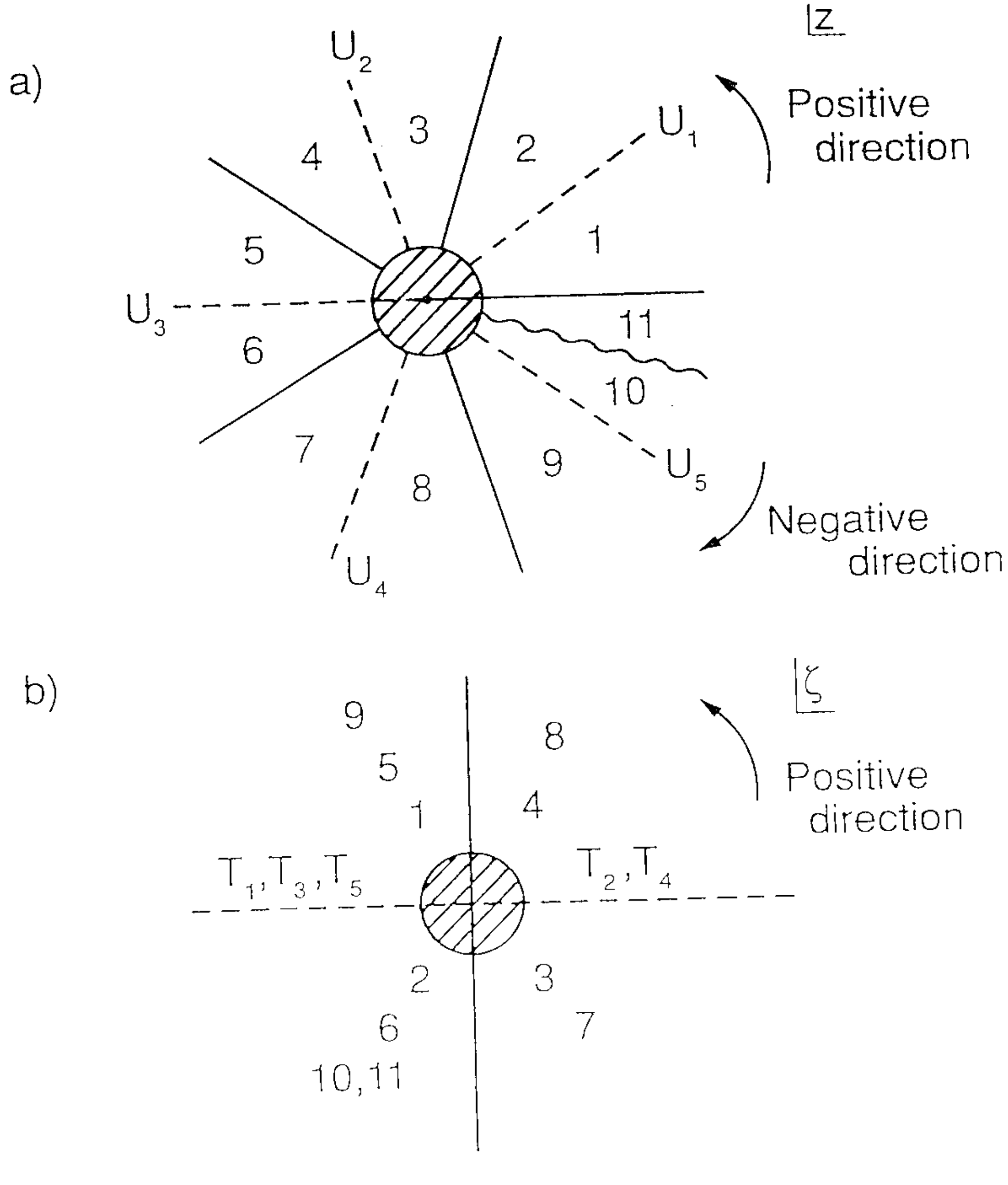



Figure 2.2: Stokes lines and anti-Stokes lines in the asymptotic region in the case (iv), in which $\arg \xi = \frac{5}{2} \arg z + \pi/2$.

$$T_3 = \overline{T}_2 e^{2i\pi Q_1}, T_4 = \overline{T}_3 e^{-2i\pi Q_1},$$

$$T_5 = \overline{T}_4 e^{2i\pi Q_1}, T_6 = \overline{T}_5 e^{-2i\pi Q_1},$$

•

•

•

$$T_{2N+1} = \overline{T}_{2N} e^{2i\pi Q_1}, T_{2N+2} = \overline{T}_{2N+1} e^{-2i\pi Q_1}, \tag{2.42}$$

where $\overline{T}_i = T_i\ (\omega^{N+1}Q_1, \omega^{N+2}Q_2, \cdots)$.

**D. Case** (ii)

In this case, by using the same procedure as in the case (iv) we obtain the following results:

$$U_i = T_i, \quad \text{for} \quad i = 1, 2, \cdots, 2N+1 \tag{2.43}$$

and

$$\overline{T}_i = T_{i+1}(Q_1, Q_2, \cdots), \quad i = 1, 2, \cdots, 2N. \tag{2.44}$$

The "-" transformation is defined as

$$\begin{aligned} \xi &\longrightarrow \xi e^{-i\pi}, \\ Q_1 &\longrightarrow \omega^{2(N+1)}Q_1, \\ Q_2 &\longrightarrow \omega^{2(N+2)}Q_2, \\ Q_3 &\longrightarrow \omega^{2(N+3)}Q_2, \end{aligned} \tag{2.45}$$

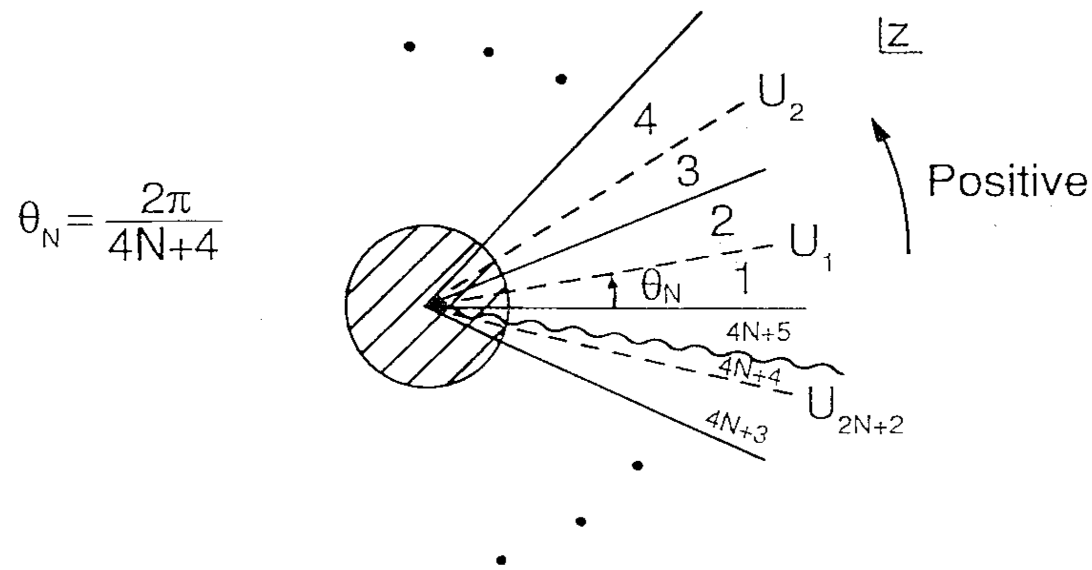
•

•

•

where $\omega = e^{-i\pi/(2N+1)}$, and $\overline{T}_i = T_i\ (\omega^{2(N+1)}Q_1, \omega^{2(N+2)}Q_2, \cdots)$. The Stokes lines and the anti-Stokes lines are shown in Fig.2.4.

In summary, the Stokes phenomena for the four cases of second-order differential equations have been analyzed here. First, one-to-one correspondence has been established between Stokes constants $U_i$ and $T_i$ in the two complex planes. Then, the transformation "-", under which the differential equation (1.6) is invariant leads to the simple rules which express all Stokes constants $T_i$ in terms of only one , for instance, $T_1$. In conclusion, the procedure here used can be extended to deal with a)




b)

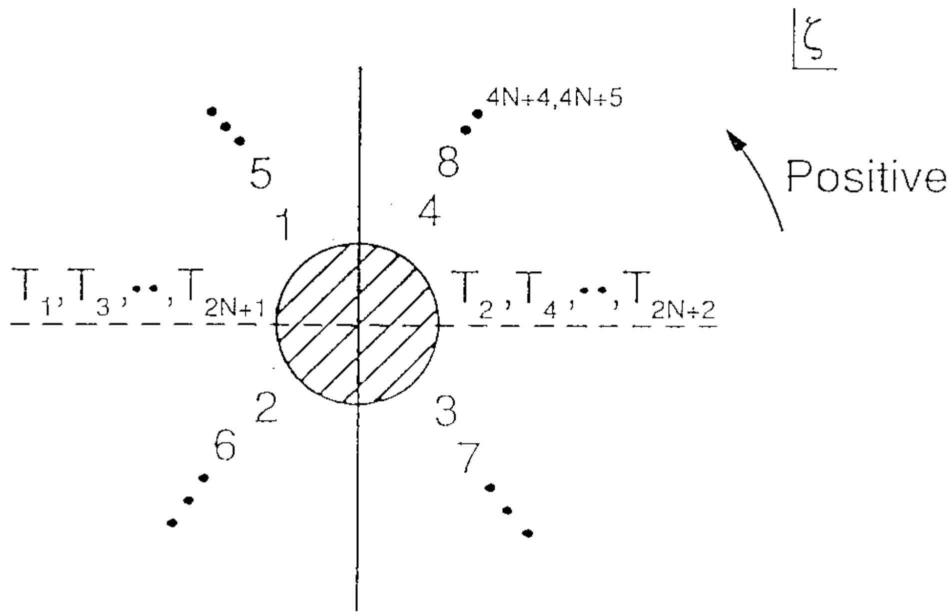



Figure 2.3: Stokes lines and anti-Stokes lines in the asymptotic region in the case (i), in which $\arg \xi = (N+1) \arg z + \pi/2$.

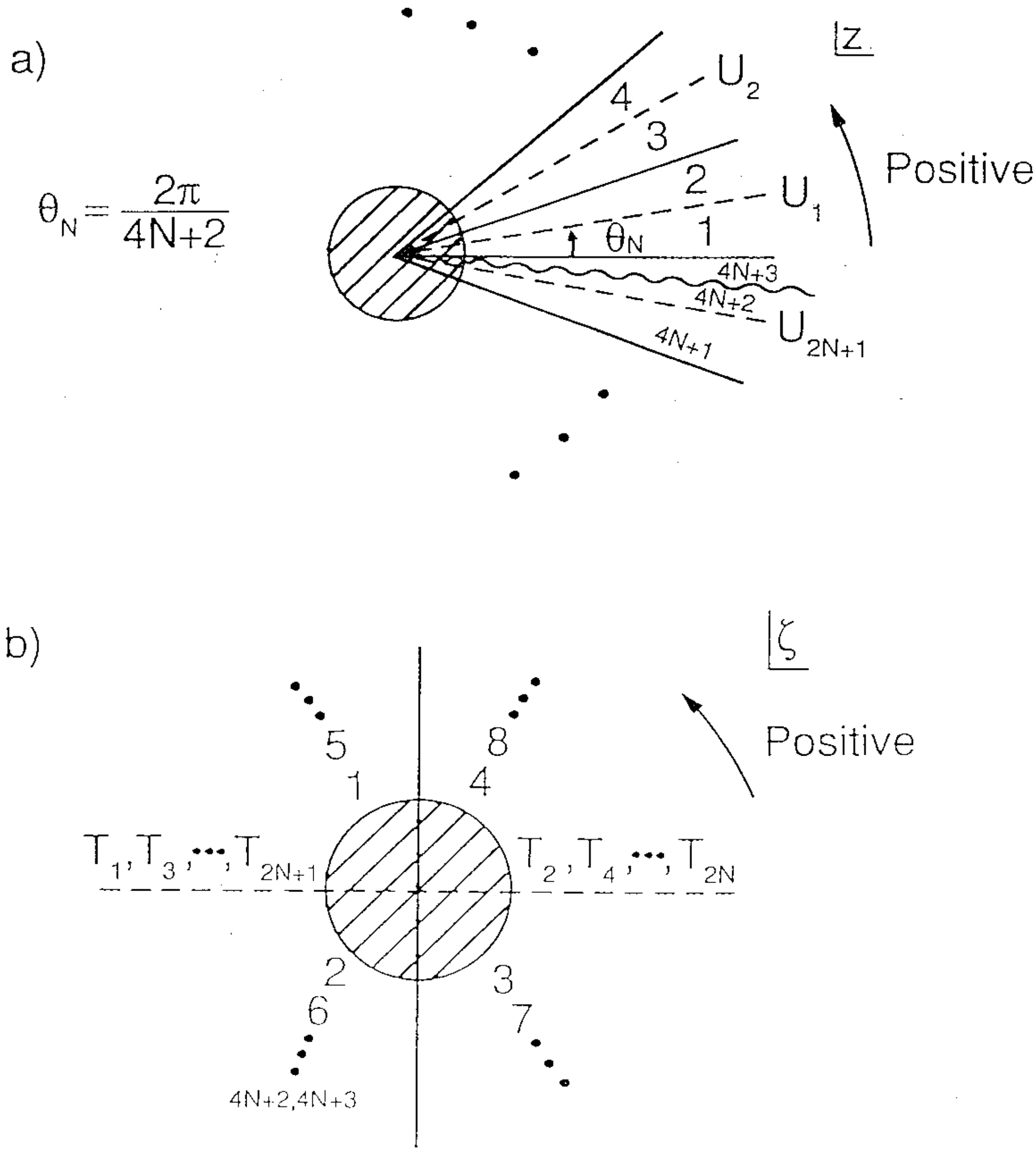



Figure 2.4: Stokes lines and anti-Stokes lines in the asymptotic region in the case (ii), in which $\arg\xi = (N+1/2)\arg z + \pi/2$.

the most general case of Eq. (1.3), relations among Stokes constants will be formally the same as in the case (i) or case (ii). What we need to do is just to redefine the transformation "-" which remains invariant to $Q(\xi)$ in the general case of Eq. (1.3).

## 2.2 Explicit expressions of the Stokes constants $T_1$

In this section, extending the method of Hinton[2], we derive explicit expressions of the Stokes constants $T_1$ for all four cases in the form of convergent infinite series. First, let us write the solution of Eq. (1.6) as a product of two functions,

$$\psi(\xi) = X(\xi)U(\xi), \tag{2.46}$$

where $X(\xi)$ is required to be a solution of

$$\frac{d^2X}{d\xi^2} + [Q(\xi) + \mu^2(\xi)]X = 0, \tag{2.47}$$

and $\mu^2$ must be chosen for Eq.(2.47) to have a regular singular point at $\xi = \infty$. The wave function $\psi$ is searched in the form,

$$\psi(\xi) = \mu(\xi)^{-1/2}\{A_1(\xi)\exp[\int \mu(\xi)d\xi] + A_2(\xi)\exp[-\int \mu(\xi)d\xi]\}, \tag{2.48}$$

where $A_1(\xi)$ and $A_2(\xi)$ satisfy coupled equations ( Eqs. (2.50) and (2.51) below). For our purpose to determine the Stokes constants $T_1$, we can assume that $\psi$ is subdominant on the Stokes line $\arg\xi = 0$. This means

$$A_1(\xi) \longrightarrow 0 \text{ and } A_2(\xi) \longrightarrow 1 \quad \text{for } \xi \to +\infty. \tag{2.49}$$

Coupled integral equations satisfied by $A_1(\xi)$ and $A_2(\xi)$ are obtained as

$$A_1(\zeta) = \int_{+\infty}^{\zeta} d\xi B(\xi)\exp[-2\int \mu(\xi)d\xi]A_2(\xi) \tag{2.50}$$

and

$$A_2(\zeta) = 1 + \int_{+\infty}^{\zeta} d\xi B(\xi)\exp[2\int \mu(\xi)d\xi]A_1(\xi), \tag{2.51}$$

where

$$B(\xi) = \frac{1}{2}\frac{\mu'}{\mu} + \frac{X'}{X}. \tag{2.52}$$

It should be noted that the formulas given above are exact and merely reformulate the original problem of solving Eq. (1.6). For later convenience, we introduce here the following two complementary expressions of the incomplete Gamma functions and its asymptotic expansion:

$$\Gamma(\beta,\zeta) = -\int_{+\infty}^{\zeta} d\xi \xi^{\beta-1} e^{-\xi}, \tag{2.53}$$

$$\int_{-\infty}^{\zeta} d\xi \xi^{\beta-1} e^{\xi} = e^{\pi i(\beta-1)} \Gamma(\beta, \zeta e^{-i\pi}), \tag{2.54}$$

and

$$\begin{aligned} e^{\zeta}\Gamma(\beta,\zeta) \quad &\sim \quad \sum_{m=0}^{\infty} (-1)^m \frac{\Gamma(1-\beta+m)}{\Gamma(1-\beta)} \zeta^{-m+\beta-1} \\ &+ \frac{2\pi i \Theta_1(\zeta)}{\Gamma(1-\beta)} e^{i\pi(\beta-1)} e^{\zeta}, \quad \text{for} \quad -\pi < \arg\zeta < 2\pi, \end{aligned} \tag{2.55}$$

where $\Theta_1$ is the step function defined in the previous section.

**A. Case(i)**

In order to obtain a solution of Eq. (2.47) which has a regular singular point at $\xi = \infty$, we choose $\mu$ as

$$\mu(\xi) = \frac{1}{2} - \sum_{n=1}^{N+1} Q_n \xi^{-\frac{N+n}{N+1}}, \tag{2.56}$$

namely,

$$\int \mu(\xi) d\xi = \frac{1}{2}\xi - Q_1 \ln \xi + \sum_{n=1}^{N} Q_{n+1} \frac{N+1}{n} \xi^{-\frac{n}{N+1}}. \tag{2.57}$$

This choice is another generalization from the Hinton's method. This $\mu(\xi)$ is substituted into Eqs. (2.50) and (2.51), and $B(\xi)$ is combined with third term of Eq. (2.57) to give

$$\begin{aligned} B_1(\xi) &= B(\xi) \exp[-2 \sum_{n=1}^{N} Q_{n+1} \frac{N+1}{n} \xi^{-\frac{n}{N+1}}] \\ &= \sum_{n=1}^{\infty} B_n^{(1)} \xi^{-\frac{N+n}{N+1}} \end{aligned} \tag{2.58}$$

and

$$\begin{aligned} B_2(\xi) &= B(\xi) \exp[2 \sum_{n=1}^{N} Q_{n+1} \frac{N+1}{n} \xi^{-\frac{n}{N+1}}] \\ &= \sum_{n=1}^{\infty} B_n^{(2)} \xi^{-\frac{N+n}{N+1}}, \end{aligned} \tag{2.59}$$

where $B(\xi)$ is calculated from Eq. (2.52). The power series expansion of $B(\xi)$ and explicit expressions of $B_n^{(1)}$ and $B_n^{(2)}$ are in Appendix A. The coupled integral equations are thus given by

$$A_1(\zeta) = \int_{+\infty}^{\zeta} d\xi B_1(\xi) \xi^{\nu} e^{-\xi} A_2(\xi) \tag{2.60}$$

and

$$A_2(\zeta) = 1 + \int_{+\infty}^{\zeta} d\xi B_2(\xi) \xi^{-\nu} e^{\xi} A_1(\xi), \tag{2.61}$$

with $\nu = 2Q_1$.

Now , we shall look for asymptotic solutions of Eqs. (2.60) and (2.61) for $-\pi < \arg \xi < 2\pi$ in the form,

$$A_1(\xi) = \xi^{\nu} e^{-\xi} \sum_{n=1}^{\infty} \alpha_n^{(1)} \xi^{-n/(N+1)} + T_1 \Theta_1(\xi) \sum_{n=0}^{\infty} \beta_n^{(2)} \xi^{-n/(N+1)}, \tag{2.62}$$

and,

$$A_2(\xi) = \sum_{n=0}^{\infty} \beta_n^{(1)} \xi^{-n/(N+1)} + T_1 \Theta_1(\xi) \xi^{-\nu} e^{\xi} \sum_{n=1}^{\infty} \alpha_n^{(2)} \xi^{-n/(N+1)}, \tag{2.63}$$

where $\beta_0^{(1)} = \beta_0^{(2)} = 1$. The other coefficients $\alpha_n^{(1)}$, $\beta_n^{(1)}$, $\alpha_n^{(2)}$, and, $\beta_n^{(2)}$, and the Stokes constant $T_1$ on $\arg \xi = \pi$ are to be determined.

Following Hinton, we introduce the quantity

$$I_{11}(\zeta) \equiv \int_{+\infty}^{\zeta} B_1(\xi) \xi^{\nu} e^{-\xi} \sum_{n=0}^{\infty} \beta_n^{(1)} \xi^{-n/(N+1)}, \tag{2.64}$$

which corresponds to the first term of Eq. (2.60) with $A_2(\xi)$ replaced by Eq. (2.63). Using Eq. (2.58) and the asymptotic expansion Eq. (2.55) of the incomplete Gamma function of Eq. (2.53), we obtain

$$\begin{aligned} I_{11}(\zeta) &= \sum_{s=0}^{\infty} [\sum_{n+m=s} B_{m+1}^{(1)} \beta_n^{(1)}] \int_{+\infty}^{\zeta} d\xi \xi^{\nu - \frac{N+s+1}{N+1}} e^{-\xi} \\ &= \zeta^{\nu} e^{-\zeta} \sum_{n=0}^{\infty} \{ \sum_{s=0}^{n} ( \sum_{p+q=s} B_{p+1}^{(1)} \beta_q^{(1)} ) (-1)^{\frac{n-s}{N+1}+1} \\ &\times \frac{\Gamma(-\nu + \frac{N+n+1}{N+1})}{\Gamma(-\nu + \frac{N+s+1}{N+1})} \gamma(\frac{n-s}{N+1}) \} \zeta^{-\frac{N+n+1}{N+1}} \\ &+ \sum_{s=0}^{\infty} ( \sum_{p+q=s} B_{p+1}^{(1)} \beta_q^{(1)} ) \frac{-2\pi i \Theta_1(\zeta)}{\Gamma(-\nu + \frac{N+s+1}{N+1})} e^{i\pi(\nu - \frac{N+s+1}{N+1})}, \end{aligned} \tag{2.65}$$

where $\gamma(X)$ is defined as

$$\gamma(X) = \begin{cases} 1, & X = 0, 1, 2 \cdots, \\ 0, & \text{otherwise}. \end{cases} \tag{2.66}$$

It should be noted that the second term of Eq. (2.65) is dependent on the variable $\zeta$ only through the step function $\Theta_1$. Next, let us consider the quantity

$$I_{12}(\zeta) \equiv \int_{+\infty}^{\zeta} B_1(\xi)\xi^{\nu} e^{-\xi}[T_1\Theta_1(\xi)\xi^{-\nu}e^{\xi}\sum_{n=0}^{\infty}\alpha_n^{(2)}\xi^{-n/(N+1)}], \tag{2.67}$$

which corresponds to the second term of Eq.(2.60) with $A_2(\xi)$ replaced by Eq. (2.63). This can be calculated straightforwardly to result in

$$I_{12}(\zeta) = -T_1\Theta_1(\zeta)\sum_{s=0}^{\infty}(\sum_{p+q=s} B_{p+1}^{(1)}\alpha_{q+1}^{(2)})\frac{N+1}{s+1}\zeta^{-\frac{s+1}{N+1}}. \tag{2.68}$$

Comparing the sum of Eqs. (2.65) and (2.68) with Eq. (2.62), we obtain

$$\begin{aligned}
\alpha_1^{(1)} &= \alpha_2^{(1)} = \cdots = \alpha_N^{(1)} = 0, \\
\alpha_{n+N+1}^{(1)} &= \sum_{s=0}^{n}(\sum_{p+q=s} B_{p+1}^{(1)}\beta_q^{(1)})(-1)^{\frac{n-s}{N+1}+1}\frac{\Gamma(-\nu+\frac{N+n+1}{N+1})}{\Gamma(-\nu+\frac{N+s+1}{N+1})} \\
&\times \gamma(\frac{n-s}{N+1}), \quad \text{for } n \geq 0,
\end{aligned} \tag{2.69}$$

$$\beta_n^{(2)} = -\frac{N+1}{n}\sum_{p+q=n-1} B_{p+1}^{(1)}\alpha_{q+1}^{(2)}, \quad \text{for } n \geq 1, \tag{2.70}$$

and

$$T_1 = -2\pi i e^{i\pi\nu}\sum_{n=0}^{\infty}(\sum_{p+q=n} B_{p+1}^{(1)}\beta_q^{(1)})\frac{e^{-i\pi(\frac{N+n+1}{N+1})}}{\Gamma(-\nu+\frac{N+n+1}{N+1})}. \tag{2.71}$$

In the same way, substituting Eq. (2.62) into Eq. (2.61) and using Eqs. (2.54) and (2.55) , we obtain

$$\begin{aligned}
&\int_{+\infty}^{\zeta} d\xi B_2(\xi)\xi^{-\nu}e^{\xi}A_1(\xi) \\
&= -\sum_{s=0}^{\infty}\frac{N+1}{s+1}(\sum_{p+q=s} B_{p+1}^{(2)}\alpha_{q+1}^{(1)})\zeta^{-\frac{s+1}{N+1}} \\
&+ T_1\Theta_1(\zeta)\zeta^{-\nu}e^{\zeta}\sum_{s=0}^{\infty}[\sum_{p+q=s} B_{p+1}^{(2)}\beta_q^{(2)}] \\
&\times \sum_{m=0}^{\infty}\frac{\Gamma(\nu+\frac{N+s+1}{N+1}+m)}{\Gamma(\nu+\frac{N+s+1}{N+1})}\zeta^{-m-\frac{N+s+1}{N+1}}.
\end{aligned} \tag{2.72}$$

Comparison with Eq. (2.63) leads to

$$\beta_n^{(1)} = -\frac{N+1}{n}\sum_{p+q=n-1} B_{p+1}^{(2)}\alpha_{q+1}^{(1)}, \quad \text{for } n \geq 1, \tag{2.73}$$

$$\alpha_1^{(2)} = \alpha_2^{(2)} = \cdots = \alpha_N^{(2)} = 0,$$

and,

$$\alpha_{n+N+1}^{(2)} = \sum_{s=0}^{n}(\sum_{p+q=s} B_{p+1}^{(2)}\beta_q^{(2)})\gamma(\frac{n-s}{N+1})\frac{\Gamma(\nu+\frac{N+n+1}{N+1})}{\Gamma(\nu+\frac{N+s+1}{N+1})},$$

$$\text{for} \quad n \geq 0. \tag{2.74}$$

We have thus obtained recurrence relations for the determination of the coefficients in Eqs. (2.62) and (2.63), and an explicit analytical expression for the Stokes constant $T_1$. Only two coefficients $\alpha_n^{(1)}$ and $\beta_n^{(1)}$ in Eqs. (2.69) and (2.73) are required for the determination of $T_1$. This is also true in the other cases.

**B. Case**(ii)

In this case we choose $\mu$ in Eq. (2.47) as

$$\mu(\xi) = \frac{1}{2} - \sum_{n=1}^{N} Q_n \xi^{-\frac{2(N+n)}{2N+1}}. \tag{2.75}$$

The coupled integral equations are the same as Eqs. (2.60) and (2.61) with $\nu = 0$. The functions $B_1$ and $B_2$ are obtained as

$$B_1(\xi) = B(\xi)\exp[-2\sum_{n=1}^{N} Q_n \frac{2N+1}{2n-1}\xi^{-\frac{2n-1}{2N+1}}]$$

$$= \sum_{n=1}^{\infty} B_n^{(1)}\xi^{-\frac{2N+n}{2N+1}} \tag{2.76}$$

and

$$B_2(\xi) = B(\xi)\exp[2\sum_{n=1}^{N} Q_n \frac{2N+1}{2n-1}\xi^{-\frac{2n-1}{2N+1}}]$$

$$= \sum_{n=1}^{\infty} B_n^{(2)}\xi^{-\frac{2N+n}{2N+1}}. \tag{2.77}$$

Explicit expressions of $B(\xi)$ and the coefficients of $B_n^{(1)}$ and $B_n^{(2)}$ are derived in Appendix A. Asymptotic solutions of $A_1(\xi)$ and $A_2(\xi)$ are given by

$$A_1(\xi) = e^{-\xi}\sum_{n=1}^{\infty}\alpha_n^{(1)}\xi^{-n/(2N+1)} + T_1\Theta_1(\xi)\sum_{n=0}^{\infty}\beta_n^{(2)}\xi^{-n/(2N+1)} \tag{2.78}$$

and

$$A_2(\xi) = \sum_{n=0}^{\infty}\beta_n^{(1)}\xi^{-n/(2N+1)} + T_1\Theta_1(\xi)e^{\xi}\sum_{n=1}^{\infty}\alpha_n^{(2)}\xi^{-n/(2N+1)}, \tag{2.79}$$

for $-\pi < \arg\xi < 2\pi$, and where $\beta_0^{(1)} = \beta_0^{(2)} = 1$. Final results for the coefficients $\alpha_n^{(1)}$, $\beta_n^{(1)}$, $\alpha_n^{(2)}$, $\beta_n^{(2)}$, and the Stokes constant $T_1$ are as follows:

$$T_1 = -2\pi i \sum_{s=0}^{\infty}\Big(\sum_{p+q=s} B_{p+1}^{(1)}\beta_q^{(1)}\Big)\frac{e^{-i\pi(\frac{2N+s+1}{2N+1})}}{\Gamma(\frac{2N+s+1}{2N+1})}. \tag{2.80}$$

$$\beta_n^{(2)} = -\frac{2N+1}{n}\sum_{m=0}^{n-1} B_{n-m}^{(1)}\alpha_{m+1}^{(2)}, \quad \text{for } n \geq 1, \tag{2.81}$$

$$\begin{aligned}
\alpha_1^{(1)} &= \alpha_2^{(1)} = \cdots = \alpha_{2N}^{(1)} = 0, \\
\alpha_{n+2N}^{(1)} &= \sum_{s=1}^{n}\Big(\sum_{q=0}^{s-1} B_{s-q}^{(1)}\beta_q^{(1)}\Big)(-1)^{\frac{n-s}{2N+1}+1}\frac{\Gamma(\frac{2N+n}{2N+1})}{\Gamma(\frac{2N+s}{2N+1})} \\
&\times \ \gamma\Big(\frac{n-s}{2N+1}\Big), \quad \text{for } n \geq 1,
\end{aligned} \tag{2.82}$$

$$\beta_n^{(1)} = -\frac{2N+1}{n}\sum_{m=1}^{n} B_{n-m+1}^{(2)}\alpha_m^{(1)}, \quad \text{for } n \geq 1, \tag{2.83}$$

$$\begin{aligned}
\alpha_1^{(2)} &= \alpha_2^{(2)} = \cdots = \alpha_{2N}^{(2)} = 0, \\
&\text{and} \\
\alpha_{n+2N}^{(2)} &= \sum_{s=1}^{n}\Big(\sum_{m=0}^{s-1} B_{s-m}^{(2)}\beta_m^{(2)}\Big)\gamma\Big(\frac{n-s}{2N+1}\Big)\frac{\Gamma(\frac{2N+n}{2N+1})}{\Gamma(\frac{2N+s}{2N+1})}, \\
&\qquad \text{for} \quad n \geq 1.
\end{aligned} \tag{2.84}$$

### C. Case(iii)

In order to obtain a solution of Eq. (2.47) with $\xi = \infty$ as regular singular point, we should choose $\mu$ as

$$\mu(\xi) = \frac{1}{2} - \frac{Q_0}{\xi^{2/3}} - \frac{Q_1}{\xi} - \frac{Q_0^2 + Q_2}{\xi^{4/3}} - \frac{2Q_0Q_1}{\xi^{5/3}}. \tag{2.85}$$

The phase integral becomes

$$\int \mu(\xi)d\xi = \frac{1}{2}(\xi - \alpha\xi^{1/3}) - Q_1\ln\xi + 3(Q_0^2 + Q_2)\xi^{-1/3} + 3Q_0Q_1\xi^{-2/3}, \tag{2.86}$$

where $\alpha = 6Q_0$ as defined in the previous chapter. The second term in Eq. (2.86) is a new term which has never appeared in the case(i) and case (ii) and can not be combined with $B$ in Eqs. (2.50) and (2.51), while the last two terms in Eq. (2.86) can be combined with $B$ as the previous cases. We obtain

$$B_1(\xi) = B(\xi)\exp[-6(Q_0^2 + Q_2)\xi^{-1/3} - 6Q_0Q_1\xi^{-2/3}]$$

$$\equiv \sum_{n=1}^{\infty} B_n^{(1)} \xi^{-\frac{n+2}{3}} \tag{2.87}$$

and

$$\begin{aligned} B_2(\xi) &= B(\xi)\exp[6(Q_0^2+Q_2)\xi^{-1/3}+6Q_0Q_1\xi^{-2/3}] \\ &\equiv \sum_{n=1}^{\infty} B_n^{(2)} \xi^{-\frac{n+2}{3}}, \end{aligned} \tag{2.88}$$

where explicit expressions of $B(\xi)$ and of the coefficients $B_n^{(1)}$ and $B_n^{(2)}$ are given in Appendix A. Coupled integral equations are slightly different from Eqs. (2.60) and (2.61), and are given by

$$A_1(\zeta) = \int_{+\infty}^{\zeta} d\xi B_1(\xi)\xi^{\nu} e^{-(\xi-\alpha\xi^{1/3})} A_2(\xi) \tag{2.89}$$

and

$$A_2(\zeta) = 1 + \int_{+\infty}^{\zeta} d\xi B_2(\xi)\xi^{-\nu} e^{(\xi-\alpha\xi^{1/3})} A_1(\xi), \tag{2.90}$$

with $\nu = 2Q_1$ and the initial conditions are the same as before. The asymptotic solutions of Eqs. (2.89) and (2.90) are different from the previous cases and given by

$$A_1(\xi) = \xi^{\nu} e^{-(\xi-\alpha\xi^{1/3})} \sum_{n=1}^{\infty} \alpha_n^{(1)} \xi^{-n/3} + T_1\Theta_1(\xi) \sum_{n=0}^{\infty} \beta_n^{(2)} \xi^{-n/3} \tag{2.91}$$

and

$$A_2(\xi) = \sum_{n=0}^{\infty} \beta_n^{(1)} \xi^{-n/3} + T_1\Theta_1(\xi)\xi^{-\nu} e^{(\xi-\alpha\xi^{1/3})} \sum_{n=1}^{\infty} \alpha_n^{(2)} \xi^{-n/3}, \tag{2.92}$$

for $-\pi < \arg\xi < 2\pi$ , and where $\beta_0^{(1)} = \beta_0^{(2)} = 1$.

In the same way as before in the case(i), we introduce the following quantities $I_{11}$ and $I_{22}$:

$$I_{11}(\zeta) \equiv \int_{+\infty}^{\zeta} d\xi B_1(\xi)\xi^{\nu} e^{-(\xi-\alpha\xi^{1/3})} \sum_{n=0}^{\infty} \beta_n^{(1)} \xi^{-n/3} \tag{2.93}$$

and

$$\begin{aligned} I_{12}(\zeta) \;&\equiv\; \int_{+\infty}^{\zeta} d\xi B_1(\xi)\xi^{\nu} e^{-(\xi-\alpha\xi^{1/3})} \\ &\times\; [T_1\Theta_1(\xi)\xi^{-\nu} e^{(\xi-\alpha\xi^{1/3})} \sum_{n=0}^{\infty} \alpha_n^{(2)} \xi^{-n/3}]. \end{aligned} \tag{2.94}$$

The quantity $I_{12}$ can be simply obtained as

$$I_{12}(\zeta) = -T_1\Theta_1(\zeta) \sum_{s=0}^{\infty} \Big( \sum_{p+q=s} B_{p+1}^{(1)} \alpha_{q+1}^{(2)} \Big) \frac{3}{s+1} \zeta^{-\frac{s+1}{3}}. \tag{2.95}$$

In order to reduce $I_{11}$ so that we can determine the Stokes constant $T_1$ , we first expand the term $e^{\alpha\xi^{1/3}}$ into power series and then use the Stokes phenomenon (the asymptotic expansion Eq. (2.55)) of the incomplete Gamma function. Then we obtain

$$
\begin{aligned}
I_{11}(\zeta) &= \sum_{s=0}^{\infty}[\sum_{p+q=s} B_{p+1}^{(1)}\beta_q^1]\sum_{n=0}^{\infty}\frac{\alpha^n}{n!}\int_{+\infty}^{\zeta} d\xi\xi^{\nu-(s+3)/3+n/3}e^{-\xi} \\
&= \sum_{s=0}^{\infty}\sum_{n=0}^{\infty}\frac{\alpha^n}{n!}(\sum_{p+q=s} B_{p+1}^{(1)}\beta_q^{(1)})\{\sum_{m=0}^{\infty}(-1)^{m+1}\frac{\Gamma(-\nu-\frac{n-s-3}{3}+m)}{\Gamma(-\nu-\frac{n-s-3}{3})} \\
&\times \ \zeta^{-m+\nu+\frac{n-s-3}{3}}e^{-\zeta}+\frac{-2\pi i\Theta_1(\zeta)}{\Gamma(-\nu-\frac{n-s-3}{3})}e^{i\pi(\nu+\frac{n-s-3}{3})}\},
\end{aligned}
\tag{2.96}
$$

where the second term depends on $\zeta$ only through the step function $\Theta_1(\zeta)$. Direct comparison of Eqs. (2.95) and (2.96) with Eq. (2.91) can not be made yet, because the first term of Eq. (2.96) does not contain the term $e^{\alpha\zeta^{1/3}}$ explicitly. In order to make this possible to obtain an explicit expression of $T_1$, rearrangement of the first term of Eq. (2.96) should be carried out. This is a tedious procedure and is given in Appendix B. We obtain finally

$$
T_1 = -2\pi i e^{i\pi\nu}\sum_{s=0}^{\infty}\sum_{n=0}^{\infty}\frac{\alpha^n}{n!}\Delta_s\frac{e^{i\pi(\frac{n-s-3}{3})}}{\Gamma(-\nu-\frac{n-s-3}{3})},
\tag{2.97}
$$

$$
\beta_n^{(2)} = -\frac{3}{n}\sum_{p+q=n-1} B_{n+1}^{(1)}\alpha_{q+1}^{(2)}, \quad \text{for } n\geq 1,
\tag{2.98}
$$

$$
\alpha_1^{(1)} = \alpha_2^{(1)} = 0,
\tag{2.99}
$$

and

$$
\alpha_{n+3}^{(1)} = -\sum_{p+q=n}\Delta_p W_{pq}, \quad \text{for } n\geq 0,
\tag{2.100}
$$

where

$$
\alpha = 6Q_0, \quad \Delta_s = \sum_{n+m=s} B_{n+1}^{(1)}\beta_m^{(1)},
\tag{2.101}
$$

$$
\begin{aligned}
W_{pq} &= \sum_{m=[q/3]}^{[q/2]}\Theta(3m-q)\sum_{n=3m-q}^{m}\frac{m!}{n!(m-n)!} \\
&\times \ \frac{\Gamma(\nu-p/3)c_{n(3m-q)}}{\Gamma(\nu-p/3-m+n)}\alpha^{3m-q},
\end{aligned}
\tag{2.102}
$$

with

$$
c_{nr} = \begin{cases} \delta_{n0}, & r=0, \\ \sum_{s=0}^{r}(-1)^{r-s}\frac{\Gamma(s/3+1)}{s!(r-s)!\Gamma(s/3-n+1)}, & r\geq 1, \end{cases}
\tag{2.103}
$$

the symbol $[x]$ means the largest integer, not larger than $x$, and $\Theta$ is the ordinary step function,

$$\Theta(X) = \begin{cases} 1, & X < 0, \\ 0, & X \geq 0. \end{cases} \tag{2.104}$$

On the other hand, substituting Eq. (2.91) to Eq. (2.90) with use of Eq. (2.88) and using the asymptotic expression Eq. (2.55) of the incomplete Gamma function, we have

$$\begin{aligned} & \int_{\infty}^{\zeta} d\xi B_2(\xi)\xi^{-\nu}e^{\xi-\alpha\xi^{1/3}}A_1(\xi) \\ = & -\sum_{s=1}^{+\infty}\frac{3}{s}\Big(\sum_{n+m=s-1} B_{n+1}^{(2)}\alpha_{m+1}^{(1)}\Big)\zeta^{-\frac{s}{3}} \\ + & \sum_{s=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-\alpha)^n}{n!}\Big[\sum_{p+q=s} B_{p+1}^{(2)}\beta_q^{(2)}\Big]T_1\Theta_1(\zeta) \\ \times & \sum_{m=0}^{\infty}\frac{\Gamma(\nu+\frac{s+3-n}{3}+m)}{\Gamma(\nu+\frac{s+3-n}{3})}\zeta^{-m-\nu-\frac{s+3-n}{3}}e^{\zeta}. \end{aligned} \tag{2.105}$$

Again we extract the term $e^{-\alpha\xi^{1/3}}$ from the second term of Eq. (2.105) and compare this equation with Eq. (2.92) to obtain

$$\beta_n^{(1)} = -\frac{3}{n}\sum_{p+q=n-1} B_{n+1}^{(2)}\alpha_{q+1}^{(1)}, \quad \text{for } n \geq 1, \tag{2.106}$$

$$\alpha_1^{(2)} = \alpha_2^{(2)} = 0, \tag{2.107}$$

and

$$\alpha_{n+3}^{(2)} = -\sum_{p+q=n} O_p X_{pq}, \quad \text{for } n \geq 0, \tag{2.108}$$

where

$$O_p = \sum_{n+m=p} B_{n+1}^{(2)}\beta_m^{(2)}, \tag{2.109}$$

$$\begin{aligned} X_{pq} = & \sum_{m=[q/3]}^{[q/2]}\Theta(3m-q)(-1)^m\sum_{n=3m-q}^{m}\frac{m!}{n!(m-n)!} \\ \times & \frac{\Gamma(-\nu-p/3)c_{n(3m-q)}}{\Gamma(-\nu-p/3-m+n)}(-\alpha)^{3m-q}. \end{aligned} \tag{2.110}$$

The coefficient $c_{n(3m-q)}$ are the same as those of Eqs. (2.103) . This completes the derivation of the coefficients $\alpha_n^{(1)}$, $\alpha_n^{(2)}$, $\beta_n^{(1)}$, $\beta_n^{(2)}$, and the Stokes constant $T_1$.

Because $Q_0 \neq 0$ in the present case, the expression of $T_1$ is more complicated than the first case. When we put $Q_0 = 0$, it is easy to confirm that all the results obtained in the present case coincide with those of the case (i) with $N = 2$ and no negative powers of $z$ in $Q(z)$. We have confirmed that our results obtained here give the exact results in the case of $a_2 = a_0 = 0$[2].

**D. Case(iv)**

In this case the function $\mu$ as is chosen as

$$\mu(\xi) = \frac{1}{2} - \frac{Q_0}{\xi^{4/5}} - \frac{Q_2}{\xi^{6/5}} - \frac{Q_0^2}{\xi^{8/5}}, \tag{2.111}$$

and the following coupled integral equations are obtained:

$$A_1(\zeta) = \int_{+\infty}^{\zeta} d\xi B_1(\xi) e^{-(\xi-\alpha\xi^{1/5})} A_2(\xi) \tag{2.112}$$

and

$$A_2(\zeta) = 1 + \int_{+\infty}^{\zeta} d\xi B_2(\xi) e^{(\xi-\alpha\xi^{1/5})} A_1(\xi), \tag{2.113}$$

where $\alpha = 10Q_0$ and

$$\begin{aligned} B_1(\xi) &= B(\xi)\exp[-10Q_2\xi^{-1/5} - \frac{10}{3}Q_0^2\xi^{-3/5}] \\ &\equiv \sum_{n=1}^{\infty} B_n^{(1)}\xi^{-\frac{n+4}{5}} \end{aligned} \tag{2.114}$$

and

$$\begin{aligned} B_2(\xi) &= B(\xi)\exp[10Q_2\xi^{-1/5} + \frac{10}{3}Q_0^2\xi^{-3/5}] \\ &\equiv \sum_{n=1}^{\infty} B_n^{(2)}\xi^{-\frac{n+4}{5}}. \end{aligned} \tag{2.115}$$

Explicit expressions of $B(\xi)$ and of the coefficients $B_n^{(1)}$ and $B_n^{(2)}$ are given in Appendix A. Asymptotic solutions of Eqs. (2.112) and (2.113) for $-\pi < \arg\xi < 2\pi$ are obtained as

$$A_1(\xi) = e^{-(\xi-\alpha\xi^{1/5})}\sum_{n=1}^{\infty}\alpha_n^{(1)}\xi^{-n/5} + T_1\Theta_1(\xi)\sum_{n=0}^{\infty}\beta_n^{(2)}\xi^{-n/5} \tag{2.116}$$

and

$$A_2(\xi) = \sum_{n=0}^{\infty}\beta_n^{(1)}\xi^{-n/5} + T_1\Theta_1(\xi)e^{(\xi-\alpha\xi^{1/5})}\sum_{n=1}^{\infty}\alpha_n^{(2)}\xi^{-n/5}. \tag{2.117}$$

The same procedure as in the case(iii) can be used to determine the coefficients in Eqs. (2.116) and (2.117), and the Stokes constant $T_1$. Here we just list the final results:

$$T_1 = -2\pi i \sum_{s=0}^{\infty}\sum_{n=0}^{\infty} \frac{\alpha^n}{n!}\Delta_s \frac{e^{i\pi(\frac{n-s-5}{5})}}{\Gamma(-\frac{n-s-5}{5})}, \tag{2.118}$$

$$\beta_{n+1}^{(2)} = -\frac{5}{n+1}\sum_{p+q=n} B_{p+1}^{(1)}\alpha_{q+1}^{(2)}, \quad \text{for } n \geq 0, \tag{2.119}$$

$$\alpha_1^{(1)} = \alpha_2^{(1)} = \alpha_3^{(1)} = \alpha_4^{(1)} = 0, \tag{2.120}$$

and

$$\alpha_{n+5}^{(1)} = -\sum_{p+q=n} \Delta_p W_{pq}, \quad \text{for } n \geq 0, \tag{2.121}$$

where

$$\Delta_s = \sum_{n+m=s} B_{n+1}^{(1)}\beta_m^{(1)}, \quad s \geq 0, \tag{2.122}$$

$$\begin{aligned} W_{pq} &= \sum_{m=[q/5]}^{[q/4]} \Theta(5m-q) \sum_{n=5m-q}^{m} \frac{m!}{n!(m-n)!} \\ &\times \frac{\Gamma(-p/5)c_{n(5m-q)}}{\Gamma(-p/5-m+n)}\alpha^{5m-q}, \end{aligned} \tag{2.123}$$

with

$$c_{nr} = \begin{cases} \delta_{n0}, & r = 0, \\ \sum_{s=0}^{r}(-1)^{r-s}\frac{\Gamma(s/5+1)}{s!(r-s)!\Gamma(s/5-n+1)}, & r \geq 1, \end{cases} \tag{2.124}$$

Following similar procedure like Eq. (2.105) in the case (iii), we can have

$$\beta_{n+1}^{(1)} = -\frac{5}{n+1}\sum_{p+q=n} B_{p+1}^{(2)}\alpha_{q+1}^{(1)}, \quad \text{for } n \geq 0, \tag{2.125}$$

$$\alpha_1^{(2)} = \alpha_2^{(2)} = \alpha_3^{(2)} = \alpha_4^{(2)} = 0, \tag{2.126}$$

and

$$\alpha_{n+5}^{(2)} = \sum_{p+q=n} O_p X_{pq}, \quad \text{for } n \geq 0, \tag{2.127}$$

where

$$O_p = \sum_{n+m=p} B_{n+1}^{(2)}\beta_m^{(2)}, \tag{2.128}$$

$$\begin{aligned} X_{pq} &= \sum_{m=[q/4]}^{[q/5]} \Theta(5m-q)(-1)^m \sum_{n=5m-q}^{m} \frac{m!}{n!(m-n)!} \\ &\times \frac{\Gamma(-p/5)c_{n(5m-q)}}{\Gamma(-p/5-m+n)}\alpha^{5m-q}. \end{aligned} \tag{2.129}$$

It should be noted that the final results of cases (iii) and (iv) are quite similar. We can again easily confirm that when $Q_0 = 0$, the present results coincide with those of case (ii) with $N = 2$ and no negative power of $z$ in $Q(z)$.

## 2.3 Concluding remarks

The standard asymptotic WKB solutions were proved to be useful for present type of analysis, especially for deriving the relations among Stokes constants. From the one-valuedness of an asymptotic solution, we have established three independent relations among Stokes constants $U_1$ defined in the complex $z$ plane. These are quite useful for many physical problems although they do not have a complete. Furthermore, one-to-one correspondence was established between $U_i$ and the Stokes constant $T_i$ in the complex $\xi$ plane.

The $z \rightarrow \xi$ transformation has many advantages. First, asymptotic solutions in the $\xi$ plane can be obtained in the form of power series with respect to $\xi^{-1}$. The explicit recurrence relations of the expansion coefficients can be derived. Second, all Stokes constants can be expressed in a compact form in terms of only one Stokes constant $T_1$. It should be noted that this can be done , even in the general case of Eq. (1.3). So, if we could obtain an analytical expression for the Stokes constant $T_1$, we could, in principle, determine all the other Stokes constants. Third, in the four cases (i)-(iv) considered in this chapter, the Stokes constant $T_1$ has actually been found to be expressed analytically in the form of a convergent infinite series as a function of the coefficients $a_j$.

A numerical test is done for the case (iii) by investigating the two-state linear curve crossing problems in chapter 4, we have encountered the same problem as that in Ref.[2] about convergence rate of the infinite series. It was found that the convergence rate for the Stokes constant $T_1$ becomes increasingly slow when the parameters in the differential equation are much bigger than unity. We conclude that this situation is generally true in any one of the four cases because of the reason explained below.

Although Stokes constants are formally defined by standard asymptotic WKB solutions that should be actually considered as the reference functions for simplicity of discussion. Precise definition of Stokes constants are related to the exactly asymptotic solutions $u$ and $v$ in the complex $\xi$-plane. Therefore, exact solutions for Stokes constants must include contribution from each term of the expansions of the asymptotic solutions. This is the reason why the Stokes constant $T_1$ is given in the form of the convergent infinite series. On the other hand, as we discussed in chapter 1, the farther from all transition points WKB solutions are, the more accurate they become. This implies that if one transition point is far from the origin, we need to consider more terms in the asymptotic solutions in order to maintain a desirable accuracy for solutions of $u$ and $v$. Thus, these result in a slow convergency rate for the solution of the Stokes constant $T_1$. Fortunately, however, when transition points are separated far away from one another, we can use other sophisticated analytical approximations which are based on the Airy or the Weber equations. These will be demonstrated in chapters 5, 6 and 7

Analysis of Stokes phenomena for the four cases (i)-(iv) provides a powerful tool to deal with many physical problems. Actually, Case (iv) represents a quantum mechanical cubic potential scattering with resonances. Case (iii) with real coefficients is similarly related to an eigenvalue problem in double minimum potential($a_4 < 0$) or to a scattering(reflection and transmission) problem in double maximum potential($a_4 > 0$). This case also includes the basic differential equation for two-state linear curve crossing problems that are our basic motivation to carry out research in this field. In the present study we have assumed that the coefficients $a_n$ of the highest order of $z$ [$n = 2N, 2N-1, 4$ and 3, corresponding to cases (i)-(iv)] is positive. Solutions for the negative $a_n$ can easily be obtained by rotating the complex $z$-plane by $\pi/2$.

# Appendix

## A. Power series solutions of $B(\xi)$ and explicit expressions of $B_n^1$ and $B_n^2$

Solution of Eq. (2.52) is divided into the following two steps:

$$B(\xi) = v(\xi) + \sigma(\xi), \tag{2.130}$$

where

$$v(\xi) \equiv \frac{X'(\xi)}{X(\xi)} \tag{2.131}$$

and

$$\sigma(\xi) \equiv \frac{\mu'(\xi)}{2\mu(\xi)}. \tag{2.132}$$

From Eq. (2.47), it is easy to prove that $v(\xi)$ satisfies the Riccati equation

$$\frac{dv}{d\xi} + v^2 + (Q + \mu^2) = 0, \tag{2.133}$$

where $\mu(\xi)$ is defined in text for each case.

**A. Case** (i)

Eqs. (1.12) and (2.56) give

$$Q(\xi) + \mu^2(\xi) = \sum_{s=N+2}^{\infty} P_s \xi^{-\frac{N+s}{N+1}}, \tag{2.134}$$

where

$$P_s = \begin{cases} Q_s + \sum_{m=1}^{s-N-1} Q_m Q_{s-N-m}, & N+2 \leq s \leq 3N+2, \\ Q_s, & s \geq 3N+3. \end{cases} \tag{2.135}$$

It is easy to see that a solution of Eq. (2.131) can be found in the form,

$$v(\xi) = \sum_{n=1}^{\infty} v_n \xi^{-\frac{N+n}{N+1}}. \tag{2.136}$$

Substitution of Eqs. (2.134) and (2.136) into Eq. (2.133) yields the following recurrence relations for $v_n$:

$$v_1^2 - v_1 + P_{N+2} = 0, \tag{2.137}$$

$$v_2 = P_{N+3}/(\frac{N+n}{N+1} - 2v_1), \tag{2.138}$$

and

$$v_n = (\sum_{m=2}^{n-1} v_m v_{n+1-m} + P_{n+N+1})/(\frac{N+n}{N+1} - 2v_1), \quad \text{for } n \geq 3. \tag{2.139}$$

By choosing $v_1$ to be the root of Eq. (2.137) with smaller real part, we can obtain one series solution which can be shown[9] to converge for sufficiently large $|\xi|$. This is true for the other cases.

From Eq. (2.56), we can easily obtain

$$\sigma(\xi) = \sum_{m=1}^{\infty} \sigma_m \xi^{-\frac{2N+1+m}{N+1}}, \tag{2.140}$$

where

$$\sigma_m = \begin{cases} Q_m \frac{N+m}{N+1}, & 1 \leq m \leq N+1, \\ \sum_{n=1}^{m-N-1} 2Q_n \sigma_{m-N-n}, & N+2 \leq m \leq 2N+2, \\ \sum_{n=1}^{N+1} 2Q_n \sigma_{m-N-n}, & 2N+3 \leq m. \end{cases} \tag{2.141}$$

Finally, from Eqs. (2.136) and (2.140) we have

$$B(\xi) = v(\xi) + \sigma(\xi) \equiv \sum_{1}^{\infty} B_n \xi^{-\frac{N+n}{N+1}}, \tag{2.142}$$

where

$$B_n = \begin{cases} v_n, & 1 \leq n \leq N+1, \\ v_n + \sigma_{n-N-1}, & N+2 \leq n. \end{cases} \tag{2.143}$$

In order to obtain explicit expressions for $B_n^1$ and $B_n^2$ in Eqs. (2.58) and (2.59), let us consider the quantity

$$T(\xi; d_1, d_2, \cdots, d_N) \equiv \exp(\sum_{n=1}^{N}) d_n \xi^{-\frac{n}{N+1}} \tag{2.144}$$

$$\begin{aligned} &= 1 + \sum_{m=1}^{\infty} \frac{1}{m!} \sum_{n_1=1}^{N} \sum_{n_2=1}^{N} \cdots \sum_{n_m=1}^{N} d_{n_1} d_{n_2} \cdots d_{n_m} \xi^{-\frac{n_1+n_2+\cdots n_m}{N+1}} \\ &\equiv 1 + \sum_{s=1}^{\infty} T_s(d_1, d_2, \cdots, d_N) \xi^{-\frac{s}{N+1}}. \end{aligned} \tag{2.145}$$

After a little effort, we can find

$$T_s(d_1, d_2, \cdots, d_N) = \sum_{m=[s/N]}^{s} \frac{1}{m!} \Theta(mN - s) \sum_{n_1+n_2+\cdots n_m = s, n_i \geq 1} d_{n_1} d_{n_2} \cdots d_{n_m}, \tag{2.146}$$

where $\Theta(X)$ is an ordinary step function.

With use of these results, we obtain finally,

$$B_1^{(1)} = B_1^{(2)} = B_1, \tag{2.147}$$

and

$$B_n^{(1)} = B_n + \sum_{s=1}^{n-1} B_{n-s} T_s(d_1, d_2, \cdots, d_N), \quad n \geq 2, \tag{2.148}$$

$$B_n^{(2)} = B_n + \sum_{s=1}^{n-1} B_{n-s} T_s(-d_1, -d_2, \cdots, -d_N), \quad n \geq 2, \tag{2.149}$$

where

$$d_n = -2Q_{n+1}\frac{N+1}{n}, \quad N \geq n \geq 1. \tag{2.150}$$

**B. Case** (ii)

Eqs. (1.23) and (2.75) give

$$Q(\xi) + \mu^2(\xi) = \sum_{s=N+1}^{\infty} P_s \xi^{-\frac{2N+2s}{2N+1}}, \tag{2.151}$$

where

$$P_s = \begin{cases} Q_{N+1}, & s = N+1, \\ Q_s + \sum_{m=1}^{s-N-1} Q_m Q_{s-N-m}, & N+2 \leq s \leq 3N, \\ Q_s, & s \geq 3N+1. \end{cases} \tag{2.152}$$

In the same way as case (i), we have

$$v(\xi) = \sum_{n=1}^{\infty} v_n \xi^{-\frac{2N+n}{2N+1}} \tag{2.153}$$

and

$$\sigma(\xi) = \sum_{m=1}^{\infty} \sigma_m \xi^{-\frac{2N+2m}{2N+1}-1}, \tag{2.154}$$

where

$$v_1^2 - v_1 + P_{N+1} = 0, \tag{2.155}$$

$$v_{2s}(-\frac{2N+2s}{2N+1}) + \sum_{m=1}^{2s} v_m v_{2s+1-m} = 0, \quad s \geq 1, \tag{2.156}$$

$$v_{2s+1}(-\frac{2N+2s+1}{2N+1}) + \sum_{m=1}^{2s+1} v_m v_{2s+2-m} + P_{s+N+1} = 0, \quad s \geq 1, \tag{2.157}$$

and

$$\sigma_m = \begin{cases} Q_m \frac{2N+2m}{2N+1}, & 1 \le m \le N, \\ \sum_{n=1}^{m-N-1} 2Q_n \sigma_{m-N-n}, & N+2 \le m \le 2N+1, \\ \sum_{n=1}^{N} 2Q_n \sigma_{m-N-n}, & 2N+2 \le m. \end{cases} \tag{2.158}$$

Thus we obtain

$$B(\xi) = v(\xi) + \sigma(\xi) \equiv \sum_{n=1}^{\infty} B_n \xi^{-\frac{2N+n}{2N+1}}, \tag{2.159}$$

where

$$B_n = v_n, \quad 1 \le n \le 2N+2, \tag{2.160}$$

$$B_{2n} = v_{2n}, \quad n \ge N+2, \tag{2.161}$$

and

$$B_{2n+1} = v_{2n+1} + \sigma_{n-N}, \quad n \ge N+1. \tag{2.162}$$

In order to derive final results for $B_n^1$ and $B_n^2$ defined by Eqs. (2.76) and (2.77), we use

$$\begin{aligned} T(\xi; d_1, d_2, \cdots, d_N) &\equiv \exp\left(\sum_{n=1}^{N} d_n \xi^{-\frac{2n-1}{2N+1}}\right) \\ &= 1 + \sum_{s=1}^{\infty} T_s(d_1, d_2, \cdots, d_N) \xi^{-\frac{s}{2N+1}}, \end{aligned} \tag{2.163}$$

where

$$\begin{aligned} T_{2s}(d_1, d_2, \cdots, d_N) &= \sum_{m=[s/(2N-1)]}^{s} \frac{1}{(2m)!} \Theta[m(2N-1) - s] \\ &\times \sum_{n_1+n_2+\cdots n_{2m}=s+m, n_i \ge 1} d_{n_1} d_{n_2} \cdots d_{n_{2m}} \end{aligned} \tag{2.164}$$

and

$$\begin{aligned} T_{2s-1}(d_1, d_2, \cdots, d_N) &= \sum_{m=[(s-N)/(2N-1)]}^{s-1} \frac{1}{(2m+1)!} \Theta[m(2N-1) - s + N] \\ &\times \sum_{n_1+n_2+\cdots n_{2m+1}=s+m, n_i \ge 1} d_{n_1} d_{n_2} \cdots d_{n_{2m+1}}. \end{aligned} \tag{2.165}$$

From these expressions we finally find

$$B_1^{(1)} = B_1^{(2)} = B_1, \tag{2.166}$$

$$B_n^{(1)} = B_n + \sum_{s=1}^{n-1} B_{n-s} T_s(d_1, d_2, \cdots, d_N), \quad n \ge 2, \tag{2.167}$$

$$B_n^{(2)} = B_n + \sum_{s=1}^{n-1} B_{n-s} T_s(-d_1, -d_2, \cdots, -d_N), \quad n \geq 2, \tag{2.168}$$

and

$$d_n = -2Q_n \frac{2N+1}{2n-1}, \quad N \geq n \geq 1. \tag{2.169}$$

**C. Case** (iii)

Eqs. (1.33) and (2.85) lead to

$$Q(\xi) + \mu^2(\xi) = \sum_{n=1}^{5} P_n \xi^{-\frac{n+5}{3}}, \tag{2.170}$$

where

$$P_1 = \frac{2}{9} + Q_1^2 + 2Q_0(Q_0^2 + Q_2), \tag{2.171}$$

$$P_2 = 4Q_0^2 Q_1 + 2Q_1(Q_0^2 + Q_2), \tag{2.172}$$

$$P_3 = 4Q_1^2 Q_0 + (Q_0^2 + Q_2)^2, \tag{2.173}$$

$$P_4 = 4Q_0 Q_1 (Q_0^2 + Q_2), \tag{2.174}$$

and

$$P_5 = 4Q_0^2 Q_1^2. \tag{2.175}$$

Solutions of $v(\xi)$ and $\sigma(\xi)$ are obtained as

$$v(\xi) = \sum_{n=1}^{\infty} v_n \xi^{-\frac{n+2}{3}} \tag{2.176}$$

and

$$\sigma(\xi) = \sum_{n=1}^{\infty} \sigma_n \xi^{-\frac{n+2}{3}}, \tag{2.177}$$

where

$$v_1^2 - v_1 + P_1 = 0, \tag{2.178}$$

$$v_2 = P_2/(\frac{4}{3} - 2v_1), \tag{2.179}$$

$$v_n = (\sum_{m=2}^{n-1} v_m v_{n+1-m} + P_n)/(\frac{n+2}{3} - 2v_1), \quad \text{for } n \geq 3, \tag{2.180}$$

$$\sigma_1 = \sigma_2 = 0, \tag{2.181}$$

$$\sigma_3 = \frac{2}{3} Q_0, \tag{2.182}$$

$$\sigma_4 = Q_1, \tag{2.183}$$

$$\sigma_5 = \frac{4}{3}(Q_0^2 + Q_2) + 2Q_0\sigma_3, \tag{2.184}$$

$$\sigma_6 = \frac{10}{3}Q_0Q_1 + 2Q_0\sigma_4 + 2Q_0\sigma_3, \tag{2.185}$$

$$\sigma_7 = 2Q_0\sigma_5 + 2Q_1\sigma_4 + 2(Q_0^2 + Q_2)\sigma_3, \tag{2.186}$$

and

$$\sigma_n = 2Q_0\sigma_{n-2} + 2Q_1\sigma_{n-3} + 2(Q_0^2 + Q_2)\sigma_{n-4} + 4Q_0Q_1\sigma_{n-5}, \quad \text{for } n \geq 8. \tag{2.187}$$

Thus,

$$\begin{aligned} B(\xi) &= \sigma(\xi) + v(\xi) \\ &= \sum_{n=1}^{\infty} B_n \xi^{-\frac{n+2}{3}} \\ &= \sum_{n=1}^{\infty} (v_n + \sigma_n)\xi^{-\frac{n+2}{3}}. \end{aligned} \tag{2.188}$$

Finally, from Eqs. (2.87) and (2.88) we have

$$B_n^{(1)} = \sum_{m=0}^{n-1} B_{n-m} T_m(d_1, d_2), \quad n \geq 1 \tag{2.189}$$

and

$$B_n^{(2)} = \sum_{m=0}^{n-1} B_{n-m} T_m(-d_1, -d_2), \quad n \geq 1, \tag{2.190}$$

where

$$T_m(d_1, d_2) = \sum_{n=[m/2]}^{m} \Theta(2n - m) \frac{(6d_1)^{2n-m}(3d_2)^{m-n}}{(2n-m)!(m-n)!}, \tag{2.191}$$

with

$$d_1 = -Q_0^2 - Q_2 \tag{2.192}$$

and

$$d_2 = -2Q_0Q_1. \tag{2.193}$$

### D. Case (iv)

Eqs. (1.45) and (2.111) lead to

$$Q(\xi) + \mu^2(\xi) = \sum_{n=1}^{7} P_n \xi^{-\frac{n+9}{5}}, \tag{2.194}$$

where

$$P_1 = 2Q_0Q_2 + \frac{21}{100}, \tag{2.195}$$
$$P_2 = 0, \tag{2.196}$$
$$P_3 = Q_2^2 + 2Q_0^3, \tag{2.197}$$
$$P_4 = 0, \tag{2.198}$$
$$P_5 = 2Q_2Q_0^2, \tag{2.199}$$
$$P_6 = 0, \tag{2.200}$$

and

$$P_7 = Q_0^4. \tag{2.201}$$

Solutions of $v(\xi)$ and $\sigma(\xi)$ are obtained as

$$v(\xi) = \sum_{n=1}^{\infty} v_n \xi^{-\frac{n+4}{5}} \tag{2.202}$$

and

$$\sigma(\xi) = \sum_{n=1}^{\infty} \sigma_n \xi^{-\frac{n+4}{5}}, \tag{2.203}$$

and

$$v_1^2 - v_1 + P_1 = 0, \tag{2.204}$$

$$v_{2n} = 0, \quad n \geq 1, \tag{2.205}$$

$$v_{2n+1} = (\sum_{m=2}^{2n} v_m v_{2n+2-m} + P_{2n+1})/(\frac{2n+5}{5} - 2v_1), \quad n \geq 1, \tag{2.206}$$

$$\sigma_1 = \sigma_2 = \sigma_3 = \sigma_4 = 0, \tag{2.207}$$
$$\sigma_{2n} = 0, \quad n \geq 1, \tag{2.208}$$
$$\sigma_5 = \frac{4}{5}Q_0, \quad \sigma_7 = \frac{6}{5}Q_2, \tag{2.209}$$
$$\sigma_9 = \frac{8}{5}Q_0^2 + 2Q_0\sigma_5, \tag{2.210}$$
$$\sigma_{11} = 2Q_2\sigma_5 + 2Q_0\sigma_7, \tag{2.211}$$

and

$$\sigma_{2n+1} = 2Q_0\sigma_{2n-3} + 2Q_2\sigma_{2n-5} + 2Q_0^2\sigma_{2n-7}, \quad n \geq 6. \tag{2.212}$$

Thus, we have

$$\begin{aligned} B(\xi) &= \sigma(\xi) + v(\xi) \\ &= \sum_{n=1}^{\infty} B_n \xi^{-\frac{n+4}{5}} \\ &= \sum_{n=1}^{\infty} (v_n + \sigma_n)\xi^{-\frac{n+4}{5}}. \end{aligned} \tag{2.213}$$

Finally, from Eqs. (2.114) and (2.115) we obtain

$$B_n^{(1)} = \sum_{m=0}^{n-1} B_{n-m} T_m(d_1, d_2), \quad n \geq 1 \tag{2.214}$$

and

$$B_n^{(2)} = \sum_{m=0}^{n-1} B_{n-m} T_m(-d_1, -d_2), \quad n \geq 1, \tag{2.215}$$

where

$$T_{2m}(d_1, d_2) = \sum_{n=[m/3]}^{m} \Theta(3n - m) \frac{(10d_1)^{3n-m}(10d_2/3)^{m-n}}{(3n-m)!(m-n)!}, \quad m \geq 1, \tag{2.216}$$

and

$$T_{2m+1}(d_1, d_2) = \sum_{n=[(m-1)/3]}^{m} \Theta(3n + 1 - m) \frac{(10d_1)^{3n+1-m}(10d_2/3)^{m-n}}{(3n+1-m)!(m-n)!}, \quad m \geq 0, \tag{2.217}$$

with

$$d_1 = -Q_2 \quad \text{and} \quad d_2 = -Q_0^2. \tag{2.218}$$

## B. Derivation of Eqs. (2.102) and (2.110)

In order to make a direct comparison of Eqs. (2.91) and (2.96) possible, we rewrite the first term of Eq. (2.96) except for $\xi^\nu e^{-\xi}$, namely,

$$\begin{aligned} I(\zeta) &= \sum_{s=0}^{\infty}\sum_{n=0}^{\infty}\frac{\alpha^n}{n!}\Delta_s\sum_{m=0}^{\infty}(-1)^{m+1}\frac{\Gamma(-\nu-\frac{n-s-3}{3}+m)}{\Gamma(-\nu-\frac{n-s-3}{3})} \\ &\times \zeta^{-m+\frac{n-s-3}{3}}, \end{aligned} \tag{2.219}$$

where $\alpha$ and $\Delta_s$ are defined in the text. First, we note that the summation with respect to m in Eq. (2.219) can rewritten as

$$\begin{aligned} J(\zeta) &\equiv \sum_{m=0}^{\infty}(-1)^{m+1}\frac{\Gamma(\delta+m)}{\Gamma(\delta)}\zeta^{-m-\delta-\nu}, \\ &= \zeta^{-\nu}\sum_{m=0}^{\infty}\frac{d^m}{d\zeta^m}\zeta^{-\delta}, \end{aligned} \tag{2.220}$$

where

$$\delta = -\nu - \frac{n-s-3}{3}. \tag{2.221}$$

Thus we obtain

$$\begin{aligned} I(\zeta) &= -\sum_{s=0}^{\infty}\sum_{n=0}^{\infty}\frac{\alpha^n}{n!}\Delta_s\zeta^{-\nu}\sum_{m=0}^{\infty}\frac{d^m}{d\zeta^m}(\zeta^{\nu+\frac{n-s-3}{3}}) \\ &= -\sum_{s=0}^{\infty}\Delta_s\zeta^{-\nu}\sum_{m=0}^{\infty}\frac{d^m}{d\zeta^m}(\zeta^{\nu-\frac{s+3}{3}}e^{\alpha\zeta^{1/3}}) \\ &= -\sum_{s=0}^{\infty}\Delta_s\sum_{m=0}^{\infty}\sum_{n=0}^{m}\frac{m!}{n!(n-m)!}\frac{\Gamma(\nu-\frac{s}{3})}{\Gamma(\nu-\frac{s}{3}-m+n)}\zeta^{-\frac{s+3}{3}-m+n} \\ &\times \left(\frac{d^n}{d\zeta^n}e^{\alpha\zeta^{1/3}}\right) \\ &= -\sum_{s=0}^{\infty}\Delta_s\sum_{m=0}^{\infty}\sum_{q=2m}^{3m}\left\{\sum_{n=3m-q}^{m}\frac{m!}{n!(n-m)!}\frac{\Gamma(\nu-s/3)c_{n(3m-q)}}{\Gamma(\nu-s/3-m+n)}\right\} \\ &\times \alpha^{3m-q}\zeta^{-(s+3+q)/3}e^{\alpha\zeta_{1/3}}. \end{aligned} \tag{2.222}$$

Here the formula of the n-th derivative of a composite function is used[10],

$$\frac{d^n}{d\zeta^n}e^{\alpha\zeta^{1/3}} = \sum_{r=0}^{n}c_{nr}\alpha^r\zeta^{r/3-n}e^{\alpha\zeta^{1/3}}, \tag{2.223}$$

where $c_{nr}$ is defined by Eq. (2.103). Finally, we exchange the summation with respect to $m$ and $q$ by using the relation,

$$\sum_{m=0}^{\infty}\sum_{q=2m}^{3m} = \sum_{q=0}^{\infty}\sum_{m=[q/3]}^{[q/2]}\Theta(3m-q). \tag{2.224}$$

Insertion of this final expression back into Eq. (2.96) yields Eq. (2.102). Derivation of Eq. (2.110) can be done in exactly the same way.

# Chapter 3

# Conection matrices

Connection matrix discussed in this chapter is a matrix that can connect solutions in one asymptotic region of complex plane to solutions in another asymptotic region. Discussions in this chapter focus on physically important connections between two anti-Stokes lines, two Stokes lines, and one anti-Stokes and Stokes lines. First, the connection matrix is exactly expressed in terms of Stokes constants that are defined by the Standard asymptotic WKB solutions, and then by evaluating the phase difference between the standard and the ordinary WKB solutions, we obtain connection matrix that connects ordinary WKB solutions. Connection matrices for one transition point and two transition points are introduced to illustrate procedure, and those for three transition points and four transition points are presented. These connection matrices construct a basis for later application in Part 2.

## 3.1 One transition point

The simplest connection problem is, of course, differential equation with one transition point written as,

$$\frac{d^2\phi(z)}{dz^2} + h^2 z\phi(z) = 0, \qquad h > 0. \tag{3.1}$$

The WKB solutions in the form of phase integral are

$$(0, z) = q^{-\frac{1}{4}}(z)\exp[i\int_0^z q^{\frac{1}{2}}(z)dz] \tag{3.2}$$

and

$$(z, 0) = q^{-\frac{1}{4}}(z)\exp[-i\int_0^z q^{\frac{1}{2}}(z)dz], \tag{3.3}$$

where $q(z) = h^2 z$.

The asymptotic solution on the anti-Stokes line of $\arg z = 0$ in Fig.3.1 is given by

$$\phi(z) \underset{z\to\infty}{=} A(0,z) + B(z,0), \tag{3.4}$$

and that on the Stokes line of $\arg z = \pi$ by

$$\phi(z) \underset{z\to-\infty}{=} C(0,z)_d + D(z,0)_s. \tag{3.5}$$

The connection matrix is defined as follows:

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv F \begin{pmatrix} A \\ B \end{pmatrix}. \tag{3.6}$$

As discussed in chapter 1, if we trace the solution (3.4) from $\arg z = 0$ to region 3, we have

$$(A + Bi)(0,z)_d + B(z,0)_s. \tag{3.7}$$

When the solution reaches on the Stokes line of $\arg z = \pi$, it becomes

$$(A + Bi)(0,z)_d + [B + \frac{i}{2}(A + Bi)](z,0)_s. \tag{3.8}$$

Here, we have used the second version of the Jeffreys' connection formula[11], in which coefficient of subdominant solution is required to have a discontinuous change according to the following rule:

New subdominant coefficient =

old subdominant coefficient + ($\frac{1}{2}\times$ Stokes constant)$\times$dominant coefficient.

Comparing Eq. (3.8) with Eq. (3.5) gives

$$C = A + Bi \tag{3.9}$$

and

$$D = B + \frac{i}{2}(A + Bi). \tag{3.10}$$

Thus, the connection matrix turns out to be

$$F = \begin{pmatrix} 1 & i \\ \frac{i}{2} & \frac{1}{2} \end{pmatrix}. \tag{3.11}$$

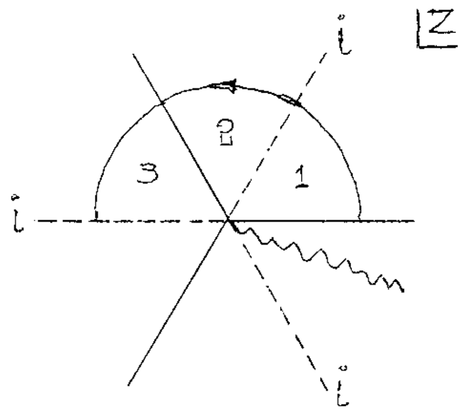



Figure 3.1.

Now, let us consider the differential equation($h^2 \to -h^2$ in Eq. (3.1) )

$$\frac{d^2\phi(z)}{dz^2} - h^2 z\phi(z) = 0. \quad h > 0 \tag{3.12}$$

The asymptotic solution on the Stokes line of $\arg z = 0$ in Fig.3.2 is given by

$$\phi(z) \underset{z\to\infty}{=} A(0,z)_s + B(z,0)_d, \tag{3.13}$$

and that on the anti-Stokes line of $\arg z = \pi$ by

$$\phi(z) \underset{z\to-\infty}{=} C(0,z) + D(z,0). \tag{3.14}$$

The connection matrix is

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} F'_{11} & F'_{12} \\ F'_{21} & F'_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv F' \begin{pmatrix} A \\ B \end{pmatrix}. \tag{3.15}$$

Tracing the solution from region 1 to 3 in Fig.3.2, we can easily obtain

$$F' = \begin{pmatrix} 1 & -\frac{i}{2} \\ -i & \frac{1}{2} \end{pmatrix}. \tag{3.16}$$

It should be noted that the two connection matrices satisfy

$$F^\dagger = F'. \tag{3.17}$$

## 3.2 Two transition points

A typical differential equation with two transition points is the Weber equation for which the connection matrix can be solved exactly in the compact form. This is

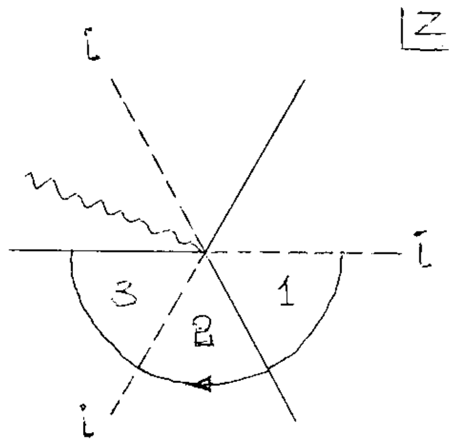



Figure 3.2.

because that the Stokes constant for Weber equation is known to be given in the compact form. Two cases will be discussed in the following for the connection matrix between anti-Stokes lines and the connection matrix between Stokes lines.

**A. Connection matrix on anti-Stokes lines**

The Weber equation is

$$\frac{d^2\phi(z)}{dz^2} + h^2(z^2 - \epsilon^2)\phi(z) = 0, \quad h > 0, \tag{3.18}$$

where $\epsilon$ can be a complex constant. The corresponding Stokes and anti-Stokes lines are shown in Fig.3.3. Asymptotic solutions on the anti-Stokes lines $\arg z = 0$ and $\arg z = \pi$ are expressed in the ordinary WKB form as

$$\phi(z) \underset{z\to+\infty}{\longrightarrow} Aq^{-1/4}(z)\exp[i\int_0^z q^{1/2}(z)dz] + Bq^{-1/4}(z)\exp[-i\int_0^z q^{1/2}(z)dz] \tag{3.19}$$

and

$$\phi(z) \underset{z\to-\infty}{\longrightarrow} Cq^{-1/4}(z)\exp[i\int_0^z q^{1/2}(z)dz] + Dq^{-1/4}(z)\exp[-i\int_0^z q^{1/2}(z)dz], \tag{3.20}$$

where

$$q(z) = h^2(z^2 - \epsilon^2). \tag{3.21}$$

The connection matrix between these two solutions is defined by

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv F \begin{pmatrix} A \\ B \end{pmatrix}. \tag{3.22}$$

In order to find the matrix $F$ we introduce the standard WKB solutions of Eq. (3.18)

$$(\bullet, z) = z^{-1/2}\exp[iP(z)] \tag{3.23}$$

and

$$(z,\bullet) = z^{-1/2}\exp[-iP(z)], \tag{3.24}$$

where

$$P(z) = \frac{h}{2}(z^2 - \epsilon^2 \ln z). \tag{3.25}$$

The asymptotic solutions (3.19) and (3.20) can be also given by

$$\phi(z) \underset{z\to+\infty}{\longrightarrow} A'(\bullet, z) + B'(z,\bullet) \tag{3.26}$$

and

$$\phi(z) \underset{z\to-\infty}{\longrightarrow} C'(\bullet, z) + D'(z,\bullet). \tag{3.27}$$

The connection matrix between the primed coefficients is given by[13]

$$\begin{pmatrix} C' \\ D' \end{pmatrix} = \begin{pmatrix} 1 & U \\ -(1+e^{2\pi\beta})/U & -e^{2\pi\beta} \end{pmatrix} \begin{pmatrix} A' \\ B' \end{pmatrix}, \tag{3.28}$$

where $U$ is a Stokes constant on the Stokes line $\arg z = \pi/4$ in Fig.3.3 and is given by

$$U = i\frac{\sqrt{2\pi}}{\Gamma(\frac{1}{2} - i\beta)} e^{-\pi\beta/2} e^{-i\beta\ln(2h)} \tag{3.29}$$

with

$$\beta = \frac{1}{2}h\epsilon^2. \tag{3.30}$$

Expanding the phase integrals in Eqs. (3.19) and (3.20) as

$$i\int_0^z q^{1/2}(z)dz \underset{z\to+\infty}{\longrightarrow} iP(z) + \delta_+ \tag{3.31}$$

and

$$i\int_0^z q^{1/2}(z)dz \underset{z\to-\infty}{\longrightarrow} -iP(z) + \delta_-, \tag{3.32}$$

and comparing Eqs. (3.19) and (3.20) with (3.26) and (3.27), then we obtain

$$\delta_+ = ih(-\frac{1}{4}\epsilon^2 - \frac{\epsilon^2}{2}\ln 2 + \frac{\epsilon^2}{2}\ln\sqrt{e^{i\pi}\epsilon^2}) \tag{3.33}$$

and

$$\delta_- = -\delta_+ + \frac{\pi}{2}h\epsilon^2. \tag{3.34}$$

Finally, we can derive

$$F \equiv F(\beta)$$

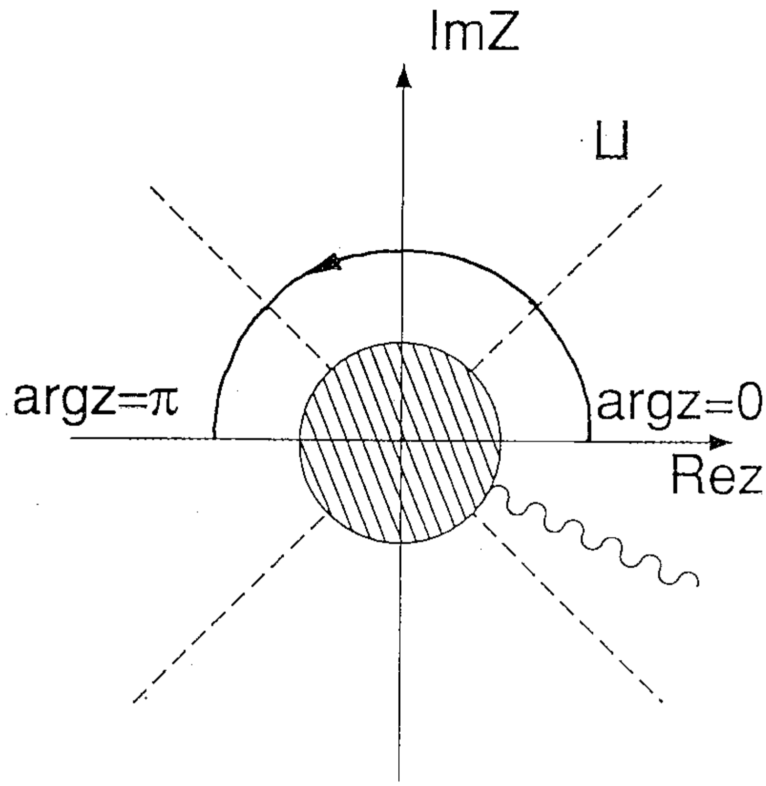



Figure 3.3.

$$= \begin{pmatrix} \sqrt{2\pi} e^{\pi\beta/2 - i\beta + i\beta \ln(e^{i\pi}\beta)}/\Gamma(1/2 + i\beta) & ie^{\pi\beta} \\ -ie^{\pi\beta} & \sqrt{2\pi} e^{\pi\beta/2 + i\beta - i\beta \ln(e^{i\pi}\beta)}/\Gamma(1/2 - i\beta) \end{pmatrix}. \tag{3.35}$$

## B. Connection matrix on the Stokes lines

Let us consider the Weber equation given by

$$\frac{d^2\phi(z)}{dz^2} - h^2(z^2 - \epsilon^2)\phi(z) = 0, \quad h > 0, \tag{3.36}$$

where $\epsilon$ can be a complex constant. The corresponding Stokes and anti-Stokes lines are shown in Fig.3.4. Asymptotic solutions on the Stokes lines $\arg z = \pi/2$ and $\arg z = -\pi/2$ now become

$$\phi(z) \underset{z \to \infty e^{i\pi/2}}{\longrightarrow} A q^{-1/4}(z) \exp[-\int_0^z q^{1/2}(z) dz] + B q^{-1/4}(z) \exp[\int_0^z q^{1/2}(z) dz] \tag{3.37}$$

and

$$\phi(z) \underset{z \to \infty e^{-i\pi/2}}{\longrightarrow} C q^{-1/4}(z) \exp[-\int_0^z q^{1/2}(z) dz] + D q^{-1/4}(z) \exp[\int_0^z q^{1/2}(z) dz], \tag{3.38}$$

where

$$q(z) = h^2(z^2 - \epsilon^2). \tag{3.39}$$

The connection matrix is now defined by

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv H \begin{pmatrix} A \\ B \end{pmatrix}. \tag{3.40}$$

Again, the standard WKB solutions are introduced as

$$(\bullet, z) = z^{-1/2} \exp[-P(z)] \tag{3.41}$$

and

$$(z, \bullet) = z^{-1/2} \exp[P(z)] \tag{3.42}$$

with

$$P(z) = \frac{h}{2}(z^2 - \epsilon^2 \ln z), \tag{3.43}$$

by which the asymptotic solutions (3.37) and (3.38) are written as

$$\phi(z) \underset{z \to \infty e^{i\pi/2}}{\longrightarrow} A'(\bullet, z)_d + B'(z, \bullet)_s \tag{3.44}$$

and

$$\phi(z) \underset{z \to \infty e^{-i\pi/2}}{\longrightarrow} C'(\bullet, z)_d + D'(z, \bullet)_s. \tag{3.45}$$

Tracing Eq. (3.44) from the Stokes line $\arg z = \pi/2$ to the Stokes line $\arg z = -\pi/2$, we have

**1.** $A'(\bullet, z)_d + (B' - \frac{U}{2}A')(z, \bullet)_s$,

**2.** $A'(\bullet, z)_s + (B' - \frac{U}{2}A')(z, \bullet)_d$,

**3.** $[A' - T(B' - \frac{U}{2}A')](\bullet, z)_s + (B' - \frac{U}{2}A')(z, \bullet)_d$,

**4.** $[A' - T(B' - \frac{U}{2}A')](\bullet, z)_d + (B' - \frac{U}{2}A')(z, \bullet)_s$,

and on $\arg z = -\pi/2$,

$$[A' - T(B' - \frac{U}{2}A')](\bullet, z)_d + \{(B' - \frac{U}{2}A') - \frac{S}{2}[A' - T(B' - \frac{U}{2}A')]\}(z, \bullet)_s. \tag{3.46}$$

Comparing this equation with Eq. (3.45), we obtain

$$C' = A' - T(B' - \frac{U}{2}A'), \tag{3.47}$$

$$D' = (B' - \frac{U}{2}A') - \frac{S}{2}[A' - T(B' - \frac{U}{2}A')], \tag{3.48}$$

where the Stokes constants $U$, $T$ and $S$ which correspond to the Stokes lines $\arg z = \pi/2, 0, -\pi/2$ in Fig.3.4 respectively, are given by

$$S = Ue^{-i2\pi\alpha}, \tag{3.49}$$

$$T = -(e^{i2\pi\alpha} + 1)/U, \tag{3.50}$$

and

$$U = i\frac{\sqrt{2\pi}}{\Gamma(\frac{1}{2} - \alpha)} e^{i\pi\alpha - \alpha\ln(2h)} \tag{3.51}$$

with

$$\alpha = \frac{1}{2}h\epsilon^2. \tag{3.52}$$

It should be noted that we have also used the second version of Jefferys' connection rule. Thus, we obtain the connection matrix as

$$\begin{pmatrix} C' \\ D' \end{pmatrix} = \begin{pmatrix} [1 - e^{2\pi i\alpha}]/2 & [1 + e^{2\pi i\alpha}]/U \\ -U[1 + e^{-2\pi i\alpha}]/4 & [1 - e^{-2\pi i\alpha}]/2 \end{pmatrix} \begin{pmatrix} A' \\ B' \end{pmatrix}. \tag{3.53}$$

In the same way as before, putting

$$\int_0^z q^{1/2}(z)dz \underset{z\to\infty e^{i\pi/2}}{\longrightarrow} P(z) - \Delta_+ \tag{3.54}$$

and

$$\int_0^z q^{1/2}(z)dz \underset{z\to\infty e^{-i\pi/2}}{\longrightarrow} -P(z) - \Delta_-, \tag{3.55}$$

then we obtain

$$\Delta_+ = \frac{h\epsilon^2}{4}(1 + 2\ln 2 - 2\ln\sqrt{e^{i\pi}\epsilon^2}) \tag{3.56}$$

and

$$\Delta_- = -\Delta_+ - \frac{i\pi}{2}h\epsilon^2, \tag{3.57}$$

with which we compare Eqs. (3.37) and (3.38) to Eqs. (3.44) and (3.45), we have

$$H \equiv H(\alpha) = \begin{pmatrix} \frac{\sqrt{2\pi}\cos(\pi\alpha)}{2\Gamma(\frac{1}{2}-\alpha)} e^{\alpha - \alpha\ln\alpha} & -\sin(\pi\alpha) \\ \sin(\pi\alpha) & \frac{\sqrt{2\pi}}{\Gamma(\frac{1}{2}+\alpha)} e^{-\alpha+\alpha\ln\alpha} \end{pmatrix}. \tag{3.58}$$

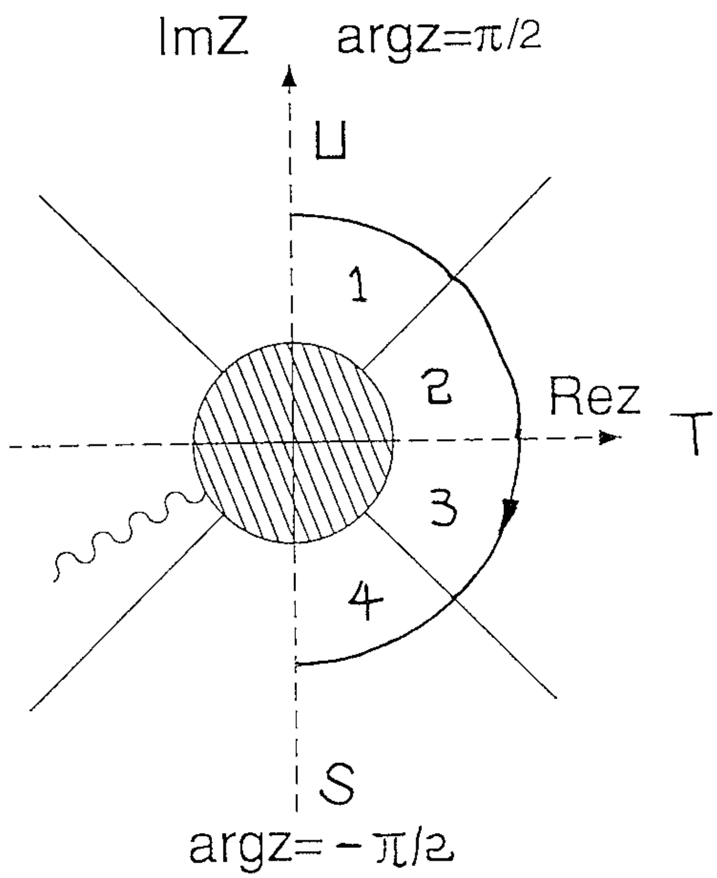



Figure 3.4.

## 3.3 Three transition points

The case (iv) discussed in the previous chapters is a typical differential equation with three transition points, which is rewritten here as

$$\frac{d^2\phi(z)}{dz^2} + (a_3 z^3 + a_1 z + a_0)\phi(z) = 0, \qquad a_3 > 0, \tag{3.59}$$

where $a_1$ and $a_0$ can be complex. By using two independent standard WKB solutions $(\bullet, z)$ and $(z, \bullet)$ shown in the case (iv) of chapter 1, the asymptotic solution on the anti-Stokes line of $\arg z = 0$ in Fig.3.5 is given by

$$\phi(z) \underset{z\to\infty}{=} A(\bullet, z) + B(z, \bullet), \tag{3.60}$$

and that on the Stokes line of $\arg z = \pi$ by

$$\phi(z) \underset{z\to-\infty}{=} C(\bullet, z)_s + D(z, \bullet)_d. \tag{3.61}$$

The connection matrix between the anti-Stokes and the Stokes lines is now defined by

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv F \begin{pmatrix} A \\ B \end{pmatrix}. \tag{3.62}$$

In order to express the connection matrix in terms of the Stokes constants, we again trace the solution (3.60) round in the complex plane of Fig.3.5, in positive sense we have

1. $A(\bullet, z)_s + B(z, \bullet)_d$,

2. $(A + BU_1)(\bullet, z)_s + B(z, \bullet)_d$,

3. $(A + BU_1)(\bullet, z)_d + B(z, \bullet)_s$,

4. $(A + BU_1)(\bullet, z)_d + [B + (A + BU_1)U_2](z, \bullet)_s$,

5. $(A + BU_1)(\bullet, z)_s + [B + (A + BU_1)U_2](z, \bullet)_d$,

and on the $\arg z = \pi$,

$$\{(A + BU_1) + [B + (A + BU_1)U_2]\tfrac{U_3}{2}\}(\bullet, z)_s + \\ [B + (A + BU_1)U_2](z, \bullet)_d. \tag{3.63}$$

Comparing this equation with Eq. (3.61), we have

$$C = A + BU_1 + [B + (A + BU_1)U_2]\frac{U_3}{2} \tag{3.64}$$

and

$$D = B + (A + BU_1)U_2. \tag{3.65}$$

Thus, the connection matrix is found to be

$$F = \begin{pmatrix} 1 + U_2U_3/2 & U_1 + (1 + U_1U_2)U_3/2 \\ U_2 & 1 + U_1U_2 \end{pmatrix}, \tag{3.66}$$

where

$$U_3 = -\frac{i + U_1}{1 + U_1U_2}. \tag{3.67}$$

This can be found from the three relations among five Stokes constants in the case (iv) of chapter 2.

The connection matrix here is defined by the standard WKB solutions, in which reference points are not specified. However, the connection matrix with other type of WKB solutions can be easily found by adding certain phase correction to Eq. (3.66). This procedure will be seen in next section for the case of four transition points.

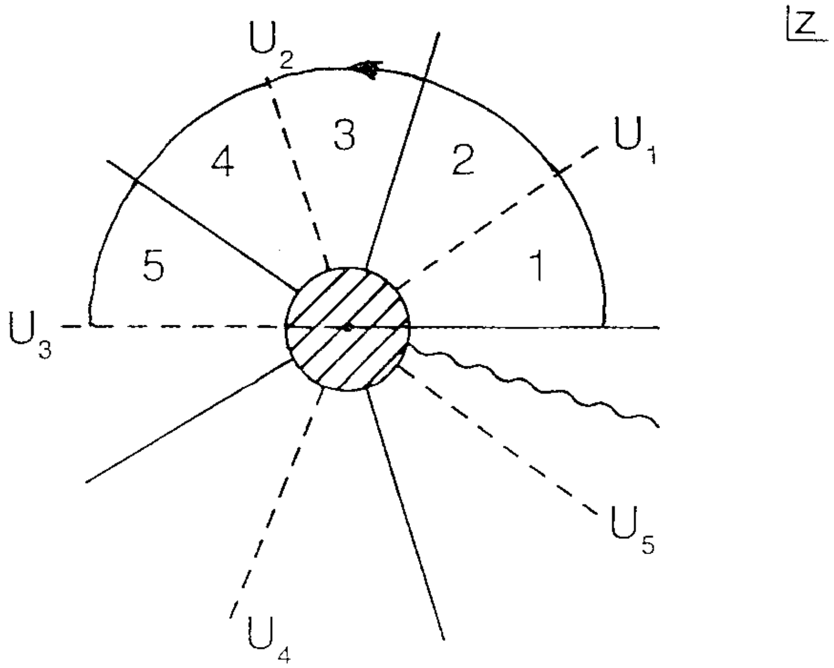



Figure 3.5.

## 3.4 Four transition points

The connection matrix for four transition points constitutes a basic framework to deal with linear curve crossing problems in Part.2 for finding both exact and semi-classical solutions of the reduced scattering matrix. Since the Stokes phenomenon of four transition points has been analyzed, we shall express the connection matrix in terms of the Stokes constants. In this section we shall first discuss the the connection matrix between two anti-Stokes lines and the connection matrix between two Stokes lines for general four-transition-point problem. Then a special distribution of four transition points will be given to illustrate how an explicit expression of the connection matrix can be obtained from the Stokes constants.

A. Connection matrix on the anti-Stokes lines

As we know from discussion of the previos chapters, the second-order differential equation with four transition points are

$$\frac{d^2\phi(z)}{dz^2} + (a_4 z^4 + a_2 z^2 + a_1 z + a_0)\phi(z) = 0, \quad a_4 > 0, \tag{3.68}$$

where $a_2$, $a_1$ and $a_0$ are complex constants. The general WKB solutions can be written as

$$\phi(z) \underset{z\to+\infty}{=} Aq^{-\frac{1}{4}}(z)\exp[i\int_{z_0}^{z} q^{\frac{1}{2}}(z)dz] + Bq^{-\frac{1}{4}}(z)\exp[-i\int_{z_0}^{z} q^{\frac{1}{2}}(z)dz] \tag{3.69}$$

and

$$\phi(z) \underset{z\to-\infty}{=} Cq^{-\frac{1}{4}}(z)\exp[i\int_{-z_0}^{z} q^{\frac{1}{2}}(z)dz] + Dq^{-\frac{1}{4}}(z)\exp[-i\int_{-z_0}^{z} q^{\frac{1}{2}}(z)dz] \tag{3.70}$$

where the reference points $z_0$ and $-z_0$ are chosen to be real and

$$q(z) = a_4 z^4 + a_2 z^2 + a_1 z + a_0. \tag{3.71}$$

The definition of connection matrix is

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv L \begin{pmatrix} A \\ B \end{pmatrix}. \tag{3.72}$$

In order to find a relation between the connection matrix and the Stokes constants, we must introduce the standard WKB solutions introduced in chapter 1,

$$\phi(z) \underset{z\to+\infty}{=} A'(\bullet, z) + B'(z, \bullet) \tag{3.73}$$

and

$$\phi(z) \underset{z\to-\infty}{=} C'(\bullet, z) + D'(z, \bullet), \tag{3.74}$$

where $(\bullet, z)$ and $(z, \bullet)$ represent the standard WKB solutions defined by

$$(\bullet, z) = z^{-1}\exp[iP(z) + i\frac{a_1}{2\sqrt{a_4}}\ln z] \tag{3.75}$$

and

$$(z, \bullet) = z^{-1}\exp[-iP(z) - i\frac{a_1}{2\sqrt{a_4}}\ln z]. \tag{3.76}$$

Here the function $P(z)$ is equal to

$$P(z) = \sqrt{a_4}(\frac{z^3}{3} + \frac{a_2}{2a_4}z), \tag{3.77}$$

and $\bullet$ simply means that the reference point (lower limit of integration) is not specified. As is shown in Fig.3.6, there are six Stokes constants associated with six Stokes lines in the asymptotic region. Let us start with a given solution $A'(\bullet, z) + B'(z, \bullet)$ on the anti-Stokes line $\arg z = 0$, in which $A'$ and $B'$ are arbitrary constants. By tracing this solution in the counter-clock wise from region 1, we obtain

1. $A'(\bullet, z)_s + B'(z, \bullet)_d$,

2. $(A' + B'U_1)(\bullet, z)_s + B'(z, \bullet)_d$,

3. $(A' + B'U_1)(\bullet, z)_d + B'(z, \bullet)_s$,

4. $(A' + B'U_1)(\bullet, z)_d + [B' + (A' + B'U_1)U_2](z, \bullet)_s$,

5. $(A' + B'U_1)(\bullet, z)_s + [B' + (A' + B'U_1)U_2](z, \bullet)_d$,

6. $\{(A' + B'U_1) + [B' + (A' + B'U_1)U_2]U_3\}(\bullet, z)_s$

$$+ [B' + (A' + B'U_1)U_2](z, \bullet)_d, \tag{3.78}$$

where the suffixes $d$ and $s$ mean dominant and subdominant as before. The last equation in Eqs. (3.78) represents a solution on the anti-Stokes line $\arg z = \pi$, on which the function in Eq. (3.74) is defined. Thus we find the following relation between $(C', D')$ and $(A', B')$:

$$\begin{aligned} \begin{pmatrix} C' \\ D' \end{pmatrix} &= \begin{pmatrix} 1 + U_2U_3 & U_1 + U_3 + U_1U_2U_3 \\ U_2 & 1 + U_1U2 \end{pmatrix} \begin{pmatrix} A' \\ B' \end{pmatrix} \\ &= \begin{pmatrix} L'_{11} & L'_{12} \\ L'_{21} & L'_{22} \end{pmatrix} \begin{pmatrix} A' \\ B' \end{pmatrix} \equiv L' \begin{pmatrix} A' \\ B' \end{pmatrix}. \end{aligned} \tag{3.79}$$

The inter-relations among six Stokes constants in the complex-$z$ plane, as discusssed in chapter 2, are rewritten as

$$(1 + U_2U_3) = (1 + U_5U_6)e^{i6\pi Q_1},$$

$$(1 + U_1U_2) = (1 + U_4U_5)e^{-i6\pi Q_1},$$

and

$$U_1 + U_3 + U_1U_2U_3 = -U_5e^{-i6\pi Q_1} \tag{3.80}$$

with

$$Q_1 = -\frac{ia_1}{6\sqrt{a_4}}. \tag{3.81}$$

These relations are very useful, but three Stokes constants still remain independent and to be determined. However, when we deal with physical problem, certain constraints of symmetry properties could give extra independent relations, as will be seen in part 2. On the other hand, in chapter 2 we developed a general procedure to express all Stokes constants in terms of only one based on the certain transformation.

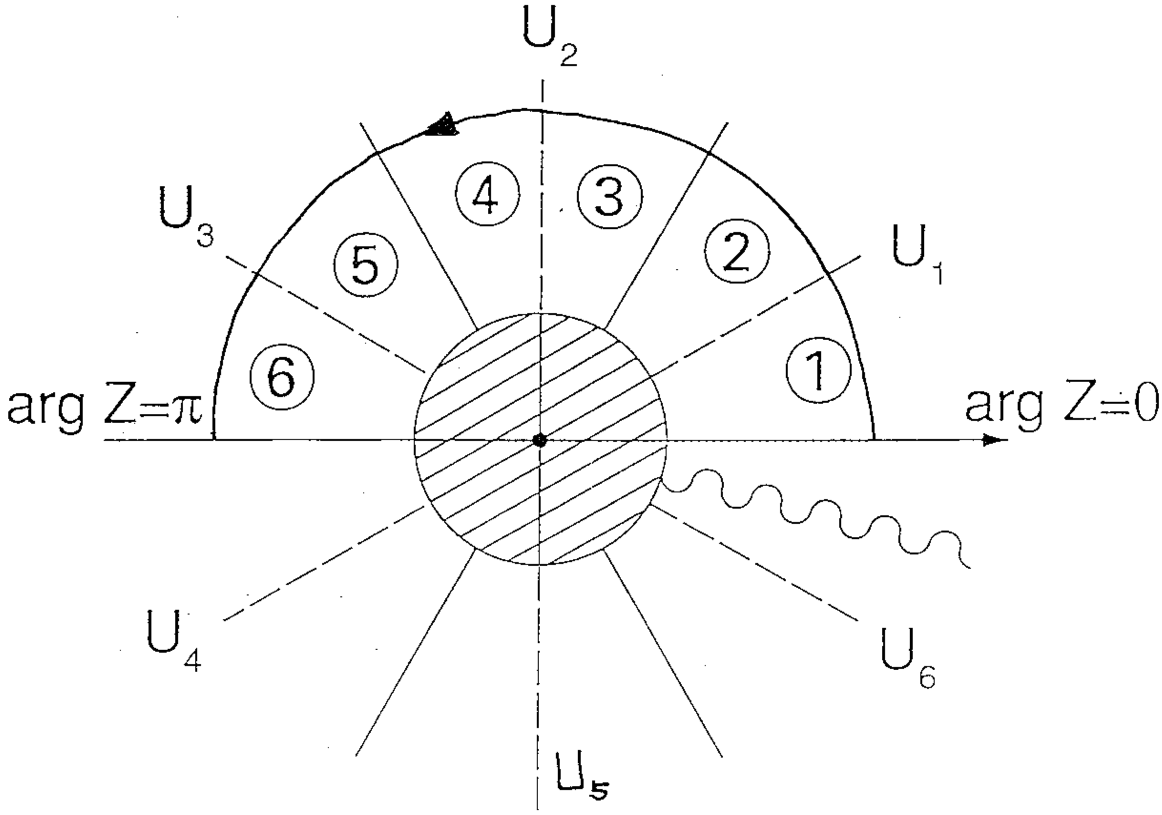



Figure 3.6.

Here we just set up a direct relation between two connection matrices $L$ and $L'$. In order to do this we calculate the phase integrals in Eqs.(3.69) and (3.70),

$$i\int_{z_0}^{z} q^{\frac{1}{2}}(z)dz \underset{z\to+\infty}{\longrightarrow} iP(z) + i\frac{a_1}{2\sqrt{a_4}}\ln z + i\delta_+(z_0) \tag{3.82}$$

and

$$i\int_{-z_0}^{z} q^{\frac{1}{2}}(z)dz \underset{z\to-\infty}{\longrightarrow} iP(z) + i\frac{a_1}{2\sqrt{a_4}}\ln z + i\delta_-(z_0) \tag{3.83}$$

where $\delta_\pm(z_0)$ are constants which are dependent on the reference point $z_0$ and on the coefficients $a_j$ in Eq. (3.68). Comparison of Eqs. (3.69) and (3.70) with Eqs. (3.73) and (3.74) with use of Eqs. (3.82) and (3.83) finally leads to

$$L = e^{-i\pi}\begin{pmatrix} L'_{11}e^{-i\delta_-+i\delta_+} & L'_{12}e^{-i\delta_--i\delta_+} \\ L'_{21}e^{i\delta_-+i\delta_+} & L'_{22}e^{i\delta_--i\delta_+} \end{pmatrix}. \tag{3.84}$$

It should be emphasized that $\delta_\pm(z_0)$ in Eqs.(3.82) and (3.83) plays an important role for determining the connection matrix; but in chapter 4 when we deal with the exact expression of reduced scattering matrix, and they can be eliminated in the final results.

## B. Connection matrix on the Stokes lines

Now we turn to describe a general procedure of connecting solutions on the Stokes lines for the differential equation (3.68). The connection should be made from $z \to \infty e^{i\pi/2}$ to $z \to \infty e^{-i\pi/2}$. Asymptotic solutions are written as

$$\phi(z) \underset{z \to \infty e^{i\pi/2}}{\longrightarrow} A(z_0, z)_d + B(z, z_0)_s \tag{3.85}$$

and

$$\phi(z) \underset{z \to \infty e^{-i\pi/2}}{\longrightarrow} C(-z_0, z)_s + D(z, -z_0)_d, \tag{3.86}$$

where $(z', z'')$ is

$$(z', z'') = q^{-1/4}(z) \exp[i \int_{z'}^{z''} q^{1/2}(z) dz]. \tag{3.87}$$

Here, the reference points $z_0$ and $-z_0$ are chosen to be pure imaginary. The connection matrix (denoted as $G$) is defined by

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv G \begin{pmatrix} A \\ B \end{pmatrix}. \tag{3.88}$$

In order to express the matrix $G$ in terms of the Stokes constants, we again use standard WKB solutions ,

$$\phi(z) \underset{z \to \infty e^{i\pi/2}}{\longrightarrow} A'(\bullet, z)_d + B'(z, \bullet)_s \tag{3.89}$$

and

$$\phi(z) \underset{z \to \infty e^{3i\pi/2}}{\longrightarrow} C'(\bullet, z)_s + D'(z, \bullet)_d. \tag{3.90}$$

It should be noted that the argument of $z$ in Eq. (3.90) is taken to be $3\pi/2$ because of a branch cut shown in Fig.3.7. Let us start with a solution in Eq. (3.89) on the Stokes line $\arg z = \pi/2$ with arbitrary constants $A'$ and $B'$ and trace this solution in the counter-clock wise to the Stokes line $\arg z = 3\pi/2$. Then, we have

4. $A'(\bullet, z)_d + (B' + U_2 A'/2)(z, \bullet)_s,$

5. $A'(\bullet, z)_s + (B' + U_2 A'/2)(z, \bullet)_d,$

6. $[A' + U_3(B' + U_2 A'/2)](\bullet, z)_s + (B' + U_2 A'/2)(z, \bullet)_d,$

7. $[A' + U_3(B' + U_2 A'/2)](\bullet, z)_d + (B' + U_2 A'/2)(z, \bullet)_s,$

8. $[A' + U_3(B' + U_2 A'/2)](\bullet, z)_d + \{(B' + U_2 A'/2) + U_4[A' + U_3(B' + U_2 A'/2)]\}(z, \bullet)_s,$

9. $[A'+U_3(B'+U_2A'/2)](\bullet,z)_s+\{(B'+U_2A'/2)+U_4[A'+U_3(B'+U_2A'/2)]\}(z,\bullet)_d$,

and on the Stokes line $\arg z = 3\pi/2$:

$$\begin{aligned}\Big\{A' &+ U_3(B'+U_2A'/2)+\frac{U_5}{2}\{(B'+U_2A'/2)\\ &+ U_4[A'+U_3(B'+U_2A'/2)]\}\Big\}(\bullet,z)_s\\ &+ \{B'+U_2A'/2+U_4[A'+U_3(B'+U_2A'/2)]\}(z,\bullet)_d. \end{aligned} \tag{3.91}$$

Comparing this equation with Eq. (3.90) and using the relations among the Stokes constants given in Eqs. (3.80), we obtain

$$\begin{pmatrix} C' \\ D' \end{pmatrix} = G' \begin{pmatrix} A' \\ B' \end{pmatrix}, \tag{3.92}$$

where

$$G' = \begin{pmatrix} [(2+U_3U_2)+(2+U_1U_2)e^{6\pi i Q_1}]/4 & [U_3-U_1e^{6\pi iQ_1}]/2 \\ [U_4-U_6e^{6\pi iQ_1}]/2 & 1+U_3U_4 \end{pmatrix} \tag{3.93}$$

with

$$Q_1 = -\frac{ia}{6\sqrt{a_4}}. \tag{3.94}$$

It should be noted that the Jeffreys' connection rule has been used again on the Stokes lines $\arg z = \pi/2$ and $3\pi/2$. Now, we can establish a relation between the two connection matrices $G$ in Eq. (3.88) and $G'$ in Eq. (3.93) by evaluating the phase-integrals of Eq. (3.87) as

$$\int_{z_0}^{z} q^{1/2}(z)dz \underset{z\to\infty e^{i\pi/2}}{\longrightarrow} P(z)+\frac{a_1}{2\sqrt{a_4}}\ln z+\Delta_+(z_0) \tag{3.95}$$

and

$$\int_{-z_0}^{z} q^{1/2}(z)dz \underset{z\to\infty e^{-i\pi/2}}{\longrightarrow} P(z)+\frac{a_1}{2\sqrt{a_4}}\ln z+\Delta_-(z_0), \tag{3.96}$$

where

$$P(z) = \sqrt{a_4}\left(\frac{z^3}{3}+\frac{a_2}{2a_4}z\right), \tag{3.97}$$

and $\Delta_\pm(z_0)$ are constants dependent upon the reference point $z_0$ and the coefficients $a_j$ in Eq. (3.68). Then, a comparison of Eqs. (3.85) and (3.86) with Eqs. (3.89) and (3.90) leads to

$$G = e^{-i\pi}\begin{pmatrix} G'_{11}e^{i\Delta_1} & G'_{12}e^{-i\Delta_2} \\ G'_{21}e^{i\Delta_2} & G'_{22}e^{-i\Delta_1} \end{pmatrix}, \tag{3.98}$$

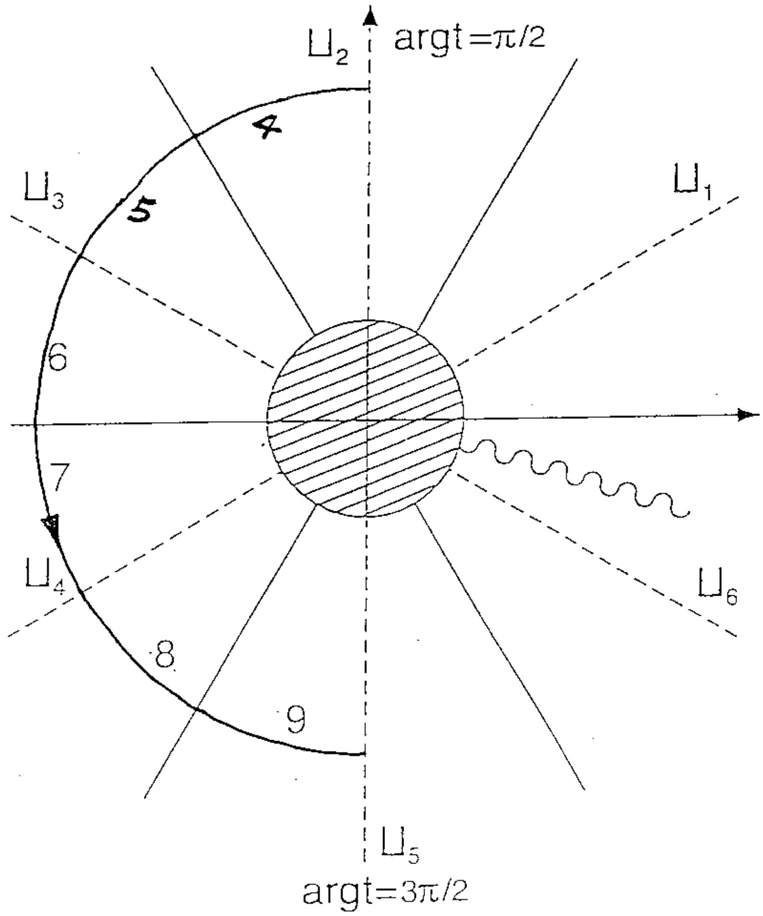


Figure 3.7.

where

$$\Delta_1 = \Delta_+ - \Delta_- - i\pi a_1/\sqrt{a_4} \tag{3.99}$$

and

$$\Delta_2 = \Delta_+ + \Delta_- + i\pi a_1/\sqrt{a_4} \tag{3.100}$$

It should be noted that the additional terms $\pm\pi a_1/\sqrt{a_4}$ come from a difference in the branch cut used for the solutions Eq. (3.86) and Eq.(3.90).

**C. Example for $q(z) = a_4 z^4 + a_1 z$**

In order to demonstrate the procedure how to obtain connection matrix in the case of four transition points, let us take $a_2 = a_0 = 0$ in Eq. (3.68) as a special distribution of four transition points in Fig.3.8, in which one of the zeros $z_0$ is located at origin and the others are symmetrically distributed on a circle. For the corresponding differential equation

$$\frac{d^2\phi(z)}{dz^2} + (a_4 z^4 + a_1 z)\phi(z) = 0, \tag{3.101}$$

the Stokes constants can be solved exactly in compact form by transforming this equation to the complex-$\xi$ plane as the Whittaker equation[2]. By directly applying

Eq. (3.84) to this special case, the connection matrix from $z \to \infty$ to $z \to -\infty$ can be given in the following way:

$$L_0 = e^{-i\pi} \begin{pmatrix} (1 + U_2^0 U_3^0) e^{-i(\delta_-^0 - \delta_+^0)} & (U_1^0 + U_3^0 + U_1^0 U_2^0 U_3^0) e^{-i(\delta_-^0 + \delta_+^0)} \\ U_2^0 e^{i(\delta_-^0 + \delta_+^0)} & (1 + U_1^0 U_2^0) e^{i(\delta_-^0 - \delta_+^0)} \end{pmatrix}, \tag{3.102}$$

where the Stokes constants $U_i$ have been replaced by $U_i^0$, and $i\delta_+^0$ and $i\delta_-^0$ are defined by

$$i \int_0^z \sqrt{a_4 z^4 + a_1 z} dz \underset{z \to +\infty}{\longrightarrow} i\sqrt{a_4}\frac{z^3}{3} + i\frac{a_1}{2\sqrt{a_4}} \ln z + i\delta_+^0 \tag{3.103}$$

and

$$i \int_0^z \sqrt{a_4 z^4 + a_1 z} dz \underset{z \to -\infty}{\longrightarrow} i\sqrt{a_4}\frac{z^3}{3} + i\frac{a_1}{2\sqrt{a_4}} \ln z + i\delta_-^0. \tag{3.104}$$

These can be exactly calculated as follows:

$$\delta_+^0 = \delta_-^0 = i[\frac{a_1}{6\sqrt{a_4}} - \frac{a_1}{3\sqrt{a_4}} \ln(\frac{1}{2}\sqrt{\frac{a_1}{a_4}})], \tag{3.105}$$

in which we have used the indefinite integral formula,

$$\int \sqrt{z^4 + az} dz = \frac{1}{3} z\sqrt{z^4 + az} + \frac{a}{3} \ln(z^{3/2} + \sqrt{z^3 + a}). \tag{3.106}$$

By using the general method in the case (iii) of chapter 2, we can first relate the Stokes constants $U_1^0, U_2^0$ and $U_3^0$ in the complex-$z$ plane to the Stokes constants $T_1^0, T_2^0$ and $T_3^0$ in the complex-$\xi$ plane, and then express all $T_i^0$ in terms of $T_1^0$, so that we have

$$U_1^0 = T_1(Q_1)(\frac{2i}{3}\sqrt{a_4})^{-2Q_1}, \tag{3.107}$$

$$U_2^0 = T_1(-Q_1)e^{-2i\pi Q_1}(\frac{2i}{3}\sqrt{a_4})^{2Q_1}, \tag{3.108}$$

and

$$U_3^0 = T_1(Q_1)e^{4i\pi Q_1}(\frac{2i}{3}\sqrt{a_4})^{-2Q_1}, \tag{3.109}$$

where $T_1(Q_1)$ is given in the compact form[2]

$$T_1(Q_1) = \frac{2\pi i e^{2\pi i Q_1}}{\Gamma(\frac{1}{3} - Q_1)\Gamma(\frac{2}{3} - Q_1)} \tag{3.110}$$

with

$$Q_1 = -\frac{ia_1}{6\sqrt{a_4}}. \tag{3.111}$$

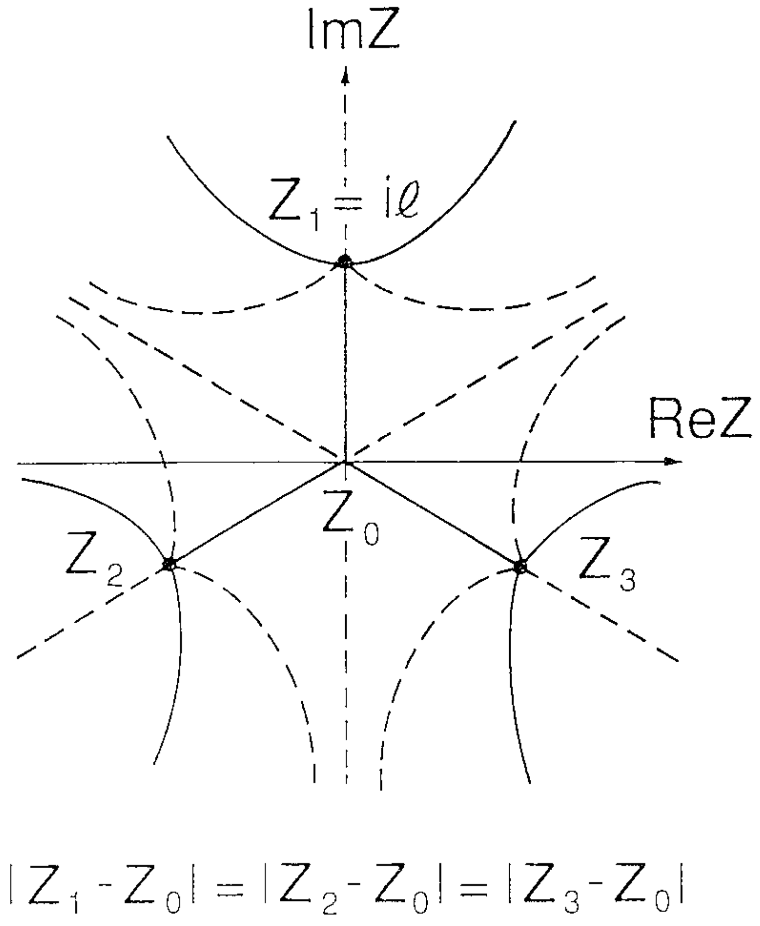



Figure 3.8.

Above equations lead to the final expression of $L_0$,

$$L_0 = e^{-i\pi} \begin{pmatrix} 1 - e^{2\pi i Q_1}[1 + 2\cos(2\pi Q_1)] & -\frac{2\pi i Q_1^{-2Q_1} e^{2\pi i Q_1 + 2Q_1}}{\Gamma(1/3 - Q_1)\Gamma(2/3 - Q_1)} \\ \frac{2\pi i Q_1^{2Q_1} e^{-2\pi i Q_1 - 2Q_1}}{\Gamma(1/3 + Q_1)\Gamma(2/3 + Q_1)} & 1 - e^{-2\pi i Q_1}[1 + 2\cos(2\pi Q_1)] \end{pmatrix}. \quad (3.112)$$

This is the explicit expression of the connection matrix between the anti-Stokes lines $\arg z = 0$ and $\arg z = \pi$ for this special four-transition-point distribution. We can apply Eq. (3.98) to this special case, the connection matrix between the Stokes lines $\arg z = \pi/2$ and $\arg z = -\pi/2$ can be also derived.

# PART 2. TWO-STATE LINEAR CURVE CROSSING PROBLEMS

As is well known, the Born-Oppenheimer adiabatic approximation, which is a separation of electronic and nuclear motions, has been proved to be a very useful approximation. As long as adiabatic potential energy surfaces remain well separated from one another, it is generally a good approximation to consider the nuclear motion to be confined onto one such surface. When two or more such surfaces intersect, or come close together, or when nuclear speeds are very high, however, transitions take place among such surfaces. These transitions are called nonadiabatic transitions which occur in various atomic and molecular dynamic processes such as atomic collisions, chemical reactions and spectroscopic processes[23−28].

A study of nonadiabatic transition has a long history with development of a host of classical, semiclassical and quantum mechanical approaches[23—86]. An analytical treatment is mostly based on the semiclassical theory which has been well developed for the one-dimensional two-state problems. As is well known, the nonadiabatic transition occurs most effectively at avoided crossings where the two adiabatic states come close together. This fact leads to the most basic and simplest model, i.e., the system of two linear diabatic potentials and constant coupling between them. However, this is not merely a hypothetical model, but can give a good basis for generalization. Analytical formulas in this model can be generalized to the cases of more realistic potentials. The two-state theories can also be applied even to multistate systems thanks to the localizability of nonadiabatic transitions[28]. The linear curve crossing problem is classified into the following two cases: (1) the same sign of slopes of the two diabatic potential curves, and (2) the opposite sign of slopes[23]. The first case is called "Landau-Zener case", and the second "nonadiabatic tunneling case" which presents a quantum mechanical tunneling accompanied by nonadiabatic transition.

Exact numerical quantal solutions for the two-states coupled differential equations with general realistic potentials are not difficult at all; but those for the linear potential problems are troublesome, because the diabatic potentials linearly diverge asymptotically and the coupling constant does not die out. Delos and Thorson treated the first case(the same sign of slopes) successfully by moving into the adiabatic-state representation in momentum space[62]. In the case of nonadiabatic tunneling, however, there appear singularities on the real axis in the adiabatic representation. Eldsberg and Oppelstrup tired to solve the coupled equations in diabatic-state representation, but their results can not be free from instability[65].

Exact analytical quantal solutions for the two-state linear curve crossing problems were tried by Bárány[63] for the first case, later by Coveney[64] for the second case. It was realized that the exact analytical solutions should involve certain unknown constants—Stokes constants. This was noticed to be a very difficult mathematical problem.

The semiclassical treatment for the two-state linear curve crossing problems was firstly proposed by Landau[29], Zener[30] and Stückelberg[68], and subsequently analyzed by many authors[61 − 68 , 73 − 78]. The analytical formulas developed so far for the scattering matrix, roughly speaking, work all right when the collision energy is higher than the crossing point of two diabatic potential curves, but they can not work at enegies lower than the crossing point.

Part 2 in this thesis will actually deal with those unsolved problems mentioned above, and successfully solve them for the first time.

# Chapter 4

# Exact quantal solutions of scattering matrices

There have been a long history about the study of classic two-state linear curve crossing problems since Landau, Zener and Stueckelberg. There are the following two cases: (1) the same sign of slopes of two diabatic potentials(Landau-Zener case), and (2) the opposite sign of slopes(nonadiabatic tunneling case). The problems were formulated to solving reduced scattering matrices which are well known to be described in terms of the two parameters $a^2$(effective coupling strength) and $b^2$(effective collision energy). Finding the exact analytical quantal solutions for the reduced scattering matrices is very challenging and a very difficult question. The answer to this question is given in this chapter. On the other hand, a new numerical method will be presented for the case of the opposite sign of slopes.

## 4.1 Introduction

Since the pioneering works done by Landau, Zener and Stueckelberg on the two-state curve crossing problem, numerous papers have been devoted to this subject[23]–[28]. This problem presents a very basic interesting mechanism of state change, and its semiclassical theory has a long history and can provide elegant analytical formulations[23]–[28]. As is well known, the dynamics of many atomic and molecular processes occur most effectively at avoided crossings where two adiabatic states come close together. This non-adiabatic transition presents a very wide interdisciplinary concept, and plays a very important role to cause a change of state in various fields of physics and chemistry, presumably even in biology[28].

The most basic and simplest model is, of course, the system of two linear diabatic potentials and a constant coupling between them. However, this is not merely one of the hypothetical models, but can give a good basis for generalization. The analytical formulas in this model can be generalized to the cases of more realistic potentials. The two-state theories can also be applied even to multi-state systems thanks to the localizability of non-adiabatic transitions[60]. The linear curve crossing problem is classified into the following two cases: (1) the same sign of slopes of the two diabatic potential curves, and (2) the opposite sign of slopes[61].

The scattering matrices for two-state curve crossing problems can be decomposed into a product of two parts[62], one of them is an elastic scattering phase shift that is easily evaluated for realistic potential, but divergent for linear potential, another part which is well defined for both realistic and linear potentials is called the reduced scattering matrix, namely $S^R$. To find out exact quantal solutions of the reduced scattering matrices for both cases mentioned above is our central topic in this chapter.

A work in finding an exact analytical solution for $S^R$ was tried by Bárány[63] in the case (1), later by Coveney[64] in the case (2). It was realized that the exact analytical solutions for both cases were involved in the certain unknown constants—Stokes constants. This is a very difficult mathematical problem.

We shall first gives a brief introduction about how the linear curve crossing problems are reduced to solutions of the second-order ordinary differential equations with quartic polynomials as coefficient functions, and the reduced scattering matrices $S^R$ satisfy extra symmetries in addition to unitarity. Since the connection matrix and Stokes constants of this differential equation have been investigated in the previous chapters in a general four-transition-point problem, its application then will show that the reduced scattering matrix in each case is exactly expressed in terms of one Stokes constant $U_1$ which is finally given analytically by a convergent infinite series.

Finally, we will report a numerical method for finding solution of $S^R$ in the case (2). Exact numerical solutions for general nonlinear realistic potentials are not difficult at all, but those of the linear potential problems are somewhat troublesome, because the diabatic potentials linearly diverge asymptotically besides the coupling constant does not die out. Delos and Thorson treated the case (1) (the case of the same sign of slopes), successfully by moving into the adiabatic-state representation in momen um s ace[ ]. In he case ( ), however, here a ear sin ulari ies on he real axis in he adiaba ic re resen a ion and i is ver difficul o ob ain exac numerical resul s. Eldsber and O els ru ried o solve he cou led e uations in the diabatic state representation, but their results can not be free from instability[65]. Their transition probabilities are sometimes even larger than unity. As far as we know, there is no reliable numerical method available for this second case. So, it is still worthwhile to have a method for obtaining exact numerical results for the case (2), considering the importance of the linear potential model which can give a good basis for a general potential case.

## 4.2 Preliminaries——

### Basic differential equations and symmetries of reduced scattering matrices

The basic equations of the two-state linear curve crossing model in the diabatic-state representation are given by[61]

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1(x)}{dx^2}+[V_{11}(x)-E]\psi_1(x)=-V_{12}(x)\psi_2(x) \tag{4.1}$$

and

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2(x)}{dx^2}+[V_{22}(x)-E]\psi_2(x)=-V_{21}(x)\psi_1(x), \tag{4.2}$$

where $m$ is the particle mass, the coordinate $x$ is defined in the range $-\infty < x < \infty$, and the collision energy $E$ can be either positive or negative measured from the crossing point. In this chapter we consider the case of linear potentials and constant coupling,

$$\begin{aligned} V_{11}(x) &= -F_1 x, \\ V_{22}(x) &= -F_2 x, \\ &\text{and} \\ V_{12}(x) &= V_{21}(x) = A > 0. \end{aligned} \tag{4.3}$$

Without loss of generality, it is assumed throughout this chapter that $F_1 > 0$ and $F_1 > F_2$. The case $F_1F_2 > 0$ corresponds to the system in which the two terms

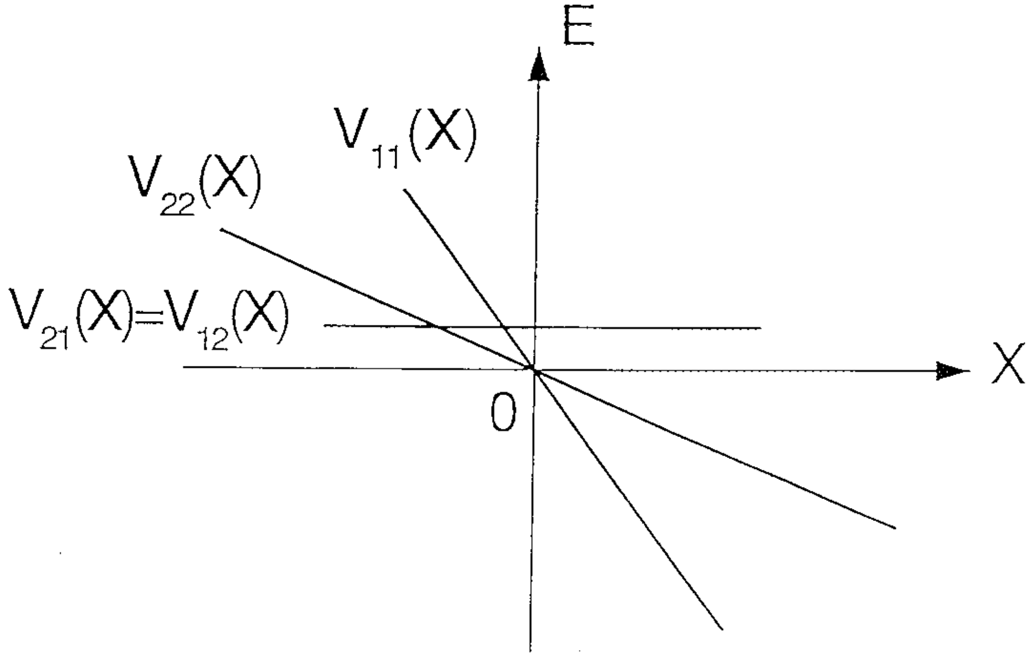



Figure 4.1: Linear curve crossing: same sign of slopes.

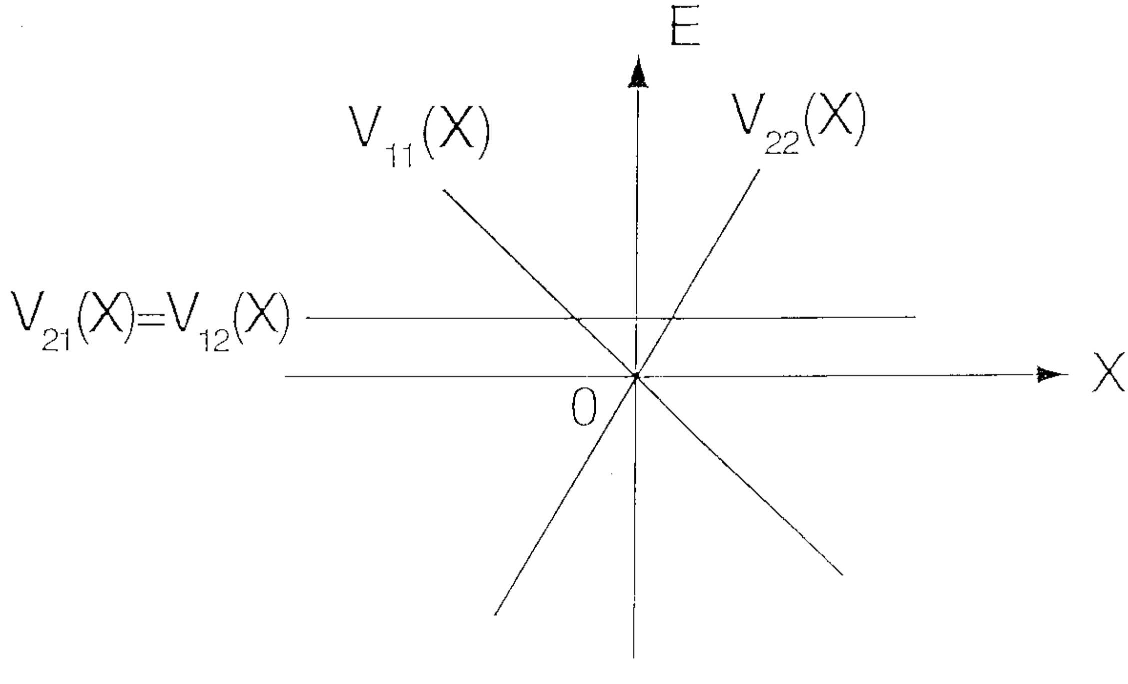



Figure 4.2: Linear curve crossing: opposite sign of slopes.

$V_{11}(x)$ and $V_{22}(x)$ intersect with the same sign of slopes in Fig.4.1, and the case $F_1F_2 < 0$ to the intersection with opposite sign of slopes in Fig.4.2.

It is well known that by using the Fourier transformation,

$$\psi_i(x) = (2\pi)^{-1} \int_{-\infty}^{+\infty} u_i(k) e^{ikx} dk, \quad i = 1, 2, \tag{4.4}$$

the second-order coupled differential equations (4.1) and (4.2) can be reduced to the first-order coupled equations in the momentum space as[26, 61]

$$(k^2 - \epsilon - if_1 \frac{d}{dk}) u_1(k) = -\alpha u_2(k) \tag{4.5}$$

and

$$(k^2 - \epsilon - if_2 \frac{d}{dk}) u_2(k) = -\alpha u_1(k), \tag{4.6}$$

where

$$\begin{aligned} \epsilon &= \frac{2mE}{\hbar^2}, \\ f_i &= \frac{2mF_i}{\hbar^2}, \\ \text{and} & \\ \alpha &= \frac{2mA}{\hbar^2}, \quad i = 1, 2. \end{aligned} \tag{4.7}$$

Further simplification is made by using the transformation,

$$u_i(k) = \sqrt{\frac{2}{|f_i|}} A_i(k) \exp[\frac{i}{f_i}(\epsilon k - k^3/3)] \quad i = 1, 2, \tag{4.8}$$

and by introducing the dimensionless variable $t$ and parameters $a^2$ and $b^2$ defined by

$$t = \left(\frac{2\alpha}{f}\right) k, \tag{4.9}$$

$$a^2 = f(f_1 - f_2)/8\alpha^3 \quad \text{and} \quad b^2 = \epsilon(f_1 - f_2)/2\alpha f \tag{4.10}$$

with

$$f = (f_1 |f_2|)^{1/2}. \tag{4.11}$$

Since the two cases ($f_1 f_2 > 0$ and $f_1 f_2 < 0$) require different treatments, we consider them separately. Although in this chapter we employ the above two parameters $a^2$ and $b^2$ introduced by Child[61], these are directly related to $\beta$ and $\epsilon$ introduced by Nikitin and coworkers[66] : the relationships are $a^2 = 1/\beta^2$ and $b^2 = \epsilon$.

**A. Same sign of slopes:** $f_1 f_2 > 0$

From Eqs. (4.5), (4.6) and (4.8) we can easily obtain the following coupled equations:

$$\frac{dA_1(t)}{dt} = -\frac{i}{2}A_2(t)\exp[-i(a^2t^3/3 - b^2t)] \tag{4.12}$$

and

$$\frac{dA_2(t)}{dt} = -\frac{i}{2}A_1(t)\exp[i(a^2t^3/3 - b^2t)]. \tag{4.13}$$

Elimination of $A_2(t)$ results in

$$\frac{d^2A_1(t)}{dt^2} + i(a^2t^2 - b^2)\frac{dA_1(t)}{dt} + \frac{1}{4}A_1(t) = 0, \tag{4.14}$$

and with further substitution

$$A_1(t) = B_1(t)\exp[-\frac{i}{2}(\frac{a^2t^3}{3} - b^2t)], \tag{4.15}$$

we obtain finally

$$\frac{d^2B_1(t)}{dt^2} + q(t)B_1(t) = 0, \tag{4.16}$$

where

$$q(t) = \frac{1}{4} - ia^2t + \frac{1}{4}(a^2t^2 - b^2)^2. \tag{4.17}$$

It is known that the scattering matrix $S$ in the semiclassical context is conveniently written as[62]

$$S_{mn} = S^R_{mn}\exp[i(\eta_m + \eta_n)], \tag{4.18}$$

where $\eta_m$ and $\eta_n$ represent semiclassical phase shifts for elastic scattering. Since we deal with the functions $A_1(t)$ and $A_2(t)$ in this chapter, $S^R$ and $\eta$ are defined in the diabatic-state representation. The matrix $S^R$ is called reduced scattering matrix and contains all the necessary information about the nonadiabatic transition. In the present case $S^R$ is defined by

$$\begin{pmatrix} A_1(+\infty) \\ A_1(+\infty) \end{pmatrix} = \begin{pmatrix} S^R_{11} & S^R_{12} \\ S^R_{21} & S^R_{22} \end{pmatrix} \begin{pmatrix} A_1(-\infty) \\ A_2(-\infty) \end{pmatrix} \tag{4.19}$$

Furthermore, we can prove that the matrix $S^R$ satisfies the following symmetries in addition to unitarity:

$$S^R_{11} = (S^R_{22})^* \quad \text{and} \quad S^R_{12} = S^R_{21} = \text{pure imag.} \tag{4.20}$$

These directly come from the properties of the evolution matrix $F(z, z_0)$ defined by

$$\begin{pmatrix} A_1(z) \\ A_2(z) \end{pmatrix} = F(z, z_0) \begin{pmatrix} A_1(z_0) \\ A_2(z_0) \end{pmatrix} \tag{4.21}$$

These properties are

$$S^R = F(+\infty, -\infty), \tag{4.22}$$

$$\det F(z, z_0) = 1, \tag{4.23}$$

$$F(x, x_0) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} F^*(x, x_0) \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \tag{4.24}$$

and

$$F(-x, 0) = F^*(x, 0). \tag{4.25}$$

**B. Opposite sign of slopes: $f_1 f_2 < 0$**

In this case Eqs. (4.5), (4.6) and (4.8) give

$$\frac{dA_1(t)}{dt} = -\frac{i}{2} A_2(t) \exp[i(a^2t^3/3 - b^2t)] \tag{4.26}$$

and

$$\frac{dA_2(t)}{dt} = \frac{i}{2} A_1(t) \exp[-i(a^2t^3/3 - b^2t)]. \tag{4.27}$$

Elimination of $A_2(t)$ results in

$$\frac{d^2 A_1}{dt^2} - i(a^2t^2 - b^2)\frac{dA_1}{dt} - \frac{1}{4} A_1 = 0 \tag{4.28}$$

and with the substitution

$$A_1(t) = B_1(t) \exp[\frac{i}{2}(\frac{a^2t^3}{3} - b^2t)] \tag{4.29}$$

we finally obtain

$$\frac{d^2 B_1}{dt^2} + q(t) B_1(t) = 0, \tag{4.30}$$

where

$$q(t) = -\frac{1}{4} + ia^2t + \frac{1}{4}(a^2t^2 - b^2)^2. \tag{4.31}$$

The reduced scattering matrix in this case is defined by

$$\begin{pmatrix} A_1(+\infty) \\ A_2(-\infty) \end{pmatrix} = \begin{pmatrix} S_{11}^R & S_{12}^R \\ S_{21}^R & S_{22}^R \end{pmatrix} \begin{pmatrix} A_1(-\infty) \\ A_2(+\infty) \end{pmatrix}, \tag{4.32}$$

where $A_1(\pm\infty)$ and $A_2(\pm\infty)$ are obtained from Eqs. (4.26) and(4.27). The off-diagonal elements of $S^R$ represent non-adiabatic tunneling. Coveney et al derived the properties of the evolution matrix $F$ defined by Eq.(4.21)[67]. They are

$$F(x, x_0) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} F^*(x, x_0) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{4.33}$$

$$\det F(z, z_0) = 1, \tag{4.34}$$

$$F(-x, 0) = F^*(x, 0). \tag{4.35}$$

From these properties we can show

$$F_{22}(+\infty, -\infty) = F_{11}^*(+\infty, -\infty) \tag{4.36}$$

and

$$F_{21}(+\infty, -\infty) = -F_{12}(+\infty, -\infty) = \text{pure imaginary}. \tag{4.37}$$

Finally, the reduced scattering matrix is proved to be given by

$$S_{11}^R = S_{22}^R = 1/F_{22}(+\infty, -\infty) \tag{4.38}$$

and

$$S_{12}^R = S_{21}^R = F_{12}(+\infty,\ -\infty)/F_{22}(+\infty,\ -\infty). \tag{4.39}$$

The unitarity of $S^R$ further requires

$$|F_{11}(+\infty, -\infty)|^2 + |F_{12}(+\infty, -\infty)|^2 = 1. \tag{4.40}$$

## 4.3 The reduced scattering matrices $S^R$ in terms of the Stokes constants $U_1$

The connection matrix $L$ of Eq. (3.72) for a general four-transition-point problem has been discussed in chapter 3. Our basic differential equations (4.16) and (4.30), for the same and opposite signs of slopes respectively, are special four-transition-point problems. Its evolution matrix $F(+\infty, -\infty)$ of Eq. (4.21) essentially represents the reduced scattering matrix $S^R$. We first establish a relation between the connection matrix $L$ and the evolution matrix $F(+\infty, -\infty)$, and then $S^R$ can be finally expressed in terms of one Stokes constant. Let us start with asymptotic solutions of the function $B_1(t)$ of Eqs. (4.16) and (4.30) (see Eq. (3.68) ):

$$B_1(t) \underset{t\to+\infty}{\longrightarrow} Aq^{-\frac{1}{4}}(t)\exp[iQ^+(t)] + Bq^{-\frac{1}{4}}(t)\exp[-iQ^+(t)] \tag{4.41}$$

and

$$B_2(t) \underset{t\to-\infty}{\longrightarrow} Cq^{-\frac{1}{4}}(t)\exp[iQ^-(t)] + Dq^{-\frac{1}{4}}(t)\exp[-iQ^-(t)], \tag{4.42}$$

where

$$Q^+(t) = \frac{1}{2}P(t) \pm \ln t + \delta_+(t_0) \tag{4.43}$$

and

$$Q^-(t) = \frac{1}{2}P(t) \pm \ln t + \delta_-(t_0) \tag{4.44}$$

with

$$P(t) = \frac{a^3}{3}t^3 - b^2 t. \tag{4.45}$$

The positive and negative signs in front of $\ln t$ in Eqs. (4.43) and (4.44) corresponds to the same sign of slopes and the opposite sign of slopes, respectively.

**A. Same sign of slopes: $f_1 f_2 > 0$**

Since from Eqs.(4.15) and (4.12) we have

$$A_1(t) = B_1(t)\exp[-\frac{i}{2}P(t)] \tag{4.46}$$

and

$$A_2(t) = \left[2i\frac{dB_1(t)}{dt} + \frac{dP(t)}{dt}B_1(t)\right]\exp\left[\frac{i}{2}P(t)\right], \tag{4.47}$$

we can easily prove

$$A_1(+\infty) = \lim_{t\to+\infty} B_1(t)\exp\left[-\frac{1}{2}P(t)\right] = A\sqrt{\frac{2}{a^2}}e^{i\delta_+(t_0)} \tag{4.48}$$

and

$$\begin{aligned} A_2(+\infty) &= \lim_{t\to+\infty}\left\{A\left[-2q^{\frac{1}{4}}(t) + \frac{dP(t)}{dt}q^{-\frac{1}{4}}(t)\right]\exp\left[iQ^+(t)\right]\right. \\ &+ \left. B\left[2q^{\frac{1}{4}}(t) + \frac{dP(t)}{dt}q^{-\frac{1}{4}}\right]\exp\left[-iQ^+(t)\right]\right\}e^{\frac{i}{2}P(t)} \\ &= B2\sqrt{2a^2}e^{-i\delta_+(t_0)}. \end{aligned} \tag{4.49}$$

In the same way we can show

$$A_1(-\infty) = Ce^{i\delta_-}\sqrt{\frac{2}{a^2}}e^{-i\pi} \tag{4.50}$$

and

$$A_2(-\infty) = D2\sqrt{2a^2}e^{-i\delta_-}e^{i\pi}. \tag{4.51}$$

Thus from Eqs. (3.72) and (3.84) we obtain the evolution matrix $F(+\infty, -\infty)$,

$$\begin{aligned}\begin{pmatrix} A_1(+\infty) \\ A_2(+\infty) \end{pmatrix} &= \begin{pmatrix} L_{22}e^{i\delta_+ - i\delta_-} & -L_{12}\frac{1}{2a^2}e^{i\delta_+ + i\delta_-} \\ -L_{21}(2a^2)e^{-i\delta_+ - i\delta_-} & L_{11}e^{-i\delta_+ + i\delta_-} \end{pmatrix} e^{i\pi} \begin{pmatrix} A_1(-\infty) \\ A_2(-\infty) \end{pmatrix} \\ &= \begin{pmatrix} 1 + U_1U_2 & -(U_1 + U_3 + U_1U_2U_3)\frac{1}{2a^2} \\ -2a^2U_2 & 1 + U_2U_3 \end{pmatrix} \begin{pmatrix} A_1(-\infty) \\ A_2(-\infty) \end{pmatrix}.\end{aligned} \tag{4.52}$$

The symmetry properties of Eq. (4.20) give the following two additional equations among the Stokes constants:

$$2a^2U_2 = (U_1 + U_3 + U_1U_2U_3)\frac{1}{2a^2} = \text{pure imaginary}, \tag{4.53}$$

and

$$U_3 = -U_1^*. \tag{4.54}$$

Since we already have three equations among $U_i$ as given in Eqs. (3.80), the reduced scattering matrix $S^R$ can be finally simplified to the following expressions in terms of only one Stokes constant $U_1$:

$$S^R = \begin{pmatrix} 1 + U_1U_2 & -2a^2U_2 \\ -2a^2U_2 & 1 - U_1^*U_2 \end{pmatrix}, \tag{4.55}$$

where

$$U_2 = \frac{U_1 - U_1^*}{4a^4 + U_1U_1^*}. \tag{4.56}$$

It should be noted that in the present case the parameter $Q_1$ in Eq. (3.80) is simply equal to $-1/3$. The other four Stokes constants can, of course, be easily expressed in terms of $U_1$ as follows:

$$U_3 = -U_1^*, \quad U_4 = -\frac{1}{4a^4}U_1,$$

$$U_5 = -4a^4U_2 \quad \text{and} \quad U_6 = \frac{1}{4a^4}U_1^*. \tag{4.57}$$

It must be emphasized that the Stokes constant $U_1$ is defined by the standard WKB solutions in Eqs. (3.73) and (3.74). From Eq. (4.55), we can immediately have expression for the important transition probability given by $P_{12} = |S^R_{12}|^2$:

$$P_{12} = \frac{16a^4(\mathrm{Im}U_1)^2}{(U_1U_1^* + 4a^4)^2}. \tag{4.58}$$

Interestingly, this expression tell that

$$P_{12} = \begin{cases} 0, & \mathrm{Im}U_1 = 0, \\ 1, & \mathrm{Re}U_1 = 0, \quad \mathrm{Im}U_1 = \pm 2a^2. \end{cases} \tag{4.59}$$

**B. Opposite sign of slopes: $f_1 f_2 < 0$**

Applying the same procedure as that in the previous case to Eqs. (4.29), we have

$$A_1(+\infty) = \lim_{t\to+\infty} B_1(t)\exp\left[\frac{i}{2}P(t)\right] = Be^{-i\delta_+}\sqrt{\frac{2}{a^2}}, \tag{4.60}$$

$$\begin{aligned} A_2(+\infty) &= \lim_{t\to+\infty}\left\{A\left[-2q^{\frac{1}{4}}(t) - \frac{dP(t)}{dt}q^{-\frac{1}{4}}(t)\right]\exp[iQ^+(t)]\right. \\ &+ \left.B\left[2q^{\frac{1}{4}}(t) - \frac{dP(t)}{dt}q^{-\frac{1}{4}}(t)\right]\exp[-iQ^+(t)]\right\}e^{-\frac{i}{2}P(t)} \\ &= -A2\sqrt{2a^2}e^{i\delta_+}, \end{aligned} \tag{4.61}$$

$$A_1(-\infty) = D\sqrt{\frac{2}{a^2}}e^{-i\delta_- - i\pi}, \tag{4.62}$$

and

$$A_2(-\infty) = -C2\sqrt{2a^2}e^{i\delta_- + i\pi}, \tag{4.63}$$

where $q(t)$ in Eq. (4.31) has been used. Finally, we have

$$\begin{aligned} \begin{pmatrix} A_1(+\infty) \\ A_2(+\infty) \end{pmatrix} &= e^{i\pi}\begin{pmatrix} L_{11}e^{-i\delta_+ + i\delta_-} & L_{21}\frac{1}{2a^2}e^{-i\delta_+ - i\delta_-} \\ L_{12}(2a^2)e^{i\delta_+ + i\delta_-} & L_{22}e^{i\delta_+ - i\delta_-} \end{pmatrix}\begin{pmatrix} A_1(-\infty) \\ A_2(-\infty) \end{pmatrix} \\ &= \begin{pmatrix} 1 + U_2U_3 & \frac{1}{2a^2}U_2 \\ (U_1 + U_3 + U_1U_2U_3)(2a^2) & 1 + U_1U_2 \end{pmatrix}\begin{pmatrix} A_1(-\infty) \\ A_2(-\infty) \end{pmatrix}. \end{aligned} \tag{4.64}$$

This defines the evolution matrix $F(+\infty, -\infty)$ in the case of opposite sign of slopes. Comparison of Eq. (4.64) with Eqs. (4.38), Eqs. (4.39) and Eqs. (4.40) gives

$$\frac{1}{2a^2}U_2 = -(U_1 + U_3 + U_1U_2U_3)(2a^2) = \text{pure imaginary} \tag{4.65}$$

and

$$U_3 = -U_1^*. \tag{4.66}$$

These two equations together with Eqs. (3.80) provide five relations among the six Stokes constants. Note that in the present case $Q_1$ in Eqs. (3.80) is simply equal to $\frac{1}{3}$. Thus, finally the reduced scattering matrix $S^R$ is expressed in terms of the Stokes constant $U_1$ as

$$S^R = \frac{1}{1+U_1U_2}\begin{pmatrix} 1 & \frac{1}{2a^2}U_2 \\ \frac{1}{2a^2}U_2 & 1 \end{pmatrix}, \tag{4.67}$$

where

$$U_2 = \frac{U_1 - U_1^*}{U_1U_1^* - \frac{1}{4a^4}}. \tag{4.68}$$

The other four Stokes constants can also be expressed in terms of $U_1$,

$$U_3 = -U_1^*, \quad U_4 = 4a^4U_1,$$

$$U_5 = \frac{1}{4a^4}U_2 \text{ and } U_6 = -4a^4U_1^*. \tag{4.69}$$

From Eq. (4.64), we can immediately have expression for the important transition probability given by $P_{12} = |S_{12}^R|^2$:

$$P_{12} = \frac{(\mathrm{Im}U_1)^2/a^4}{[U_1U_1^* - 1/(4a^4)]^2 + (\mathrm{Im}U_1)^2/a^4}. \tag{4.70}$$

Interestingly, this expression tell that

$$P_{12} = \begin{cases} 0, & \mathrm{Im}U_1 = 0, \\ 1, & |U_1| = 1/(2a^2). \end{cases} \tag{4.71}$$

It should be noted that when $\mathrm{Im}U_1 = 0$ and $\mathrm{Re}U_1 = \pm 1/(2a^2)$ are both satisfied simultaneously, $P_{12}$ can take a finite value other than 0.

## 4.4 Exact expressions of the Stokes constants $U_1$

In the previous section, the reduced scattering matrices $S^R$ are expressed in terms of the Stokes constant $U_1$ by Eqs.(4.55) and (4.67) for the same and the opposite sign of slopes, respectively . Since the basic equations (4.16) and (4.30) by which the Stokes constant $U_1$ are defined are included in the general four-transition-point case discussed in chapters 2 and 3, here we just use the results obtained in the previous chapters to denote Stokes constants $U_1$ in a unified way for both cases of linear curve crossings. So, final analytical expression of $U_1$ is given as follows:

$$
\begin{aligned}
U_1 &= U_1(a_4,\ Q_0,\ Q_1,\ Q_2) \\
&= T_1(Q_0,\ Q_1,\ Q_2)[\frac{2}{3}i\sqrt{a_4}]^{-2Q_1},
\end{aligned} \tag{4.72}
$$

where $T_1$ is given below and the quantities $Q_0$, $Q_1$ and $Q_2$ are defined by

$$
\begin{aligned}
Q_0 &= -a_2(12a_4)^{-\frac{2}{3}}e^{i\frac{\pi}{3}}, \\
Q_1 &= -a_1(36a_4)^{-\frac{1}{2}}e^{i\frac{\pi}{2}},
\end{aligned}
$$

and

$$
Q_2 = -a_0(18^2a_4)^{-\frac{1}{3}}e^{i\frac{2\pi}{3}}. \tag{4.73}
$$

The function $T_1$ is given in the form of a convergent infinite series,

$$
T_1 = -2\pi i e^{i2\pi Q_1}\sum_{s=0}^{\infty}\sum_{n=0}^{\infty}\frac{(6Q_0)^n}{n!}\Delta_s\frac{e^{i\pi(n-s-3)/3}}{\Gamma(-2Q_1-\frac{n-s-3}{3})}, \tag{4.74}
$$

where

$$
\begin{aligned}
\Delta_s &= \sum_{n+m=s} B_{n+1}^{(1)}\beta_m^{(1)}, \qquad s \geq 0, \\
\beta_n^{(1)} &= -\frac{3}{n}\sum_{p+q=n-1} B_{p+1}^{(2)}\alpha_{q+1}^{(1)}, \qquad n \geq 1, \\
\alpha_{n+3}^{(1)} &= -\sum_{p+q=n}\Delta_p W_{pq} \qquad n \geq 0,
\end{aligned} \tag{4.75}
$$

$$
\begin{aligned}
W_{pq} &= \sum_{m=[q/3]}^{[p/2]}\Theta(3m-q)\sum_{n=3m-q}^{m}\frac{m!}{n!\,(m-n)!} \\
&\times \frac{\Gamma(2Q_1-\frac{p}{3})C_{n(3m-q)}}{\Gamma(2Q_1-\frac{p}{3}-(m-n))}(6Q_0)^{3m-q},
\end{aligned} \tag{4.76}
$$

and

$$
c_{nr} = \begin{cases} \delta_{n0}, & r = 0, \\ \sum_{s=0}^{r}(-1)^{r-s}\frac{\Gamma(s/3+1)}{s!(r-s)!\Gamma(s/3-n+1)}, & r \geq 1, \end{cases} \tag{4.77}
$$

with $\beta_0^{(1)} = 1$ and $\alpha_1^{(1)} = \alpha_2^{(1)} = 0$. The constants $B_n^{(1)}$ and $B_n^{(2)}$ in Eqs. (4.75) are defined by

$$
B_n^{(1)} = \sum_{k=0}^{n-1} B_{n-k}T_k(d_1,\ d_2), \qquad n \geq 1, \tag{4.78}
$$

and

$$B_n^{(2)} = \sum_{k=0}^{n-1} B_{n-k} T_k(-d_1,\ -d_2), \qquad n \geq 1, \tag{4.79}$$

where

$$T_k(d_1,\ d_2) = \sum_{n=[k/2]}^{k} \Theta(2n-k) \frac{(6d_1)^{2n-k}(3d_2)^{k-n}}{(2n-k)!\ (k-n)!} \tag{4.80}$$

$$d_1 = -Q_0^2 - Q_2 \quad \text{and} \quad d_2 = -2Q_0Q_1. \tag{4.81}$$

The sequence $B_n$ in Eqs. (4.78) and (4.79) is given by

$$B_n = v_n + \sigma_n, \qquad n \geq 1, \tag{4.82}$$

where $v_n$ is obtained from the recurrence relations,

$$v_1^2 - v_1 + P_1 = 0, \tag{4.83}$$

$$v_2 = P_2/(\frac{4}{3} - 2v_1), \tag{4.84}$$

and

$$v_n = (\sum_{m=2}^{n-1} v_m v_{n+1-m} + P_n)/(\frac{n+2}{3} - 2v_1), \qquad n \geq 3 \tag{4.85}$$

with

$$\begin{aligned} P_1 &= \frac{2}{9} + Q_1^2 + 2Q_0(Q_0^2 + Q_2), \\ P_2 &= 4Q_0^2 Q_1 + 2Q_1(Q_0^2 + Q_2), \\ P_3 &= 4Q_0Q_1^2 + (Q_0^2 + Q_2)^2, \\ P_4 &= 4Q_0Q_1(Q_0^2 + Q_2), \\ P_5 &= 4Q_0^2 Q_1^2 \end{aligned}$$

and

$$P_n = 0, \quad \text{for} \quad n \geq 6. \tag{4.86}$$

The constants $\sigma_n$ are also given by recurrence relations,

$$\begin{aligned} \sigma_1 &= \sigma_2 = 0 \\ \sigma_3 &= \frac{2}{3} Q_0, \\ \sigma_4 &= Q_1, \\ \sigma_5 &= \frac{4}{3}(Q_0^2 + Q_2) + 2Q_0\sigma_3, \\ \sigma_6 &= \frac{10}{3} Q_0 Q_1 + 2Q_0\sigma_4 + 2Q_1\sigma_3, \\ \sigma_7 &= 2Q_0\sigma_5 + 2Q_1\sigma_4 + 2(Q_0^2 + Q_2)\sigma_3, \end{aligned}$$

and

$$\sigma_n = 2Q_0\sigma_{n-2} + 2Q_1\sigma_{n-3} + 2(Q_0^2 + Q_2)\sigma_{n-4} + 4Q_0Q_1\sigma_{n-5}, \quad \text{for } n \geq 8. \tag{4.87}$$

The notations appearing in Eqs.(4.75)–(4.83) have the following meanings: $\Gamma(x)$ is the Gamma function, $[x]$ means the largest integer not larger than $x$, and $\Theta(x)$ is the step function, i.e. $\Theta(x) = 0$ when $x < 0$ and $\Theta(x) = 1$ when $x \geq 0$. Although there are two roots for $v_1$, as is easily seen from Eq. (4.83), we can select the one with smaller real part or anyone of the two if two roots have the same real part. In the above summations and recurrence relations, we can easily see that all of them are given in the form of finite series except Eq. (4.74). It should also be noted that a direct recurrence relation for $\Delta_s$ can be obtained from Eqs.(4.75) as follows:

$$\begin{aligned} \Delta_s &= B_{s+1}^{(1)} - V_{(s-1)2}\Delta_0 W_{00} - \Delta_0 \sum_{n=1}^{s-3} V_{(s-1)(n+2)} W_{0n} \\ &- \sum_{k=1}^{s-3} \left\{ \sum_{n=k}^{s-3} V_{(s-1)(n+2)} W_{k(n-k)} \right\} \Delta_k, \end{aligned} \tag{4.88}$$

where

$$V_{pq} = \begin{cases} -3\sum_{m=q}^{p} \frac{1}{m+1} B_{p+1-m}^{(1)} B_{m+1-q}^{(2)}, & \text{for } p \geq q \geq 0, \\ 0 & \text{otherwise.} \end{cases} \tag{4.89}$$

Now, let us go back to our linear curve crossing problems. We can immediately see that what we have to do is just to replace $Q_0$, $Q_1$ and $Q_2$ in Eqs. (4.73) by the following expressions (see Eqs. (4.17) and (4.31) ):

$$\begin{aligned} Q_0 &= \frac{1}{2} b^2 (9a^2)^{-\frac{1}{3}} e^{i\frac{\pi}{3}}, \\ Q_1 &= -\frac{1}{3} \\ \text{and} \\ Q_2 &= -\frac{1}{4}(1 + b^4)(9a^2)^{-\frac{2}{3}} e^{i\frac{2\pi}{3}} \end{aligned} \tag{4.90}$$

for the same sign of slopes, and

$$\begin{aligned} Q_0 &= \frac{1}{2} b^2 (9a^2)^{-\frac{1}{3}} e^{i\frac{\pi}{3}}, \\ Q_1 &= \frac{1}{3} \\ \text{and} \\ Q_2 &= \frac{1}{4}(1 - b^4)(9a^2)^{-\frac{2}{3}} e^{i\frac{2\pi}{3}} \end{aligned} \tag{4.91}$$

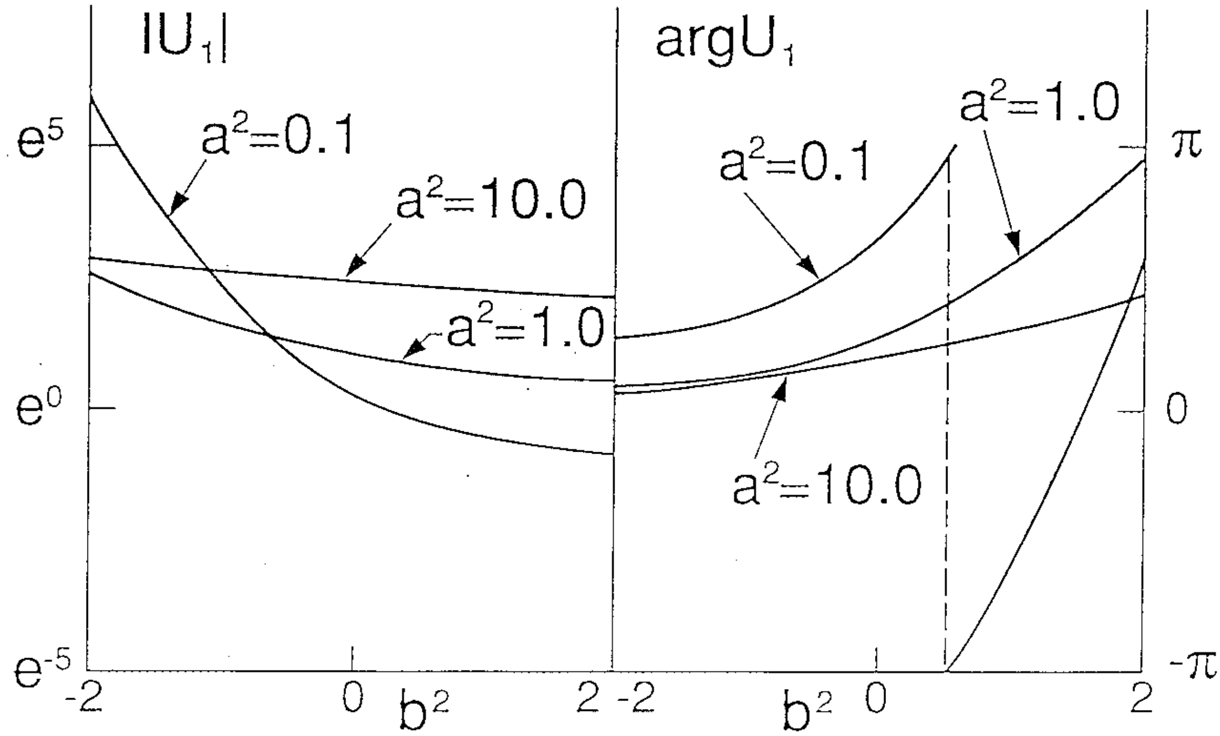



Figure 4.3: Modulus and argument of the Stokes constant $U_1$: same sign of slopes.

for the opposite sign of slopes. The parameters $a^2$ and $b^2$ are defined by Eq. (4.10).

Eqs. (4.55) and (4.67) with $U_1$ given by Eqs. (4.72) and (4.74) provide the exact analytical expressions of the reduced scattering matrices which can, of course, cover the whole range of the two parameters $a^2$ and $b^2$, i.e., the whole variety of coupled linear potentials (slopes and coupling constant) and the whole range of collision energy. One big drawback is, however, that the analytical expression of the Stokes constant $U_1$ is quite cumbersome and not very transparent with respect to the dependencies on $a^2$ and $b^2$. Numerical computations confirmed that this expression surely gives the exact results, and that the infinite series of Eq. (4.74) converges reasonably fast in the region $|\frac{b^2}{a^2}| \leq 1$, where no good approximations are available yet. The convergence becomes slower, however, in the region of large values of the parameters, where various good approximations are available.

In order to give a rough idea about the Stokes constant $U_1$, $|U_1|$ and $\arg U_1$ are shown in Fig.4.3 for same sign of slopes and Fig.4.4 for opposite sign of slopes, as a function of $b^2$ for some values of $a^2$.

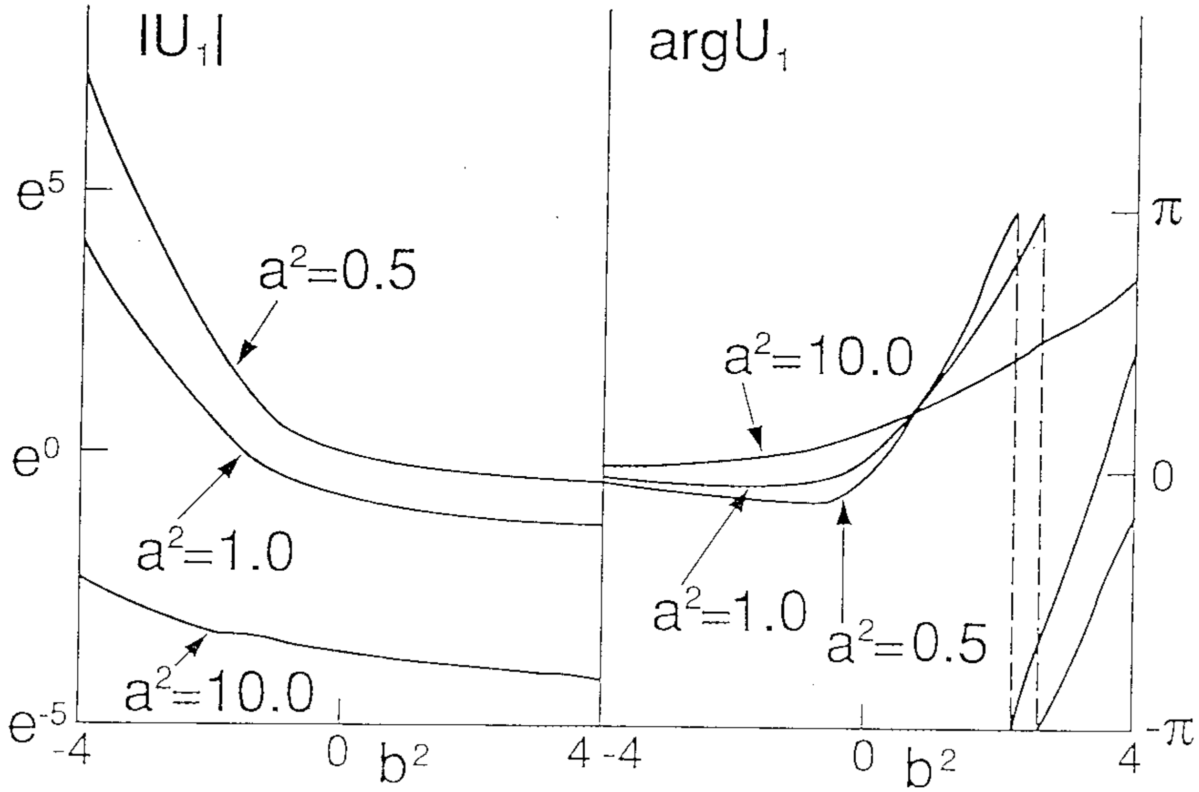



Figure 4.4: Modulus and argument of the Stokes constant $U_1$: opposite sign of slopes.

## 4.5 Numerical solution for the case of $f_1 f_2 < 0$

Our purpose in this section is to find out numerical method to calculate the reduced scattering matrix $S^R$ for the case of the opposite sign of slopes. Based on the symmetry properties of the $S^R$ in Eqs. (4.38), (4.39) and (4.40), we can have a convenient expression given by

$$S^R = \frac{1}{T^*}\begin{pmatrix} 1 & W \\ W & 1 \end{pmatrix}, \tag{4.92}$$

where

$$|T|^2 + W^2 = 1 \tag{4.93}$$

with $W$ being pure imaginary. It is easily seen that what we need to calculate are two quantities $W$ and $\arg T$. In order to make both stable and accurate numerical results, we must establish new coupled equations which are our starting point in the following.

**A. New coupled equations**

Let us first go back the original coupled equations in the momentum space given in Eqs. (4.5) and (4.6), rewritten as

$$(K^2 - \varepsilon - if_1\frac{d}{dK})u_1(K) = -\alpha u_2(K)$$

and

$$(K^2 - \varepsilon - if_2\frac{d}{dK})u_2(K) = -\alpha u_1(K). \tag{4.94}$$

Since the reduced scattering matrix is dependent only on the two parameters $a^2$ and $b^2$, it is sufficient to consider the special case $f_1 = -f_2 = f > 0$. In other words, the results of this special case can cover the whole general cases of $f_1 \neq -f_2$. Let us introduce a transformation,

$$V_+(K) = u_1(K) + u_2(K)$$

and

$$V_-(K) = u_1(K) - u_2(K), \tag{4.95}$$

a new variable,

$$X = \frac{K}{\sqrt{|\varepsilon| + \alpha}}, \tag{4.96}$$

and parameters,

$$c^2 = \frac{f}{(|\varepsilon| + \alpha)^{3/2}} = \frac{2\sqrt{a^2}}{(|b^2| + 1)^{3/2}} \tag{4.97}$$

and

$$\gamma = \frac{|\varepsilon| - \alpha}{|\varepsilon| + \alpha} = \frac{|b^2| - 1}{|b^2| + 1}. \tag{4.98}$$

Further introducing a variable transformation,

$$y = \frac{X^3}{3} + X, \tag{4.99}$$

and substituting these equations into Eqs. (4.94), we find new coupled equations for $V_+(y)$ and $V_-(y)$. Here, we treat the positive energy case ($b^2 \geq 0$) and the negative energy case ($b^2 \leq 0$) separately, because the convenient coupled equations have different forms in these two cases. Then the following coupled equations can be easily derived:

$$V_+(y) = ic^2 \frac{dV_-(y)}{dy}, \tag{4.100}$$

$$\frac{X^2(y) + \gamma}{X^2(y) + 1} V_-(y) = ic^2 \frac{dV_+(y)}{dy}, \quad \text{for } b^2 \leq 0, \tag{4.101}$$

and

$$\frac{X^2(y) - \gamma}{X^2(y) + 1} V_+(y) = ic^2 \frac{dV_-(y)}{dy},$$

$$\frac{X^2(y) - 1}{X^2(y) + 1} V_-(y) = ic^2 \frac{dV_+(y)}{dy} \quad \text{for } b^2 \geq 0, \tag{4.102}$$

It can be easily seen that the new coupled equations are very suitable for numerical calculation, because the coefficient functions never diverge anywhere. Actually, they are smaller than unity. From Eq. (4.99), $X(y)$ can be directly solved as

$$X(y) = \{\sqrt{1 + (3y/2)^2} + 3y/2\}^{1/3} - \{\sqrt{1 + (3y/2)^2} - 3y/2\}^{1/3}. \tag{4.103}$$

### B. The reduced scattering matrix

In order to obtain the reduced scattering matrix, we have to express the quantities $T$ and $W$ in Eq. (4.92) in terms of the solutions of the new coupled Eqs. (4.100), (4.101) and (4.102). From Eqs.(4.32) and (4.8), we have

$$\begin{pmatrix} u_1(K) \\ u_2(K) \end{pmatrix} = \begin{pmatrix} \exp[-2i\phi(K)]T & W \\ -W & \exp[2i\phi(K)]T^* \end{pmatrix} \begin{pmatrix} u_1(-K) \\ u_2(-K) \end{pmatrix}, \quad \text{for } K \to \infty, \tag{4.104}$$

where

$$\phi(K) = \frac{1}{f}(\frac{K^3}{3} - \varepsilon K). \tag{4.105}$$

Eqs. (4.95) simply give

$$W = \frac{1}{2}\frac{[V_-^2(K) - V_+^2(K)] - [V_-^2(-K) - V_+^2(-K)]}{V_-(K)V_+(-K) + V_+(K)V_-(-K)}, \quad \text{for } K \to \infty, \tag{4.106}$$

and

$$\begin{aligned} \arg T &= \arg\{[(V_+(K) + V_-(K))(V_-(-K) - V_+(-K)) \\ &+ W(V_-(-K) - V_+(-K))^2]\exp[2i\phi(K)]\}, \quad \text{for } K \to \infty, \end{aligned} \tag{4.107}$$

It should be noted that

$$\begin{aligned} \arg S_{11}^R &= \arg S_{22}^R = \arg T, \\ \arg S_{12}^R &= \arg S_{21}^R = \pm\pi/2 + \arg T \end{aligned} \tag{4.108}$$

and

$$P_{12} \equiv |S_{12}^R|^2 = |S_{21}^R|^2 = \frac{|W|^2}{1 + |W|^2}. \tag{4.109}$$

Since Eqs. (4.106) and (4.107) are not yet numerically stable and convenient, we transform them further as described below. Multiplying $V_-(y)$ to Eq. (4.100) and $V_+(y)$ to Eq. (4.101), subtracting these equations, and integrating the resultant equation over $y$ in the range$(-\infty, \infty)$, then we obtain

$$\begin{aligned} &[V_-^2(K) - V_+^2(K)] - [V_-^2(-K) - V_+^2(-K)] \\ = \; & -\frac{2i}{c^2}(1-\gamma)\int_{-K}^{K} \frac{1}{X^2(y)+1} V_+(y)V_-(y)dy, \quad \text{for } K \to \infty, \end{aligned} \tag{4.110}$$

On the other hand, multiplying $V_+(y)$ to Eq. (4.100) with $y$ replaced by $-y$ and $V_-(-y)$ to Eq. (4.101), subtracting these equations, and integrating over $y$ in the ranges $(0, \pm\infty)$, then we get

$$V_-(-K)V_+(K) + V_-(K)V_+(-K) = 2V_+(0)V_-(0), \quad \text{for } K \to \infty, \tag{4.111}$$

From Eqs. (4.106), (4.110) and (4.111) we finally obtain the following integral expression for $W$:

$$W = \frac{1-\gamma}{2ic^2 V_+(0)V_-(0)} \int_{-\infty}^{\infty} \frac{V_+(y)V_-(y)}{X^2(y)+1} dy. \tag{4.112}$$

This expression is very convenient for numerical solution. Interestingly, by using the same manipulation mentioned above, exactly the same expression as Eq. (4.112) can be found for the case $b^2 \geq 0$.

Since $X(y) \rightarrow \pm(3|y|)^{1/3}$ for $y \rightarrow \pm\infty$, it can be shown that the asymptotic solutions of $V_{\pm}(y)$ are given by the following expressions for both $b^2 \geq 0$ and $b^2 \leq 0$:

$$V_-(K) \stackrel{K\to\infty}{\longrightarrow} A \sin\phi(K) + B\cos\phi(K), \tag{4.113}$$

$$V_+(K) \stackrel{K\to\infty}{\longrightarrow} i[A\cos\phi(K) - B\sin\phi(K)] \tag{4.114}$$

and

$$V_-(K) \stackrel{K\to-\infty}{\longrightarrow} A' \sin\phi(K) + B'\cos\phi(K), \tag{4.115}$$

$$V_+(K) \stackrel{K\to-\infty}{\longrightarrow} i[A'\cos\phi(K) - B'\sin\phi(K)], \tag{4.116}$$

where $\phi(K)$ is defined by Eq. (4.105). Then we obtain

$$\arg T = \arctan\{\frac{B'A - A'B - iW[B'^2 - A'^2]}{A'A + B'B - 2iWA'B'}\}. \tag{4.117}$$

It should be noted that $\phi(K)$ cancels out exactly in Eq. (4.117). Thus when the solutions are well extended into the asymptotic regions, the phase $\arg T$ can be easily evaluated from this equation.

### C. Numerical results

The nonadiabatic tunneling probability $P_{12}$ of Eq. (4.109) and the phase $\arg T$ of Eq. (4.108) can now be stably and accurately calculated by using Eqs. (4.112) and (4.117). It should be noted that we can solve the coupled equations (4.100), (4.101) and (4.102) under the boundary conditions,

$$V_+(y_0) = iV_{+0} \quad \text{and} \quad V_-(y_0) = V_{-0}, \tag{4.118}$$

where $y_0, V_{+0}$ and $V_{-0}$ can be *any* real numbers except for the case $V_{+0} = V_{-0} = 0$. Eqs. (4.118) never represent unphysical boundary conditions. It is actually numerically confirmed that $P_{12}$ and $\arg T$ are completely the same for different values of $y_0, V_{+0}$ and $V_{-0}$.

As is easily seen from Eqs. (4.100), (4.101) and (4.102), the solutions $V_{\pm}(y)$ are oscillatory. Thus in order to have a rapid convergence in the calculation of $W$, it is better to transform the integral in Eq. (4.112) by an integration by parts with use of Eqs. (4.100), (4.101) and (4.102). This is especially effective in the strong coupling (small $a^2$) case, since the solutions oscillate rapidly because of the factor $1/c^2$(see Eqs. (4.119) and (4.120) below). We can repeat the integrations by parts as many times as we want for the required accuracy.

In the calculation of $\arg T$ the numerical solutions should be fitted to analytical asymptotic solutions so as to determine the coefficients $(A, B)$ and $(A', B')$. This can be done by using the WKB asymptotic solutions. In the case of $b^2 \leq 0$, the WKB solutions are given as

$$V_-(y) = q(y)^{-1/4}\{A\sin[\frac{1}{c^2}\int q^{1/2}(y)dy] + B\cos[\frac{1}{c^2}\int q^{1/2}(y)dy]\}, \tag{4.119}$$

and

$$V_+(y) = iq(y)^{-1/4}\{A\cos[\frac{1}{c^2}\int q^{1/2}(y)dy] - B\sin[\frac{1}{c^2}\int q^{1/2}(y)dy]\}, \quad \text{for} \quad y \to \pm\infty, \tag{4.120}$$

where

$$q(y) = \frac{X^2(y)+\gamma}{X^2(y)+1}. \tag{4.121}$$

The phase integral in Eqs. (4.119) and (4.120) can be easily expanded as

$$\begin{aligned} \lim_{y\to\pm\infty}\int q^{1/2}(y)dy &= \lim_{X\to\pm\infty}\int\sqrt{(X^2+\gamma)(X^2+1)}dX \\ &= y + \frac{\gamma-1}{2}X(y) + \frac{(\gamma-1)^2}{8X(y)} + O(X^{-3}), \\ & \quad y \to \pm\infty. \end{aligned} \tag{4.122}$$

The similar expressions as Eqs. (4.119) $\sim$ (4.122) can be easily obtained for the case $b^2 \geq 0$.

Numerical results for $a^2 = 0.1, 1.0$ and $10.0$ are given in Fig.4.5 and Table 4.1. It should be noted that $\arg T$ changes by $\pi$ at the complete reflection resonances[81]. It is easily confirmed that the present method is very stable and reliable even in a strong coupling regime. Even very small values of transition probabilities can be easily reproduced, and the unitarity is never broken. As a demonstration, Table 4.2 shows five sharp resonances in the strong coupling case ($a^2 = 0.1$) (see Fig.4.5). These sharp resonances are seen to become slightly broader with increasing $b^2$.

## 4.6 Concluding remarks

At first glance it may be surprising that the exact analytical quantal solutions for the reduced scattering matrices $S^R$ have been obtained without solving the basic

Table 4.1: Nonadiabatic transition probabilities ($P_{12}$) and phases ($\arg T$).

| $b^2$ \ $a^2$ | 0.1 | | 1 | | 10 | |
|---|---|---|---|---|---|---|
| | $P_{12}$ | arg T | $P_{12}$ | arg T | $P_{12}$ | arg T |
| -4.0 | $0.27 \cdot 10^{-13}$ | 1.25 | $0.16 \cdot 10^{-4}$ | 0.40 | $0.46 \cdot 10^{-2}$ | 0.129 |
| -3.8 | $0.35 \cdot 10^{-12}$ | 1.28 | $0.37 \cdot 10^{-4}$ | 0.41 | $0.60 \cdot 10^{-2}$ | 0.132 |
| -3.6 | $0.42 \cdot 10^{-11}$ | 1.32 | $0.82 \cdot 10^{-4}$ | 0.42 | $0.785 \cdot 10^{-2}$ | 0.136 |
| -3.4 | $0.47 \cdot 10^{-10}$ | 1.36 | $0.178 \cdot 10^{-3}$ | 0.43 | $0.102 \cdot 10^{-1}$ | 0.141 |
| -3.2 | $0.5 \cdot 10^{-9}$ | 1.40 | $0.382 \cdot 10^{-3}$ | 0.45 | $0.131 \cdot 10^{-1}$ | 0.145 |
| -3.0 | $0.49 \cdot 10^{-8}$ | 1.45 | $0.801 \cdot 10^{-3}$ | 0.46 | $0.167 \cdot 10^{-1}$ | 0.150 |
| -2.8 | $0.457 \cdot 10^{-7}$ | 1.50 | $0.164 \cdot 10^{-2}$ | 0.48 | $0.212 \cdot 10^{-1}$ | 0.156 |
| -2.6 | $0.393 \cdot 10^{-6}$ | 1.56 | $0.330 \cdot 10^{-2}$ | 0.50 | $0.267 \cdot 10^{-1}$ | 0.161 |
| -2.4 | $0.314 \cdot 10^{-5}$ | 1.63 | $0.646 \cdot 10^{-2}$ | 0.52 | $0.335 \cdot 10^{-1}$ | 0.167 |
| -2.2 | $0.233 \cdot 10^{-4}$ | 1.71 | $0.123 \cdot 10^{-1}$ | 0.55 | $0.415 \cdot 10^{-1}$ | 0.174 |
| -2.0 | $0.160 \cdot 10^{-3}$ | 1.81 | $0.229 \cdot 10^{-1}$ | 0.59 | $0.511 \cdot 10^{-1}$ | 0.180 |
| -1.8 | $0.101 \cdot 10^{-2}$ | 1.92 | $0.411 \cdot 10^{-1}$ | 0.62 | $0.623 \cdot 10^{-1}$ | 0.187 |
| -1.6 | $0.583 \cdot 10^{-2}$ | 2.07 | $0.712 \cdot 10^{-1}$ | 0.67 | $0.753 \cdot 10^{-1}$ | 0.193 |
| -1.4 | $0.302 \cdot 10^{-1}$ | 2.26 | 0.118 | 0.72 | $0.903 \cdot 10^{-1}$ | 0.200 |
| -1.2 | 0.131 | 2.54 | 0.184 | 0.77 | 0.107 | 0.206 |
| -1.0 | 0.400 | 2.89 | 0.271 | 0.83 | 0.126 | 0.211 |
| -0.8 | 0.726 | -3.08 | 0.373 | 0.88 | 0.147 | 0.216 |
| -0.6 | 0.904 | -2.94 | 0.480 | 0.91 | 0.169 | 0.220 |
| -0.4 | 0.968 | -2.97 | 0.580 | 0.92 | 0.192 | 0.222 |
| -0.2 | 0.988 | 3.13 | 0.667 | 0.91 | 0.217 | 0.223 |
| 0 | 0.995 | 2.84 | 0.737 | 0.88 | 0.242 | 0.222 |
| 0.2 | 0.998 | 2.45 | 0.791 | 0.83 | 0.268 | 0.219 |
| 0.4 | 0.999 | 1.99 | 0.830 | 0.74 | 0.293 | 0.213 |
| 0.6 | 0.999 | 1.46 | 0.857 | 0.63 | 0.318 | 0.207 |
| 0.8 | 0.999 | 0.88 | 0.874 | 0.50 | 0.340 | 0.195 |
| 1.0 | 0.999 | 0.23 | 0.884 | 0.36 | 0.362 | 0.184 |
| 1.2 | 0.997 | -0.45 | 0.886 | 0.21 | 0.381 | 0.168 |
| 1.4 | 0.970 | -1.06 | 0.881 | $0.51 \cdot 10^{-1}$ | 0.397 | 0.152 |
| 1.6 | 0.977 | 0.96 | 0.863 | -0.11 | 0.411 | 0.130 |
| 1.8 | 0.993 | 0.21 | 0.825 | -0.27 | 0.422 | 0.110 |
| 2.0 | 0.937 | -0.59 | 0.743 | -0.38 | 0.429 | $0.85 \cdot 10^{-1}$ |
| 2.2 | 0.123 | 0.32 | 0.558 | -0.43 | 0.432 | $0.61 \cdot 10^{-1}$ |
| 2.4 | 0.984 | 0.48 | 0.184 | -0.27 | 0.432 | $0.35 \cdot 10^{-1}$ |
| 2.6 | 0.983 | -0.42 | $0.37 \cdot 10^{-1}$ | 0.12 | 0.426 | $0.91 \cdot 10^{-2}$ |
| 2.8 | $0.74 \cdot 10^{-1}$ | -0.24 | 0.404 | 0.36 | 0.416 | $-0.17 \cdot 10^{-1}$ |
| 3.0 | 0.977 | 0.44 | 0.643 | 0.35 | 0.400 | $-0.42 \cdot 10^{-1}$ |
| 3.2 | 0.971 | -0.52 | 0.740 | 0.22 | 0.379 | $-0.65 \cdot 10^{-1}$ |
| 3.4 | 0.684 | 0.77 | 0.766 | $0.34 \cdot 10^{-1}$ | 0.350 | $-0.85 \cdot 10^{-1}$ |
| 3.6 | 0.976 | 0.12 | 0.740 | -0.15 | 0.315 | -0.100 |
| 3.8 | 0.894 | -0.79 | 0.638 | -0.30 | 0.273 | -0.111 |
| 4.0 | 0.945 | 0.63 | 0.375 | -0.31 | 0.226 | -0.115 |

Table 4.2: Reflection resonances for $a^2 = 0.1$ in the renge $b^2 \in [1, 4]$.

| $b^2$ | $P_{12}$ |
|---|---|
| 1.4841 | $0.57*10^{-3}$ |
| 1.4844 | $0.22*10^{-4}$ |
| 1.4847 | $0.21*10^{-3}$ |
| 2.1919 | $0.33*10^{-3}$ |
| 2.1922 | $0.13*10^{-4}$ |
| 2.1925 | $0.12*10^{-3}$ |
| 2.8063 | $0.12*10^{-3}$ |
| 2.8066 | $0.44*10^{-5}$ |
| 2.8069 | $0.22*10^{-3}$ |
| 3.3625 | $0.12*10^{-3}$ |
| 3.3628 | $0.11*10^{-5}$ |
| 3.3631 | $0.17*10^{-3}$ |
| 3.8777 | $0.14*10^{-3}$ |
| 3.8780 | $0.31*10^{-6}$ |
| 3.8783 | $0.12*10^{-3}$ |

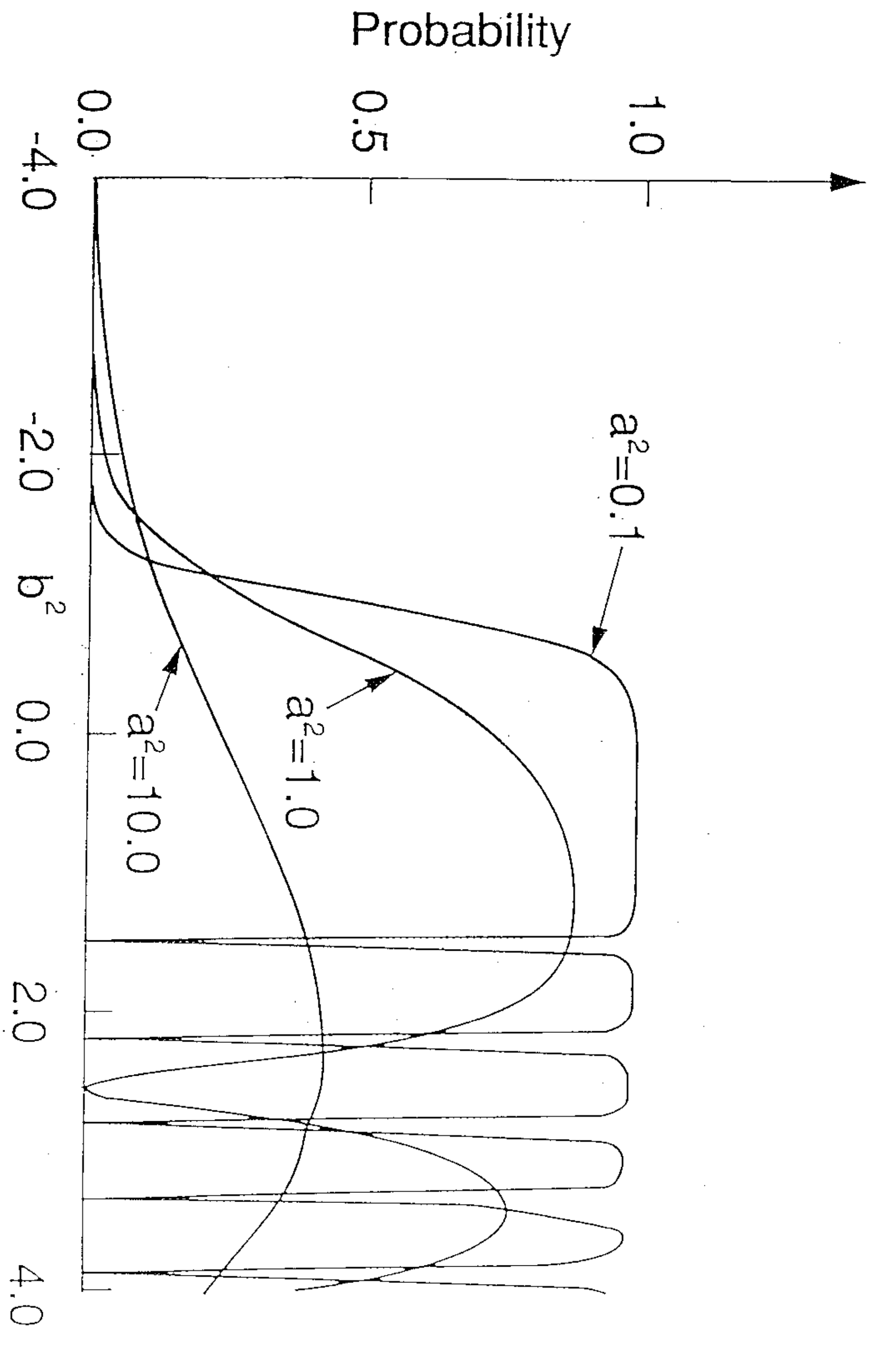



Figure 4.5: Nonadiabatic tunneling probabilities $P_{12}$ as function $b^2$ for three typical coupling regimes: $a^2 = 0.1$(strong coupling) $a^2 = 1.0$(intermediate), and $a^2 = 10.0$(weak).

equations (4.16) and (4.30) for two-state linear curve crossing problems. Actually, the exact analytical solutions of these two basic equations can hardly be found. But in the view of finding solutions of physical quantity, reduced scattering matrix, what we need is the connection matrix which connects asymptotic solutions of the basic equations (4.16) and (4.30) from $x \to +\infty$ to $x \to -\infty$. This connection matrix has been expressed in terms of three Stokes constants for the general four-transition-point problem in chapter 3. For these special four-transition-point problems of two-state linear curve crossing with the same and opposite sign of slopes, two extra symmetry conditions of $S^R$ in addition to unitarity could be obtained, so that the reduced scattering matrix for each case has been expressed in terms of only one Stokes constant which was found in chapter 2 in the form of a analytical convergent infinite series. That is to asy, the exact analytical expressions of scattering matrices are derived for the first time, although the convergent infinite series are very complicated, unfortunately.

Although we have employed the diabatic-state representation in this chapter, the total scattering matrix given by Eq. (4.18) does not depend on the representation, as far as we solve the problem exactly. Thus, if we want, we can easily obtain the reduced scattering matrix in the adiabatic-state representation which is generally superior to the diabatic-state representation for comprehending the underlying physics in various processes.

We have estimated the constants $T_1$ of Eq. (4.74) numerically and found that the convergence rate of the infinite series is fast when the four transition points are close together near the origin, and becomes slower as the points move far away from the origin. As explained in chapter 1, because if the transition points are far away from the origin, the convergence of the WKB solutions, and consequently the convergence of the Stokes constants, is expected to become slower. Fortunately, however, in this case we can construct good analytical approximations by replacing the four transition points by a pair of two transition points. Even in the former case in which the four points sit close together, however, it is still very important to develop a good simple analytical approximation, especially in the case of opposite sign of slopes. Those approximate solutions for reduced scattering matrices $S^R$ will be discussed in the subsequent chapters.

Besides, for the case of the opposite sign of slopes, we proposed new coupled equations which overcome the famous difficulty of the numerical solution[63]–[65]

and can provide very accurate results for both amplitude and phase of the reduced scattering matrix for any coupling regimes from weak to strong.

# Chapter 5

# Distributions of transition points and Stokes lines

From the standpoint of exact quantal treatment of the reduced scattering matrices discussed in chapter 4, should be considered only asymptotic Stokes lines which are absolutely far away from all transition points in the complex plane. We do not have to care about where the exact positions of transition points are, if we know the exact solutions of Stokes constants. The connection matrix can be exactly expressed in terms of Stokes constants by tracing the WKB solutions in the region $|z| \rightarrow +\infty$ where the asymptotic Stokes lines are just straight lines with equal angular interval.

From the standpoint of the semiclassical treatment of the reduced scattering matrix, however, we want to figure out analytical solution in the compact form, and to understand various limiting cases how the connection matrix is approximated and what is the valid condition for semiclassical solution. So, we have to know the distribution of transition points and Stokes ( and anti-Stokes ) lines around them accurately. Transition points are nothing but zero points of $q(t)$ in Eqs. (4.17) and (4.31), and the Stokes and anti-Stokes lines emanate from each transition point. Stokes lines represent the lines on which the dominancy (subdominancy) of dominant (subdominant) solutions becomes strongest and are defined by

$$\mathrm{Re} \int_{t_0}^{t} q^{1/2}(t')dt' = 0, \tag{5.1}$$

where $t_0$ usually represents a transition point. Anti-Stokes lines, on the other hand, represent the lines across which the dominancy and subdominancy interchange and are defined by

$$\mathrm{Im}\int_{t_0}^{t} q^{1/2}(t')dt' = 0. \tag{5.2}$$

The basic differential equations (4.16) and (4.30) governing the two-state linear curve crossing problems look like similar in the coefficient functions (4.17) and (4.31), in which the two terms have different sign. But this makes a big difference in the distributions of both transition points and Stokes lines; and the difference has much influence on analytical expressions of the reduced scattering matrices. We shall see in the next two chapters.

## 5.1 Same sign of slopes: $f_1 f_2 > 0$

The transition points are zero points of Eq. (4.17) in the complex t-plane rewritten in the from,

$$t^4 - 2(\frac{b^2}{a^2})t^2 - i\frac{4}{a^2}t + (\frac{b^2}{a^2})^2 + \frac{1}{a^4} = 0, \tag{5.3}$$

in which the parameters $a^2$ and $b^2$ defined by Eq. (4.10) can vary in the ranges $[0,\infty)$ and $(-\infty,+\infty)$, respectively. Using the facts that these parameters are real and that $-t_j^*$ can be a root if $t_j$ is a root, we can analyze Eq. (5.3) by putting

$$t_1 = x_1 + iy, \quad t_2 = -x_1 + iy \tag{5.4}$$

and

$$t_3 = -x_2 - iy, \quad t_4 = x_2 - iy, \tag{5.5}$$

where $y > 0$, $x_1 > 0$, and $x_2^2$ is real (it can be negative). These should satisfy the following relations:

$$\begin{aligned} x_1^2 + x_2^2 &= 2y^2 + 2\frac{b^2}{a^2}, \\ y(x_1^2 - x_2^2) &= \frac{2}{a^2} \\ &\text{and} \\ (x_1^2 + y^2)(x_2^2 + y^2) &= (\frac{b^2}{a^2})^2 + \frac{1}{a^4}. \end{aligned} \tag{5.6}$$

This means that the roots $t_1$ and $t_2$ are symmetric with respect to the imaginary axis. For the other two roots $t_3$ and $t_4$, there are the following three cases depending on the sign of $x_2^2$:

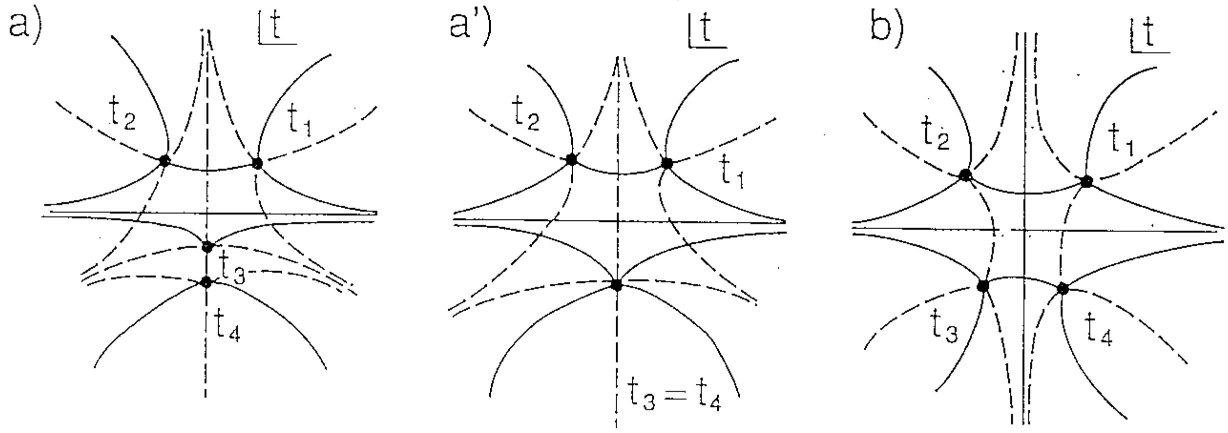



Figure 5.1: Distribution of transition points ($t_j$) in the case of same sign sign slopes. (a) $x_2^2 < 0$, ($a'$) $x_2^2 = 0$, (b) $x_2^2 > 0$.

(a) $x_2^2 > 0$: $t_3$ and $t_4$ are symmetric with respect to imaginary axis,

(a') $x_2^2 = 0$: double pure imaginary roots $t_3 = t_4$,

and

(b) $x_2^2 < 0$: two pure imaginary roots $t_3 \neq t_4$.

The Stokes and anti-Stokes lines are depicted in Fig.5.1 for these three cases. Finally, the four roots can be obtained analytically. Eqs. (5.6) are easily reduced to

$$x_1^2 = y^2 + (\frac{b^2}{a^2}) + \frac{1}{a^2 y}, \tag{5.7}$$

$$x_2^2 = y^2 + (\frac{b^2}{a^2}) - \frac{1}{a^2 y} \tag{5.8}$$

and

$$y^6 + (\frac{b^2}{a^2})y^4 - \frac{1}{4a^4}y^2 - \frac{1}{4a^4} = 0. \tag{5.9}$$

Eq. (5.9) is just a cubic polynomial of $y^2$ and can be solved analytically, although we do not do that explicitly here. It only suffices to say that only one positive root of $y^2$ is shown to exist in the region

$$x < y^2 < 2x + 1, \tag{5.10}$$

where

$$x = \frac{1}{3}\Big\{\sqrt{(\frac{b^2}{a^2})^2 + \frac{3}{4a^4}} - (\frac{b^2}{a^2})\Big\}. \tag{5.11}$$

The boundary curve ($x_2^2 = 0$) between the two cases (a) and (b) can be easily obtained from Eqs. (5.8) and (5.9) as (see Fig.5.2)

$$a^2 = \Big[\frac{2}{3}\sqrt{b^4 + 3/4} - \frac{1}{3}b^2\Big] / \Big[2\sqrt{b^4 + \frac{3}{4}} - 2b^2\Big]^2. \tag{5.12}$$

On this curve $y$ and $x_1^2$ are given by

$$y = 2\Big[\sqrt{b^4 + \frac{3}{4}} - b^2\Big] \tag{5.13}$$

and

$$x_1^2 = 4\Big[\sqrt{b^4 + \frac{3}{4}} - b^2\Big] / \Big[\frac{2}{3}\sqrt{b^4 + \frac{3}{4}} - \frac{1}{3}b^2\Big]. \tag{5.14}$$

## 5.2 Opposite sign of slopes: $f_1 f_2 < 0$

In this case, the transition points are the zeros of Eq. (4.31) which is rewritten as

$$t^4 - 2(\frac{b^2}{a^2})t^2 + i\frac{4}{a^2}t + (\frac{b^2}{a^2})^2 - \frac{1}{a^4} = 0. \tag{5.15}$$

In spite of the fact that only two signs are different from Eq. (5.3), the situation in this case is more complicated. Eq. (5.15) can also be solved in the similar way as before by using Eqs. (5.4) and (5.5), so that we obtain

$$x_1^2 = y^2 + \frac{b^2}{a^2} - \frac{1}{a^2 y}, \tag{5.16}$$

$$x_2^2 = y^2 + (\frac{b^2}{a^2}) + \frac{1}{a^2 y} \tag{5.17}$$

and

$$y^6 + (\frac{b^2}{a^2})y^4 + \frac{1}{4a^4}y^2 - \frac{1}{4a^4} = 0. \tag{5.18}$$

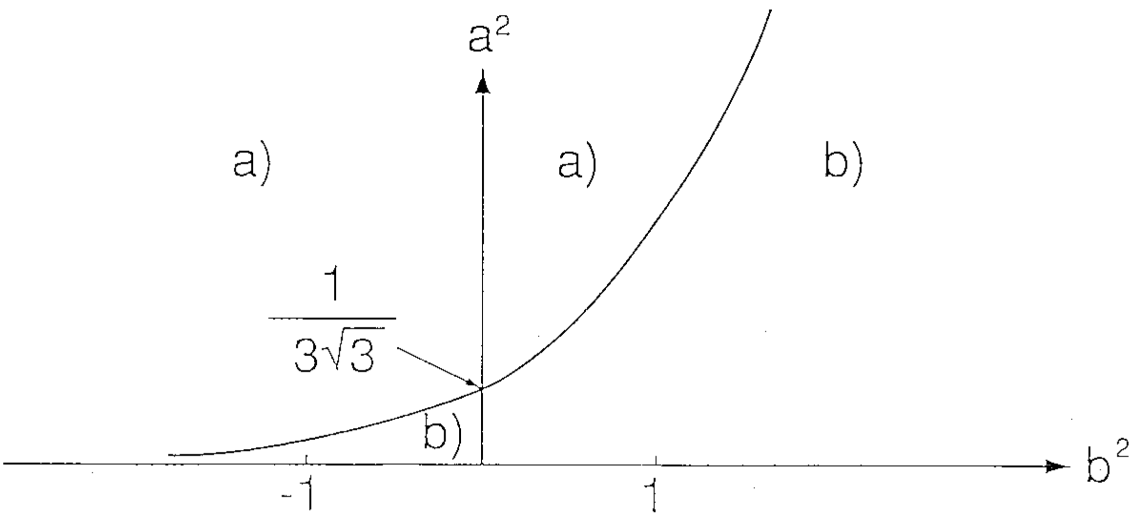



Figure 5.2: Regions of $x_2^2 < 0$ and $x_2^2 > 0$ in the $(a^2, b^2)$ plane corresponding to the cases (a) and (b) of Fig.5.1.

where $y > 0$, but both $x_1^2$ and $x_2^2$ can be negative. Analysis of Eq. (5.18) first leads to the following broad classification:

(i) $b^2 \geq 1 :\quad x_2^2 > 0$ and $x_1^2$ real,

(ii) $-\sqrt{\frac{3}{4}} < b^2 < 1 :\quad x_2^2 > 0$ and $x_1^2 < 0$

and

(iii) $b^2 \leq -\sqrt{\frac{3}{4}} :\quad x_2^2$ real and $x_1^2 < 0$.

In order to fully understand distributions of the transition points and Stokes lines, each case above should be further classified into some subcases as discussed below.

**Case(i)** $b^2 \geq 1$

In this case the transition points $t_3$ and $t_4$ are always symmetric with respect to the imaginary axis. The distribution of the other two roots $t_1$ and $t_2$ can be classified according to the sign of $x_1^2$ as follows:

(a) $x_1^2 > 0$ : symmetric with respect to the imaginary axis (Fig.5.3a),

(a') $x_1^2 = 0$ : double pure imaginary roots $t_1 = t_2$

and

(b) $x_1^2 < 0$ : two pure imaginary roots $t_1 \neq t_2$. (Fig.5.4b)

These are shown in Figs.5.3a and 5.3b together with the associated Stokes and anti-Stokes lines. From Eq. (5.18), it can be proved that only one positive root of $y^2$ exist in the region $0 < y^2 < 1$.

Also from Eqs. (5.16) and (5.18) we can find the boundary ($x_1^2 = 0$) curve $L_0$ as is shown in Fig.5.4,

$$L_0(x_1^2 = 0) \quad : \quad a^2 = \left[\frac{2}{3}\sqrt{b^4 - \frac{3}{4}} - \frac{b^2}{3}\right] \Big/ \left\{4\left[b^2 - \sqrt{b^4 - \frac{3}{4}}\right]^2\right\}, \quad \text{for} \quad b^2 \geq 1. \tag{5.19}$$

On this line $y$ and $x_2^2$ are given by

$$y = y_0 = 2\left[b^2 - \sqrt{b^4 - \frac{3}{4}}\right] \tag{5.20}$$

and

$$x_2^2 = 4\left[b^2 - \sqrt{b^4 - \frac{3}{4}}\right] \Big/ \left[\frac{2}{3}\sqrt{b^4 - \frac{3}{4}} - \frac{b^2}{3}\right]. \tag{5.21}$$

In Fig.5.4 $x_1^2 > 0$ ($< 0$) corresponds to the right (left) side of the curve $L_0$.

**Case** (ii) $-\sqrt{\frac{3}{4}} < b^2 \leq 1$

The roots $t_3$ and $t_4$ are always symmetric with respect to the imaginary axis as in case (i), and $t_1$ and $t_2$ are always pure imaginary as in case (b). However, $\mathrm{Im}(t_2)$ is negative in this case ($t_2 = 0$ when $b^2 = 1$) and accordingly the Stokes line structure is different from the case (b). Only one positive root of $y^2$ exists in the region $0 < y^2 < 1 + |\frac{b^2}{a^2}|$.

Another interesting boundary is the case that the three roots $t_2$, $t_3$ and $t_4$ lie on one line parallel to the real axis. Redefining the roots $t_1$ and $t_2$ as

$$t_1 = i(y + |x_1|) \quad \text{and} \quad t_2 = i(y - |x_1|), \tag{5.22}$$

we can find this boundary curve $L_1$ as (see Fig.5.4)

$L_1(t_2, t_3, t_4$, on the line):

$$\begin{aligned} a^2 &= \frac{1}{21^3}[5\sqrt{21 - 12b^4} + 6b^2]^2[\sqrt{21 - 12b^4} - 3b^2], \\ &- \sqrt{\frac{3}{4}} \leq b^2 \leq 1, \end{aligned} \tag{5.23}$$

on which $y$ is given by

$$y = y_1 = 21/[5\sqrt{21 - 12b^4} + 6b^2]. \tag{5.24}$$

Concerning to this boundary, we have the following two cases:

(c) above $L_1$ : $\mathrm{Im}(t_2) > \mathrm{Im}(t_3) = \mathrm{Im}(t_4)$ (Fig.5.3c)

and

(d) below $L_1$ : $\mathrm{Im}(t_2) < \mathrm{Im}(t_3) = \mathrm{Im}(t_4)$. (Fig.5.3d)

**Case** (iii) $b^2 \leq -\sqrt{\frac{3}{4}}$

The two roots $t_1$ and $t_2$ are always pure imaginary ($t_1 \neq t_2$). As for $t_3$ and $t_4$, there are following three cases according to the sign of $x_2^2$:

(e) $x_2^2 > 0$ : $t_3$ and $t_4$ are symmetric with respect to the imaginary axis (Fig.5.3e),

(e') $x_2^2 = 0$ : double pure imaginary roots $t_3 = t_4$

and

(f) $x_2^2 < 0$ : two pure imaginary roots (Fig.5.3f).

Now, it should be noted that there are two boundary curves corresponding to $x_2^2 = 0$.

From Eqs. (5.17) and (5.18) we obtain the following two roots for $y$:

$$y = y_2 = 2\left[\sqrt{b^4 - \frac{3}{4}} - b^2\right] \tag{5.25}$$

and

$$y = y_3 = \frac{3}{2}\left[\sqrt{b^4 - \frac{3}{4}} - b^2\right]^{-1}, \tag{5.26}$$

which lead to the boundary curves $L_2$ and $L_3$ given by

$$L_2(x_2^2 = 0) : a^2 = \frac{1}{4}\left[\frac{2}{3}\sqrt{b^4 - \frac{3}{4}} - \frac{1}{3}b^2\right] / \left[\sqrt{b^4 - \frac{3}{4}} - b^2\right]^2 \quad \text{for } b^2 \leq -\sqrt{\frac{3}{4}} \tag{5.27}$$

and

$$L_3(x_2^2 = 0) \quad : \quad a^2 = \frac{2}{9}\left[\sqrt{b^4 - \frac{3}{4}} - b^2\right]\left\{1 + \frac{2}{3}b^2\left[\sqrt{b^4 - \frac{3}{4}} - b^2\right]\right\},$$
$$\text{for} \quad -1 \leq b^2 \leq -\sqrt{\frac{3}{4}}. \tag{5.28}$$

It is easily seen that $x_2^2 < 0$ corresponds to the region bounded by $L_2$, $L_3$ and real axis. It should also be noted that since $\mathrm{Im}(t_2) < 0$ in $-1 < b^2 < -\sqrt{\frac{3}{4}}$, the Stokes line structure shown in Fig.5.3c actually corresponds to the region of $b^2 < -1$ and above $L_2$. The curves $L_1$ and $L_2$ are not smoothly connected, and the point $P$ in Fig.5.4 represents a triple point where three roots coalesce.

Before closing this section the following remark should be made about the number of positive roots of $y^2$ of Eq. (5.18) and its consequence on the distribution of the transition points. From the analysis of Eq. (5.18) we can easily find that there is only one positive root in the region $0 < y^2 < 1$ for $b^2 \geq 0$, and in the region $0 < y^2 < 1 + |\frac{b^2}{a^2}|$ for $-\sqrt{\frac{3}{4}} < b^2 \leq 0$. Furthermore, we also find in the case of $b^2 \leq -\sqrt{\frac{3}{4}}$ that there are two positive roots on the boundary curves $L_2$ and $L_3$, three roots in the region bounded by $L_2$ and $L_3$, and only one elsewhere. In any case, however, we confirmed that the existence of multiple roots of $y^2$ only requires renaming of the transition points and never change the distribution we found above.

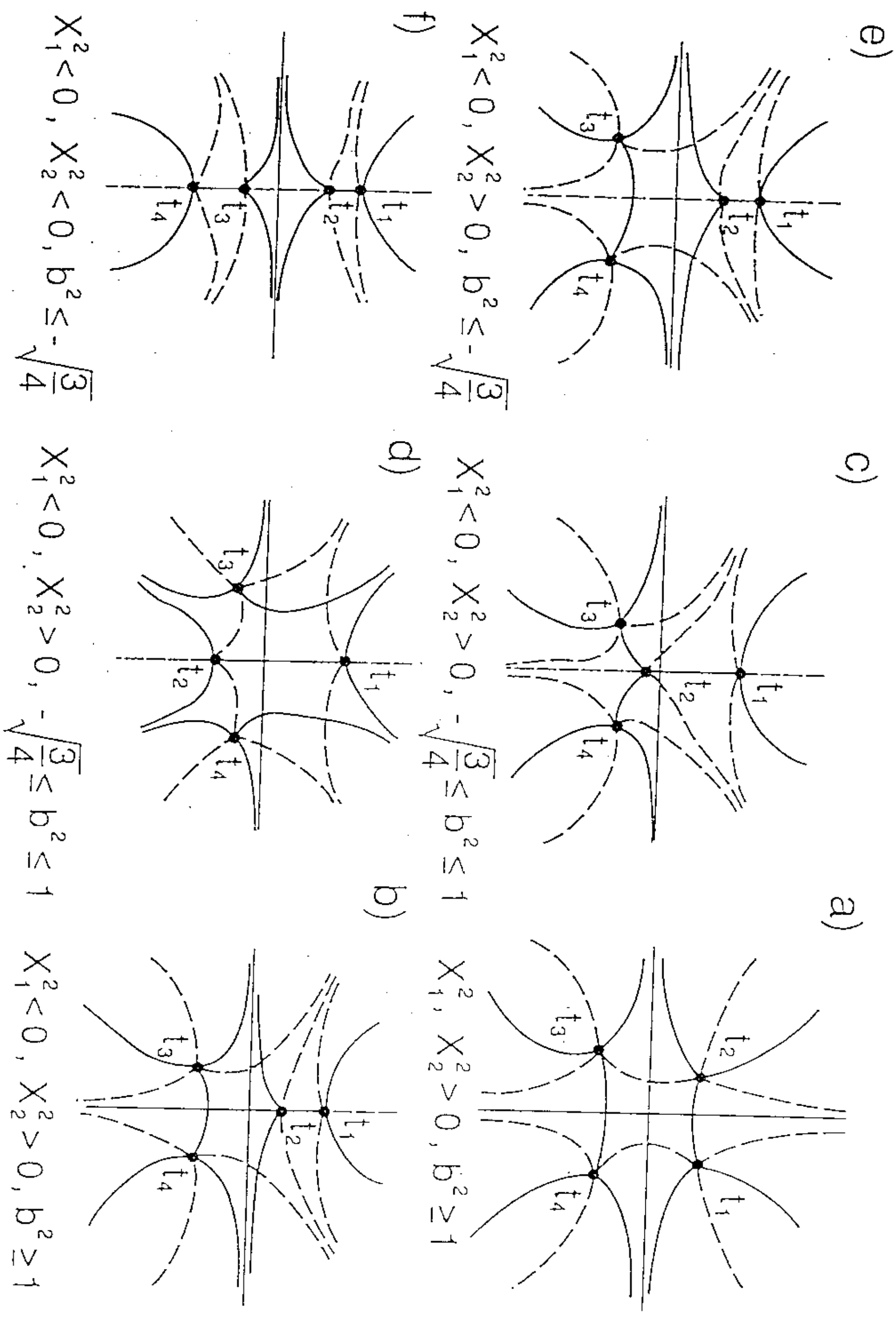



Figure 5.3: Distribution of transition points ($t_j$) in the case of opposite sign sign slopes. Case (a)–(f) are explained in the text and correspond to each region in Fig.5.4.

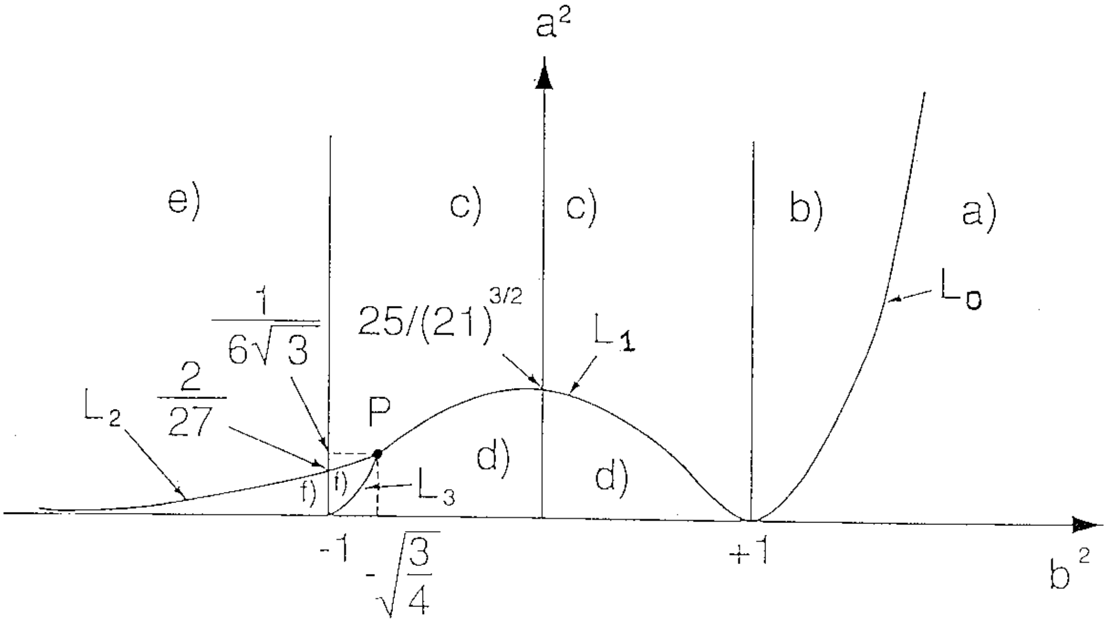



Figure 5.4: Two-dimensional diagram in $(a^2, b^2)$ plane to represent the various cases of Fig.5.3. The boundaries $L_j(j = 0 - - - 3)$ are defined in the text.

# Chapter 6

# Analytical approximations for the Stokes constant and scattering matrix: Landau-Zener case

Based on the analysis about distributions of the transition points and the Stokes lines in chapter 5, the semiclassical solution of the reduced scattering matrix for the Landau-Zener case is obtained in this chapter. This is made possible by reducing the four-transition-point problem to two two-transition-point problems. The new analytical formulas obtained in this chapter are simple and explicit functions of the two parameters $a^2$ and $b^2$. Especially, a simple formula which works much better than the conventional Landau-Zener formula is obtained.

## 6.1 Introduction

In chapter 4 the *quantum mechanically exact* expressions of the reduced scattering matrices $S^R$ have been derived for the two cases of the linear curve crossing problem, i.e., the same sign and the opposite sign of slopes of the two diabatic potentials. The scattering matrix $S^R$ in each case was expressed in terms of only one (complex) Stokes constant $U_1$; furthermore, this Stokes constant was found to be exactly and analytically given in the form of a convergent infinite series as a function of the two basic parameters which effectively represent collision energy and coupling strength.

In this chapter analytical approximations are proposed and reviewed for the case of the same sign of slopes (Landau-Zener case). The distribution of the four transition points and the Stokes lines in the complex plane, as was analyzed in chapter 5, is very crucial for deriving approximate analytical formulas and for clarifying their validity conditions. As is conjectured from Fig.5.1, there are the following three limiting cases in which approximate analytical solutions can be figured out: (a) Four transition points are well separated into two pairs along the real axis (anti-Stokes lines) (see Fig.6.2a), (b) they are well separated into two pairs along the imaginary axis (Stokes lines) (see Fig.6.3), and (c) they are very close together to the origin. Since there have been published numerous papers on the semiclassical treatments of the present Landau-Zener type of problem, let us first briefly review the history.

One of the phase-integral methods proposed by Zwaan and Stueckelberg[68] has been utilized for long time to provide the approximate semiclassical expressions for the two-state scattering matrix.[69]–[72] Later, an improvement was carried out by Crothers[73] who gave a general expression for the reduced scattering matrix involving the phase-integrals along the two adiabatic potentials analytically continued into the complex plane. On the other hand, the reduced scattering matrix for the linear curve crossing was also investigated in the diabatic state representation,[74] by using the WKB solutions associated with the parabolic cylinder functions. The results were directly expressed in terms of two basic parameters $a^2$ and $b^2$. These approximations are valid in the limiting case (a) mentioned above. In the limiting case (b) which corresponds to the collision energy lower than the crossing point of the two diabatic potentials, however, such a method was employed that takes into account only one pair of transition points in the upper half plane.[75] This method can not provide scattering matrix, but only give non-adiabatic transition probability. More importantly, it should be pointed out that the basic idea of this approximation is actually not appropriate, because the four transition points are not symmetrically distributed with respect to the real axis (see Fig.6.3) and should be treated as a whole. More sophisticated formulas for the reduced scattering matrices in the two limiting cases (a) and (b) were derived by Bárány[63, 76] in the adiabatic state representation based on the phase-integral method of Fröman and Fröman.[77] In this chapter, contributions from the two pairs of points in the upper and lower half planes are properly taken into account by going back to the diabatic state representation. In the limiting case (c), the perturbative method originally devised by Nikitin and co-workers[26, 75] works all right. The reduced scattering matrix is expressed in terms of Airy functions. Later, the formula has been rederived and interpreted more clearly by other authors[62, 63], but its validity condition has not yet been made very clear. Another different way of reducing the total scattering matrix was made by Nakamura in the context of semiclassical approximation.[78, 28] The scattering matrix is expressed as a product of matrices, each of which represents one of the basic events in the whole scattering process, namely, nonadiabatic transition at avoided crossing in incoming or outgoing segment, adiabatic wave propagation without any transition, and reflection at turning point. This reduction is very useful for dealing with a general multi-level problem. The idea of our present treatment is inspired by this method, although the connection matrices in this chapter are utilized to derive approximate analytical expressions of Stokes constant.

In this chapter two new approximate analytical expressions of the reduced scattering matrix are derived and are compared with the other available formulas. The treatment employed here is based on the phase-integral method developed by Heading.[4] Approximate connection matrices are used to derive analytical expressions of the Stokes constant $U_1$. For the limiting case (b) a new method of connection along the Stokes lines is proposed. The validity of each formula is made clear, and the whole two-parameter $(a^2, b^2)$-plane is divided into five regions; and recommended formulas in each region are presented. Furthermore, fitting formulas for the Stokes constant $U_1$ are also proposed for a region which is difficult to be covered by the analytical formulas.

This chapter is organized as follow: In the section 6.2, comparison of the exact connection matrix with approximate one will be explored for the Weber equation in order to completely understand a criteria of semiclassical approximation, and its underlying idea will be generalized to treat more complicated two limiting distributions of four transition points: Limiting case (a) in the section 6.3 and limiting case (b) in the section 6.4. The section 6.5 summarizes various analytical formulas of the reduced scattering matrix and clarifies their mutual relations. Elaborate numerical comparison is presented in the section 6.6 and the best working formulas are recommended. Concluding remarks is given in the section 6.7.

## 6.2 Semiclassical solution for the Weber equation

Since the connection matrix of the Weber equation can be both exactly and approximately solved in the compact form, we can clearly understand the criteria of the semiclassical approximation and its relation to distributions of transition points. Let us restart with the Weber equation:

$$\frac{d^2\phi(z)}{dz^2} + h^2(z^2 - \epsilon^2)\phi(z) = 0, \qquad h > 0, \tag{6.1}$$

where $\epsilon$ can be a complex constant; and assume $\mathrm{Re}\epsilon > 0$ without losing generality.

Two independent WKB solutions are given by

$$(\epsilon, z) = q^{-1/4}(z) \exp[i \int_{\epsilon}^{z} q^{1/2}(z) dz] \tag{6.2}$$

and

$$(z, -\epsilon) = q^{-1/4}(z) \exp[-i \int_{-\epsilon}^{z} q^{1/2}(z) dz] \tag{6.3}$$

where $q(z) = h^2(z^2 - \epsilon^2)$. It should be noted that the reference points for these two solutions are different, one at $\epsilon$ and the other at $-\epsilon$. The connection matrix, however, is defined in the same way as in the section 3.2. First we define general solutions on both sides of asymptotic regions as

$$\begin{aligned}\phi(z) &\underset{z\to+\infty}{=} A(\epsilon, z) + B(z, \epsilon) \\ &= A[\epsilon, 0](0, z) + B(z, 0)[0, \epsilon]\end{aligned} \tag{6.4}$$

and

$$\begin{aligned}\phi(z) &\underset{z\to+\infty}{=} C(-\epsilon, z) + D(z, -\epsilon) \\ &= C[-\epsilon, 0](0, z) + D(z, 0)[0, -\epsilon],\end{aligned} \tag{6.5}$$

in which the second equalities shift the reference points from $\pm\epsilon$ to 0, [ , ] represents WKB solution without $q^{-\frac{1}{4}}(z)$. The connection matrix is defined by

$$\begin{pmatrix} C \\ D \end{pmatrix} = F_{ext} \begin{pmatrix} A \\ B \end{pmatrix}, \tag{6.6}$$

where

$$F_{ext} = \begin{pmatrix} [-\epsilon, 0] & 0 \\ 0 & [0, -\epsilon] \end{pmatrix}^{-1} F \begin{pmatrix} [\epsilon, 0] & 0 \\ 0 & [0, \epsilon] \end{pmatrix}, \tag{6.7}$$

in which $F$ is the connection matrix of the WKB solutions with reference point at zero and is given by Eq. (3.35) of chapter 3. Finally, we have

$$F_{ext} = \begin{pmatrix} \sqrt{2\pi} e^{\pi\beta/2 - i\beta + i\beta\ln\beta}/\Gamma(1/2 + i\beta) & ie^{\pi\beta} \\ -ie^{\pi\beta} & \sqrt{2\pi} e^{\pi\beta/2 + i\beta - i\beta\ln\beta}/\Gamma(1/2 - i\beta) \end{pmatrix} \tag{6.8}$$

with

$$\beta = \frac{1}{2} h\epsilon^2. \tag{6.9}$$

Now suppose that the two transition points $\pm\epsilon$ can be separately taken into account. By tracing the WKB solution on path 2 of Fig.6.1, we obtain the connection matrices $F_1$ and $F_2$ which can be approximately found by the Airy equation. The procedures is the same as in the section 3.1. Consequently, the approximate connection matrix $F_{app}$ is obtained as

$$F_{app} = F_2 F_0 F_1, \tag{6.10}$$

where $F_2$ and $F_1$ have been given in Eqs. (3.11) and (3.16), respectively, and

$$F_0 = \begin{pmatrix} e^{\beta\pi} & 0 \\ 0 & e^{-\beta\pi} \end{pmatrix}, \tag{6.11}$$

which comes form continuity of the WKB solution and its first derivative at origin. Finally, we have

$$F_{app} = \begin{pmatrix} e^{\beta\pi} + \frac{1}{4}e^{-\beta\pi} & ie^{\beta\pi} - i\frac{1}{4}e^{-\beta\pi} \\ -ie^{\beta\pi} + i\frac{1}{4}e^{-\beta\pi} & e^{\beta\pi} + \frac{1}{4}e^{-\beta\pi} \end{pmatrix}. \tag{6.12}$$

Generally speaking, the connection matrix $F_{ext}$ in Eq. (6.8) and $F_{app}$ in Eq. (6.12) are different as is easily seen. But, if we consider a condition $|\beta| \gg 1$, $F_{ext}$ and $F_{app}$ approach the same limit $F_m$:

$$F_m = \begin{pmatrix} e^{\beta\pi} & ie^{\beta\pi} \\ -ie^{\beta\pi} & e^{\beta\pi} \end{pmatrix}, \tag{6.13}$$

where $\beta$ is defined in Eq. (6.9).

In the sense of semiclassical solution of $F_{app}$ the condition $|\beta| \gg 1$ has two implications. One is that for given $h$ , the distance between the two transition points $\epsilon$ and $-\epsilon$ should be relatively large, resulting in that WKB solution on path 2 is relatively far from the transition points. The other is that for given $\epsilon$, $h$ should be relatively large , resulting in classical limit of WKB solution. Thus, the strict condition is as follows:

$$|\beta| \gg 1. \tag{6.14}$$

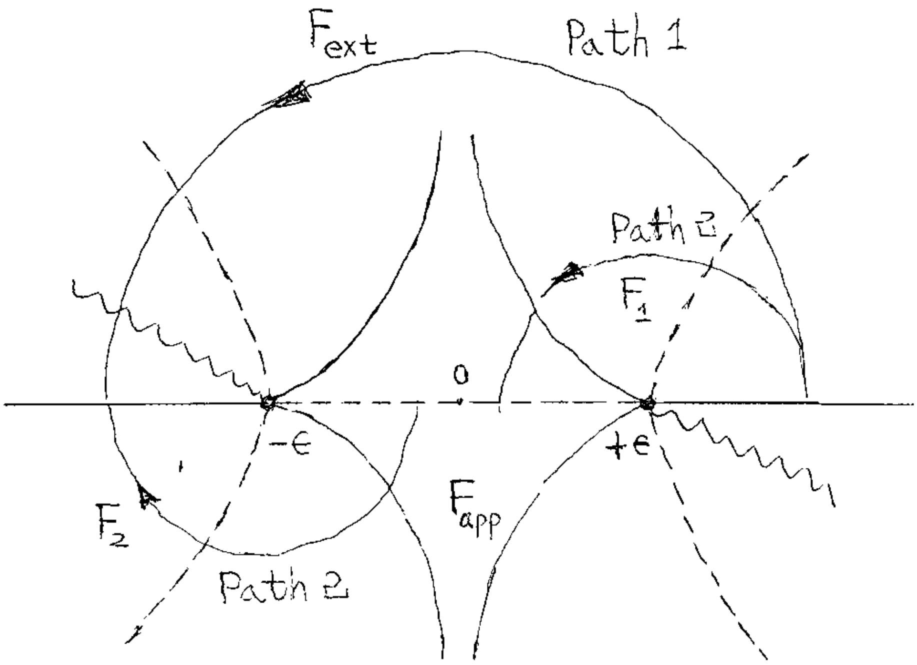



Figure 6.1.

## 6.3 Limiting case (a)

Roughly speaking, it is the limiting case (a) that the four transition points are separated into two paris along the anti-Stokes lines in Fig.6.2a. The procedure to derive our approximate matrix which connects the WKB solutions at $t \rightarrow +\infty$ and $t \rightarrow -\infty$ on the anti-Stokes lines gives us strict condition like Eq. (6.14) to define the limiting case (a). Actually, when the approximate matrix is compared with the exact one expressed in terms of the Stokes constant $U_1$, we can derive an analytical approximate expression for $U_1$. Two conditions for the validity of this approximation are obtained. These are separability condition (see Eq. (6.25)) and consistency condition (see Eq. (6.45)). First, let us apply the differential equation (3.68) of the section 3.4A for general four transition points to the basic differential equation (4.16) of the section 4.2A for this special four transition points. The exact connection matrix can be obtained in the following way. The asymptotic solutions of the basic differential equation (4.16) are written as

$$\phi(t) \underset{t\rightarrow+\infty}{\longrightarrow} Aq^{-1/4}(t)\exp[i\int_{x_0}^{t} q^{1/2}(t)dt] + Bq^{-1/4}(t)\exp[-i\int_{x_0}^{t} q^{1/2}(t)dt] \qquad (6.15)$$

and

$$\phi(t) \underset{t\to-\infty}{\longrightarrow} Cq^{-1/4}(t)\exp[i\int_{-x_0}^{t} q^{1/2}(t)dt] + Dq^{-1/4}(t)\exp[-i\int_{-x_0}^{t} q^{1/2}(t)dt], \quad (6.16)$$

where the reference points $x_0$ and $-x_0$ will be specified later (see Fig.6.2). In our linear curve crossing problem, $q(t)$ is given by Eq. (4.17). The exact connection matrix is defined by

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv L \begin{pmatrix} A \\ B \end{pmatrix}, \quad (6.17)$$

where $L$ is expressed in terms of the Stokes constant $U_1$ and phase-integrals as (see Eqs. (3.84), (3.79) and (3.80) of the section 3.4A with Eqs. (4.57) of the section 4.3A),

$$L = e^{-i\pi} \begin{pmatrix} (1 - U_1^* U_2)e^{-i\delta_- + i\delta_+} & 4a^4 U_2 e^{-i\delta_- - i\delta_+} \\ U_2 e^{i\delta_- + i\delta_+} & (1 + U_1 U_2)e^{i\delta_- - i\delta_+} \end{pmatrix}, \quad (6.18)$$

where $\delta_+$ and $\delta_-$ are estimated from the phase integrals,

$$i\int_{x_0}^{t} q^{1/2}(t)dt \underset{t\to+\infty}{\longrightarrow} iP(t) + \ln t + i\delta_+$$

and

$$i\int_{-x_0}^{t} q^{1/2}(t)dt \underset{t\to-\infty}{\longrightarrow} iP(t) + \ln t + i\delta_-, \quad (6.19)$$

where

$$P(t) = (\frac{1}{3}a^2t^3 - b^2t)/2. \quad (6.20)$$

Now the exact connection matrix in Eq. (6.18) has been derived from path 1 in Fig.6.2b.

In order to find an approximate connection matrix, we start from the distribution of the four transition points fully analyzed in the section 5.1. Instead of using $x_1$ and $x_2$, here we use $x_0$ and $\Delta x$ defined by

$$x_0 = (x_1 + x_2)/2 \quad (6.21)$$

and

$$\Delta x = (x_1 - x_2)/2. \quad (6.22)$$

Then, from Eqs. (5.6) of chapter 5 we obtain

$$\begin{aligned} x_0^2 + (\Delta x)^2 &= y^2 + b^2/a^2, \\ y(\Delta x)x_0 &= \frac{1}{2a^2}, \\ &\text{and} \\ (2x_0^2 - \frac{b^2}{a^2})^2 + \frac{1}{a^4x_0^2} &= (\frac{b^2}{a^2})^2 + \frac{1}{a^4}. \end{aligned} \quad (6.23)$$

In these new notations $q(t)$ can be rewritten as

$$q(t) = \frac{a^4}{4}[(t-x_0)^2 - (\Delta x + iy)^2][(t+x_0)^2 - (\Delta x - iy)^2]. \tag{6.24}$$

Since we obtained the approximate connection matrix of the Weber equation last section by reducing two-transition-point problem to two one-transition-point problems, this idea can be generalized here to reducing four-transition-point problem to two two-transition-point problems. Therefore, The first evident condition for the limiting case (a) is that the distance between the two pairs of transition points should be much larger than the distance between the two transition points in each pair (see Fig.6.2a). This separability condition is explicitly expressed as

$$x_0^2 \gg |\Delta x \pm iy|^2. \tag{6.25}$$

Since the distributions of Stokes lines around $x_0$ and $-x_0$ are topologically the same as that of the two-transition-point problem of the Weber equation, we can trace the WKB solutions in Eqs. (6.15) and (6.16) on path 2 from $t \to +\infty$ to $t \to 0^+$ and from $t \to 0^-$ to $t \to -\infty$ (Fig.6.2b). Then the whole connection matrix can be decomposed as

$$L^{app} = F_1 F_0 F_2 = F(-\beta_1) F_0 F(-\beta_2), \tag{6.26}$$

where the matrix $F$ is obtained from the Weber equation as is given in Eq. (3.35) of chapter 3, and the matrix $F_0$ is defined as

$$F_0 = \begin{pmatrix} e^{-i\Phi} & 0 \\ 0 & e^{i\Phi} \end{pmatrix} \tag{6.27}$$

with

$$\Phi = \int_{-x_0}^{x_0} q^{1/2}(t)dt. \tag{6.28}$$

It should be noted that in the present semiclassical treatment of the limiting case (a) the WKB solutions in Eqs. (6.15) and (6.16) are considered to be good at $t \sim 0$ and that the matrix $F_0$ is required for the continuity of the WKB solutions and its derivative at origin. The parameters $\beta_1$ and $\beta_2$ in Eq. (6.26) can be determined by the comparison equation method.[79] Here we explain the procedure, taking $\beta_1$ as an example. At $t \simeq -x_0$, the basic differential equation (4.16) with Eq. (6.24) can be approximately rewritten as

$$\frac{d^2\phi(t)}{dt^2} + \frac{1}{4}a^4\lambda^2[(t+x_0)^2 - (\Delta x - iy)^2]\phi(t) = 0. \tag{6.29}$$

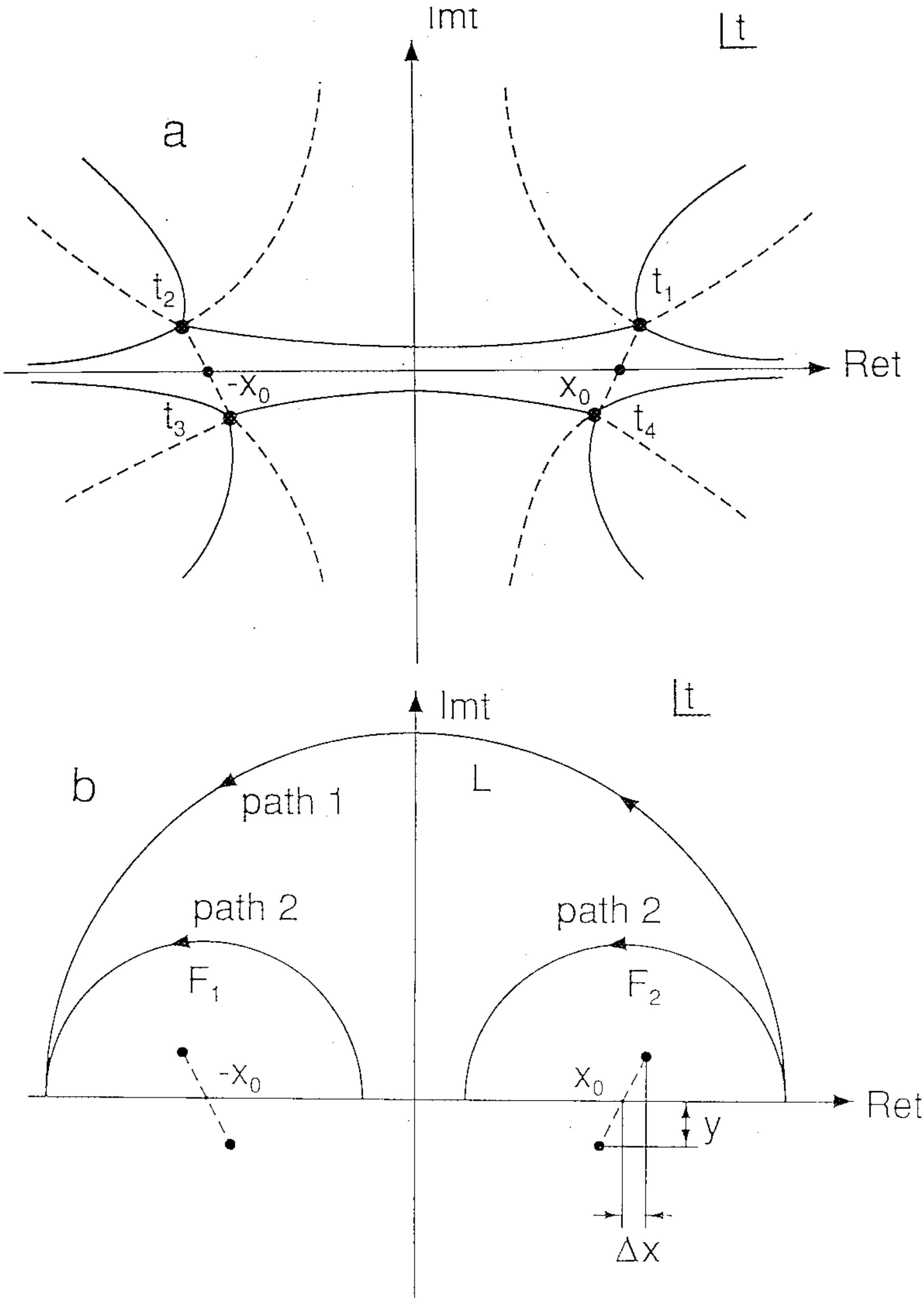



Figure 6.2: Limiting case (a): (a) $t_j$ are transition points and $\pm x_0$ the reference points. (b) Phase-integral paths.

Comparing Eq. (6.29) with Eq. (3.18) of the section 3.2A, we have

$$\beta_1 = -\frac{1}{4}a^2\lambda(\Delta x - iy)^2. \tag{6.30}$$

The requirement that the phase integrals from $t_2$ to $t_3$ for Eqs. (6.29) and (6.24) must be equal leads to

$$\begin{aligned} & \frac{1}{2}\int_{-x_0-(\Delta x-iy)}^{-x_0+(\Delta x-iy)} \sqrt{[(t-x_0)^2-(\Delta x+iy)^2][(t+x_0)^2-(\Delta x-iy)^2]}dt \\ = \; & \frac{1}{2}\lambda a^2 \int_{-x_0-(\Delta x-iy)}^{-x_0+(\Delta x-iy)} \sqrt{(t+x_0)^2-(\Delta x-iy)^2}dt. \end{aligned} \tag{6.31}$$

Under the separability condition Eq. (6.25) we have $\lambda \simeq 2x_0$, and thus

$$\beta_1 = -\frac{1}{2}a^2 x_0(\Delta x - iy)^2. \tag{6.32}$$

In the same way as above we can obtain

$$\beta_2 = -\frac{1}{2}a^2 x_0(\Delta x + iy)^2. \tag{6.33}$$

A simple manipulation with use of Eqs.(6.23) gives

$$2\beta_0 \equiv \beta_1 + \beta_2 = \frac{1}{4a^2 x_0}(1 - \frac{1}{x_0^2}) \tag{6.34}$$

and

$$\beta_1 - \beta_2 = i. \tag{6.35}$$

Finally, the matrix $L^{app}$ in Eq. (6.26) turns out to be explicitly given by

$$\begin{aligned} L_{11}^{app} &= \frac{2\pi}{\Gamma(1-i\beta_0)\Gamma(-i\beta_0)} e^{-\pi\beta_0} e^{2i\beta_0 - i\phi - i\Phi} + e^{-2\pi\beta_0} e^{i\Phi}, \\ L_{12}^{app} &= \frac{\sqrt{2\pi}i}{\Gamma(1-i\beta_0)} e^{-\pi\beta_1/2-\pi\beta_2} e^{i\beta_1 - i\beta_1 \ln\beta_1 - i\Phi} \\ &+ \frac{\sqrt{2\pi}i}{\Gamma(1+i\beta_0)} e^{-\pi\beta_2/2-\pi\beta_1} e^{-i\beta_2 + i\beta_2 \ln\beta_2 + i\Phi}, \\ L_{21}^{app} &= \frac{-\sqrt{2\pi}i}{\Gamma(-i\beta_0)} e^{-\pi\beta_2/2-\pi\beta_1} e^{i\beta_2 - i\beta_2 \ln\beta_2 - i\Phi} \\ &- \frac{\sqrt{2\pi}i}{\Gamma(i\beta_0)} e^{-\pi\beta_1/2-\pi\beta_2} e^{-i\beta_1 + i\beta_1 \ln\beta_1 + i\Phi}, \end{aligned}$$

and

$$L_{22}^{app} = e^{-2\pi\beta_0} e^{-i\Phi} + \frac{2\pi}{\Gamma(i\beta_0)\Gamma(1+i\beta_0)} e^{-\pi\beta_0} e^{-2i\beta_0 + i\phi + i\Phi}, \tag{6.36}$$

where

$$\phi = \beta_1 \ln \beta_1 + \beta_2 \ln \beta_2. \tag{6.37}$$

Next, the phase-integrals defined by Eqs. (6.19) and (6.28) should be explicitly determined under the separability condition Eq. (6.25). By defining

$$\delta_1 \equiv \delta_+ - \delta_- - \pi \tag{6.38}$$

and

$$\delta_2 \equiv \delta_+ + \delta_- + \pi, \tag{6.39}$$

and using the integral formulas given in Appendix of this chapter, we finally obtain

$$\Phi = \frac{2a^2 x_0^3}{3} - \beta_0 - \frac{1}{2}\phi + 2\beta_0 \ln(x_0\sqrt{a^2 x_0}), \tag{6.40}$$

$$\delta_1 = \Phi \tag{6.41}$$

and

$$i\delta_2 = \ln 2 + \frac{1}{2} + \frac{i}{2}[\beta_1 \ln \beta_1 - \beta_2 \ln \beta_2] + \ln \sqrt{a^2/(8x_0)}. \tag{6.42}$$

It should be noted that the first and higher order terms with respect to $|\Delta x \pm iy|^2/x_0^2$ are neglected under the separability condition. As is seen from Eq. (6.18), the ratio between $L_{12}$ and $L_{21}$ does not depend on the Stokes constants; thus it is natural to require

$$\frac{L_{12}^{app}}{L_{21}^{app}} = \frac{L_{12}}{L_{21}} = 4a^4 e^{-2i\delta_2}. \tag{6.43}$$

From this requirement we find

$$\beta_0 = \frac{1}{8a^2 x_0}, \tag{6.44}$$

which, in comparison with Eq. (6.34), leads to the second condition (consistency condition),

$$x_0^2 \gg 1. \tag{6.45}$$

It should be noted that Eq. (6.43) is equivalent to the symmetry $S_{12}^R = S_{21}^R$ and that $L^{app}$ already satisfies the other symmetry $S_{22}^R = (S_{11}^R)^*$(see the section 4.2A). Furthermore from Eq. (6.18) we find that the Stokes constant $U_1$ should satisfy

$$U_1 = (L_{22}e^{i\delta_1} - 1)e^{i\delta_2}/L_{21}. \tag{6.46}$$

If we use $L^{app}$ given by Eqs. (6.36), then we obtain

$$U_A^{ZN}(\equiv \text{approximate } U_1) = 2a^2(e^{2\pi\beta_0} - 1)^{1/2}e^{i\psi}, \tag{6.47}$$

where

$$\psi = 2a^2x_0^3/3 + \beta_0 \ln x_0^2 - 2\beta_0 - \beta_0 \ln \beta_0 - \arg\Gamma(i\beta_0) - \pi/4, \tag{6.48}$$

$\beta_0$ is defined by Eq. (6.44), and $x_0^2$ is approximately solved as

$$x_0^2 = \frac{1}{2}[\frac{b^2}{a^2} + \sqrt{\frac{b^4}{a^4} + \frac{1}{a^4}}] \tag{6.49}$$

under the consistency condition (6.45).

In conclusion, we have found an analytical approximate expression [Eq. (6.47)] for $U_1$ in a compact form under the two conditions [Eqs. (6.25) and (6.45)], which define the validity region of the limiting case (a). Numerical calculation shows that the formula works all right in a region wider than that defined by these strong inequalities. This will be discussed later in this chapter.

## 6.4 Limiting case (b)

Roughly speaking, it is the limiting case (b) that the four transition points are separated into two pairs on the imaginary axis (Stokes lines) (see Fig.6.3). The connection matrix must be evaluated along the Stokes lines rather than the anti-Stokes lines. Although this connection matrix does not represent the reduced scattering matrix anymore, this can be expressed in terms of the Stokes constants and phase-integrals along the Stokes lines; and an approximate analytical expression for $U_1$ can be derived by using the similar method to that in the previous section.

Let us next apply the results obtained in the section 3.4B for general four-transition-point problem to this special case. What we have to do is just to replace $q(t)$ of the section 3.4B by Eq. (4.17) of the section 4.2A. With use of the explicit relations among the Stokes constants given by Eqs. (4.57) of the section 4.3A, the connection matrix in Eq. (3.98) finally turns out to be

$$G = e^{-i\pi} \begin{pmatrix} e^{i\Delta_1}[16a^4 + (U_1 + U_1^*)^2]/[16a^4 + 4U_1U_1^*] & -e^{-i\Delta_2}[U_1 + U_1^*]/2 \\ -e^{i\Delta_2}[U_1 + U_1^*]/[8a^4] & e^{-i\Delta_1}(1 + U_1U_1^*/4a^4) \end{pmatrix} \tag{6.50}$$

with the phase-integrals,

$$\int_{iy}^{t} q^{1/2}(t)dt \underset{t\to\infty e^{i\pi/2}}{\longrightarrow} P(t) - i\ln t + \Delta_+$$

and

$$\int_{-iy}^{t} q^{1/2}(t)dt \underset{t\to\infty e^{-i\pi/2}}{\longrightarrow} P(t) - i\ln t + \Delta_-, \tag{6.51}$$

where

$$P(t) = (\frac{1}{3}a^2t^3 - b^2t)/2, \tag{6.52}$$

and reference points $\pm iy$ are specified later. The factor $\pi a_1/\sqrt{a_4}$ in the section 3.4B is omitted, because now this is equal to $-2\pi i$.

A procedure similar to that in the section 6.2 is employed. The coordinate $y$ to define the reference point is a solution of the following equation (Eq. (5.9) of chapter 5):

$$y^6 + \frac{b^2}{a^2}y^4 - \frac{1}{4a^4}y^2 - \frac{1}{4a^4} = 0. \tag{6.53}$$

The function $q(t)$ of Eq. (4.17) is rewritten for the present purpose as

$$q(t) = \frac{a^4}{4}[(t-iy)^2 - x_1^2][(t+iy)^2 - x_2^2]. \tag{6.54}$$

The separability condition in the present limiting case (b) may be expressed as

$$y^2 \gg x_1^2 + |x_2^2|. \tag{6.55}$$

The distribution of the four transition points is shown in Fig.6.3. It should be noted that $x_2^2$ can be negative and that the transition points $t_3$ and $t_4$ either lie parallel to real axis or sit on imaginary axis, whereas the points $t_1$ and $t_2$ always lie parallel to real axis. This indicates that an approximation which takes into account only one pair of transition points[61, 75] is not appropriate and the procedure used here is required. The distributions of Stokes lines around $iy$ and $-iy$ are topologically the same as two-transition-point problem studied in the section 3.2B. Thus, the whole connection matrix along the imaginary axis can be approximately decomposed into three parts. If we trace the solutions on path 1 in Fig.6.3, then the exact connection matrix of Eq. (6.50) is obtained. Going along path 2, we obtain

$$G^{app} = H_2H_0H_1 = H(\alpha_2)H_0H(\alpha_1), \tag{6.56}$$

where the matrix $H$ is given by Eq. (3.58) of the section 3.2B, and $H_0$ can be found in the same way as before:

$$H_0 = \begin{pmatrix} e^{-i\tilde{\Phi}} & 0 \\ 0 & e^{i\tilde{\Phi}} \end{pmatrix}, \tag{6.57}$$

where

$$\tilde{\Phi} = \int_{-iy}^{iy} q^{1/2}(t)dt \tag{6.58}$$

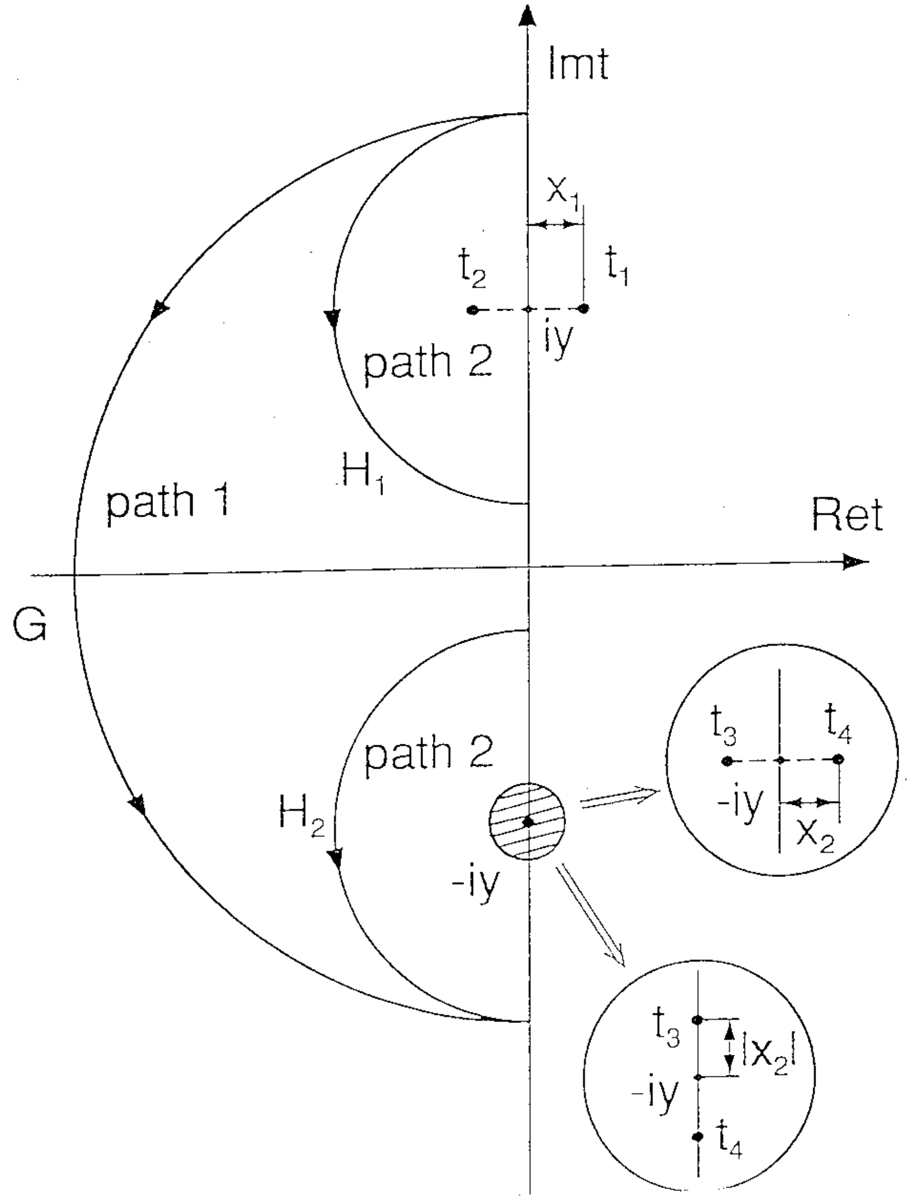



Figure 6.3: Limiting case (b): phase-integral paths.

with $q(t)$ given by Eq. (4.17). The comparison equation method same as before gives

$$\alpha_1 = \frac{1}{2}a^2 y x_1^2 \tag{6.59}$$

and

$$\alpha_2 = \frac{1}{2}a^2 y x_2^2. \tag{6.60}$$

With the aid of Eq. (5.7) and (5.8) of chapter 5, we can show

$$\alpha_0 \equiv (\alpha_1 + \alpha_2)/2 = \frac{1}{8a^2 y}(1 + \frac{1}{y^2}) \tag{6.61}$$

and

$$\alpha_1 - \alpha_2 = 1. \tag{6.62}$$

Finally, $G^{app}$ in Eq. (6.56) can be explicitly obtained as

$$\begin{aligned}
G_{11}^{app} &= -\frac{\pi}{2}\sin^2(\pi\alpha_0)\frac{e^{2\alpha_0-\phi}}{\Gamma(1-\alpha_0)\Gamma(-\alpha_0)}e^{-i\tilde{\Phi}} + \cos^2(\pi\alpha_0)e^{i\tilde{\Phi}}, \\
G_{12}^{app} &= -\frac{\sqrt{\pi}\sin(2\pi\alpha_0)e^{\alpha_2-\alpha_2\ln\alpha_2}}{2\sqrt{2}\Gamma(1-\alpha_0)}e^{-i\tilde{\Phi}} + \cos(\pi\alpha_0)\frac{\sqrt{2\pi}e^{-\alpha_1+\alpha_1\ln\alpha_1}}{\Gamma(1+\alpha_0)}e^{i\tilde{\Phi}}, \\
G_{21}^{app} &= \frac{\sqrt{\pi}\sin(2\pi\alpha_0)e^{\alpha_1-\alpha_1\ln\alpha_1}}{2\sqrt{2}\Gamma(-\alpha_0)}e^{-i\tilde{\Phi}} + \cos(\pi\alpha_0)\frac{\sqrt{2\pi}e^{-\alpha_2+\alpha_2\ln\alpha_2}}{\Gamma(\alpha_0)}e^{i\tilde{\Phi}}, \\
&\text{and} \\
G_{22}^{app} &= \cos^2(\pi\alpha_0)e^{-i\tilde{\Phi}} + \frac{2\pi e^{-2\alpha_0+\phi}}{\Gamma(\alpha_0)\Gamma(1+\alpha_0)}e^{i\tilde{\Phi}},
\end{aligned} \tag{6.63}$$

where

$$\phi = \alpha_1\ln\alpha_1 + \alpha_2\ln\alpha_2. \tag{6.64}$$

Our next task now is to determine the phase-integrals defined in Eqs. (6.51) and Eq. (6.58). With the help of the integral formulas in Appendix of this chapter, we obtain the following expressions under the separability condition (6.55):

$$i\tilde{\Phi} = 2a^2y^3/3 - \alpha_0 + 2\alpha_0\ln(2\sqrt{2y^3a^2}) - \phi/2, \tag{6.65}$$

$$\Delta_1 = \tilde{\Phi} - \pi, \tag{6.66}$$

and

$$i\Delta_2 = 1/2 + \ln\sqrt{a^2/(2y)} - \frac{1}{2}\alpha_1\ln\alpha_1 + \frac{1}{2}\alpha_2\ln\alpha_2. \tag{6.67}$$

The ratio between $G_{12}$ and $G_{21}$ does not depend on the Stokes constants and we can require

$$\frac{G_{12}^{app}}{G_{21}^{app}} = \frac{G_{12}}{G_{21}} = 4a^4e^{-2i\Delta_2}, \tag{6.68}$$

from which we obtain

$$\alpha_0 = \frac{1}{8a^2 y}. \tag{6.69}$$

A comparison with Eq. (6.61) leads to another condition (consistency condition),

$$y^2 \gg 1. \tag{6.70}$$

On the other hand, we see that the Stokes constant $U_1$ in Eq. (6.50) satisfies

$$\mathrm{Re}U_1 = G_{12} e^{i\Delta_2} \tag{6.71}$$

and

$$U_1 U_1^* = -4a^4 (G_{22} e^{i\Delta_1} + 1). \tag{6.72}$$

If we insert $G^{app}$ of Eqs. (6.63), then we have

$$\mathrm{Re}U_B^{ZN} \equiv \mathrm{Re}[\text{approximate } U_1] = \frac{2a^2}{\sqrt{\alpha_0}} \cos(\pi\alpha_0)[\frac{\sqrt{2\pi}}{\Gamma(\alpha_0)} e^{\psi_0} + \sqrt{\frac{\pi}{2}} \sin(\pi\alpha_0) \frac{e^{-\psi_0}}{\Gamma(-\alpha_0)}] \tag{6.73}$$

and

$$\mathrm{Im}U_B^{ZN} = \frac{2a^2}{\sqrt{\alpha_0}} \sin(\pi\alpha_0)[\frac{2\pi e^{2\psi_0}}{\Gamma^2(\alpha_0)} - \frac{\pi}{2}\cos^2(\pi\alpha_0)\frac{e^{-2\psi_0}}{\Gamma^2(-\alpha_0)} + \alpha_0 \cos(2\pi\alpha_0)]^{1/2}, \tag{6.74}$$

where

$$\psi_0 = \frac{2a^2 y^3}{3} - 2\alpha_0 + \alpha_0 \ln(\frac{y^2}{\alpha_0}), \tag{6.75}$$

with $\alpha_0$ given by Eq. (6.69). Under the consistency condition of Eq. (6.70), $y^2$ can be approximately solved as

$$y^2 = \frac{1}{2}[-\frac{b^2}{a^2} + \sqrt{\frac{b^4}{a^4} + \frac{1}{a^4}}]. \tag{6.76}$$

In conclusion, we have found the analytical approximate expressions for $U_1$ in Eqs. (6.73) and (6.74) under the two conditions Eqs. (6.55) and (6.70), which define the validity region of the limiting case (b). As will be discussed later, Eq. (6.74) is slightly modified so that this approximation can work well in a region much wider than that defined by these strong inequalities. This will be discussed in the next of this chapter.

## 6.5 Mutual relations among analytical formulas

Now it is time for us to make clear the mutual relations between the presently derived formulas and the other available analytical approximations for scattering matrix. The formulas by other authors we have selected here are the most sophisticated ones in each limiting case. They are reformulated in terms of the Stokes constant $U_1$, and the comparison is made at the level of $U_1$. The reduced scattering matrix is, of course, given by Eq. (4.55) of the section 4.3A.

**A. Limiting case (a)** $[x_0^2 \gg (\Delta x)^2 + y^2$ and $x_0^2 \gg 1]$

Analytical approximation for the Stokes constant $U_1$ can be generally expressed in a unified form as (see Eq. (6.47))

$$U_A = 2a^2(e^{2\Gamma} - 1)^{1/2} e^{i\psi}. \tag{6.77}$$

The following three approximations are considered:

**1. Present formula:**$U_A = U_A^{ZN}$ (Eq. (6.47)).

$$\Gamma = \Gamma_{ZN} = \pi\beta_0 \tag{6.78}$$

and

$$\begin{aligned} \psi = \psi_{ZN} &= \frac{2a^2x_0^3}{3} + \beta_0 \ln x_0^2 - 2\beta_0 - \beta_0 \ln \beta_0 - \arg\Gamma(i\beta_0) - \pi/4 \\ &\equiv \frac{2a^2x_0^3}{3} + \beta_0 \ln(\frac{x_0^2}{\beta_0^2}) - \beta_0 + \phi_S^{ZN}, \end{aligned} \tag{6.79}$$

with

$$\phi_S^{ZN} = \beta_0 \ln \beta_0 - \beta_0 - \arg\Gamma(i\beta_0) - \pi/4, \tag{6.80}$$

where

$$\beta_0 = \frac{1}{8a^2x_0} \tag{6.81}$$

and

$$x_0^2 = \frac{1}{2}\Big(\frac{b^2}{a^2} + \sqrt{\frac{b^4}{a^4} + \frac{1}{a^4}}\Big). \tag{6.82}$$

**2. Formula of Bárány:**[63] $U_A = U_A^B$.

$$\Gamma = \Gamma_B = \delta$$

and

$$\psi = \psi_B = \sigma - \frac{\delta}{\pi} + \frac{\delta}{\pi}\ln(\delta/\pi) - \arg\Gamma(i\delta/\pi) - \pi/4$$
$$\equiv \sigma + \phi_S^B, \tag{6.83}$$

where $\sigma$ and $\delta$ are defined by

$$\sigma + i\delta = \frac{1}{2\sqrt{a^2}}\int_{-b^2}^{i}[\frac{1+t^2}{b^2+t}]^{1/2}dt. \tag{6.84}$$

**3. Formula of Child:**[61] $U_A = U_A^C$.

$$\Gamma = \Gamma_C = \pi\delta_0. \tag{6.85}$$

and

$$\psi = \psi_C = \frac{2b^3}{3a} + \delta_0\ln(b^2/a^2) - \delta_0\ln\delta_0 - \arg\Gamma(i\delta_0) - \pi/4, \tag{6.86}$$

where

$$\delta_0 = \frac{1}{8ab}. \tag{6.87}$$

As is seen from the above three formulas, there holds the following correspondence among the parameters:

$$\beta_0 \Longleftrightarrow \delta/\pi \xrightarrow[b^2\gg 1]{} \delta_0, \tag{6.88}$$

$$\frac{2a^2x_0^3}{3} + \beta_0\ln(x_0^2/\beta_0^2) - \beta_0 \Longleftrightarrow \sigma \xrightarrow[b^2\gg 1]{} \frac{2b^3}{3a} + \delta_0\ln(b^2/a^2\delta_0^2) \tag{6.89}$$

and

$$\phi_S^{ZN} \Longleftrightarrow \phi_S^B, \tag{6.90}$$

where $\phi_S$ corresponds to the phase called "Stokes phase correction." Since $\beta_0 \to \delta_0[1 + o(b^{-4})]$ and $x_0 \to [b + o(b^{-3})]/a$ in the limit $b^2 \gg 1$, the phase $\psi_C$ is not necessarily a consistent limit of $\psi_{ZN}$ or $\psi_B$. Numerical comparisons indicate that $U_A^{ZN}$ and $U_A^B$ are better than $U_A^C$ and that all three coincide in the limit $b^2 \gg 1$.

It should be noted that $p \equiv e^{-2\Gamma}$ represents the nonadiabatic transition probability by one passage of avoided crossing point and that $p_{LZ} = e^{-2\pi\delta_0}$ is nothing but the conventional Landau-Zener probability. As will be explained later in detail (see Eqs. (6.113) and (6.114)), $p_A^{ZN} = e^{-2\pi\beta_0}$ is a very simple function of $a^2$ and $b^2$, and yet much better than $p_{LZ}$.

**B.Limiting case (b)** $[y^2 \gg x_1^2 + |x_2^2|$ and $y^2 \gg 1]$

Following the representation of Eqs. (6.73) and (6.74), we give here approximate analytical expressions of Re$U_1$ and Im$U_1$ also for the Bárány's approximation.

**1. Present formula:** $U_B = U_B^{ZN}$

$$\mathrm{Re}U_B^{ZN} = \frac{2a^2}{\sqrt{\alpha_0}}\cos(\pi\alpha_0)[\frac{\sqrt{2\pi}}{\Gamma(\alpha_0)}e^{\psi_0} + \sqrt{\frac{\pi}{2}}\sin(\pi\alpha_0)\frac{e^{-\psi_0}}{\Gamma(-\alpha_0)}] \tag{6.91}$$

and

$$\begin{aligned} \mathrm{Im}U_B^{ZN} &= \frac{2a^2}{\sqrt{\alpha_0}}\sin(\pi\alpha_0)[\frac{2\pi e^{2\psi_0}}{\Gamma^2(\alpha_0)} - \frac{\pi}{2}\cos^2(\pi\alpha_0)\frac{e^{-2\psi_0}}{\Gamma^2(-\alpha_0)} \\ &+ 3\alpha_0\cos^2(\pi\alpha_0) - 2\alpha_0\sin^2(\pi\alpha_0)]^{1/2} \end{aligned} \tag{6.92}$$

where

$$\psi_0 = \frac{2a^2y^3}{3} - 2\alpha_0 + \alpha_0\ln(y^2/\alpha_0), \tag{6.93}$$

$$\alpha_0 = \frac{1}{8a^2y} \tag{6.94}$$

and

$$y^2 = \frac{1}{2}\left(-\frac{b^2}{a^2} + \sqrt{\frac{b^4}{a^4} + \frac{1}{a^4}}\right). \tag{6.95}$$

Eq. (6.92) is slightly modified from Eq. (6.74). This modification is made by a numerical comparison with the exact results of Im$U_1$ and enables the present approximation to be applicable in a much wider region (region II in Fig.6.4) than that required by the two conditions given above. The difference between Eq. (6.74) and Eq. (6.92) appears only at $y^2 < 1$ which corresponds to the region $a^2 \geq -b^2 (b^2 < 0)$ in Fig.6.4. The real part of $U_B^{ZN}$ given by Eq. (6.91) remains still good in this region.

**2. Formula of Bárány:[63]** $U_B = U_B^B$.

$$\begin{aligned} \mathrm{Re}U_B^B &= \frac{2a^2}{\sqrt{\rho}}\cos(\pi\rho)\frac{\sqrt{2\pi}}{\Gamma(\rho)}e^{\delta-\rho+\rho\ln\rho} \\ &\text{and} \\ \mathrm{Im}U_B^B &= \frac{2a^2}{\sqrt{\rho}}\sin(\pi\rho)\frac{\sqrt{2\pi}}{\Gamma(\rho)}e^{\delta-\rho+\rho\ln\rho} \end{aligned} \tag{6.96}$$

or

$$|U_B^B| = \frac{2a^2}{\sqrt{\rho}}\frac{\sqrt{2\pi}}{\Gamma(\rho)}e^{\delta-\rho+\rho\ln\rho} \tag{6.97}$$

and

$$\arg U_B^B = \pi\rho. \tag{6.98}$$

with

$$\rho = \sigma/\pi, \tag{6.99}$$

where $\delta$ and $\sigma$ are defined again by Eq. (6.84).

**3. Formula of Bykhovskii,Nikitin and Ovchinnikova.[62, 65]**

In this approximation it is not possible to obtain an expression of the Stokes constant $U_1$; and only the nonadiabatic transition probability is given as follows:

$$P_B^{BNO} = \frac{2\delta_0}{\pi}\sin^2(\pi\delta_0)\Gamma^2(\delta_0)\delta_0^{-2\delta_0}e^{2\delta_0+4|b|^3/3a}, \tag{6.100}$$

where

$$\delta_0 = \frac{1}{8a|b|}. \tag{6.101}$$

This was derived by going around in the upper half complex $t-$plane from $t = -\infty$ to $+\infty$ by taking into account only one pair of transition points in Im$t > 0$. Since the distribution of the four transition points are not symmetric at all with respect to the real axis, as was discussed in the section 5.1, this approximation is not appropriate and the procedure proposed in the previous section should be utilized to take into account the effects of all the four transition points.

Correspondence among the parameters in the above three approximations is found to be as follows:

$$\alpha_0 \Longleftrightarrow \rho \underset{b^2 \ll -1}{\longrightarrow} \delta_0 = \frac{1}{8a|b|} \tag{6.102}$$

and

$$\frac{2a^2y^3}{3} + \alpha_0 \ln(y^2/\alpha_0^2) - \alpha_0 \Longleftrightarrow \delta. \tag{6.103}$$

It should be noted that Eqs. (6.91) and (6.92) contain extra terms compared to Eqs. (6.96). These represent a contribution from the subdominant solutions on the Stokes lines. This difference makes the present approximation better than Eqs. (6.96) at $a^2 \geq 2|b^2|$. The detailed comparison is made later.

Finally, it is interesting to note that the relations

$$\delta(-b^2) = \sigma(b^2) \tag{6.104}$$

and

$$x_0^2(b^2) = y^2(-b^2) \tag{6.105}$$

**C. Limiting case (c)** $[x_0^2 + y^2 \ll 1]$

When the diabatic coupling is weak ($a^2 \gg 1$), the first order perturbation theory should work all right.[75, 63, 26] This corresponds to the situation that all four transition points are located very close to the origin. In this case, the Stokes constant $U_1 \simeq U_C^{BNO}$ can also be expressed in the form of Eq. (6.77) with the parameters $\Gamma_C^{BNO}$ and $\psi_C^{BNO}$ given as,[62]

$$\Gamma \equiv \Gamma_C^{BNO} = \frac{1}{2}\ln\{1+\frac{1}{4}a^{-4/3}\pi^2[A_i^2(-\nu)+B_i^2(-\nu)]\} \tag{6.106}$$

and

$$\psi \equiv \psi_C^{BNO} = \arctan[A_i(-\nu)/B_i(-\nu)], \tag{6.107}$$

where

$$\nu = b^2/a^{2/3} \tag{6.108}$$

and $A_i(X)$ and $B_i(X)$ are the Airy functions.[80]

Since the Airy functions should be small enough in this approximation, another condition $|b^3/a| \leq 1$ may be required. Considering this condition the following simplified formula for transition probability is often utilized.[75]

$$\tilde{P}_C^{BNO} = \pi^2 a^{-4/3} A_i^2(-b^2 a^{-2/3}). \tag{6.109}$$

However, the numerical comparison indicates that the formula based on Eqs. (6.106) and (6.107) works better than Eq. (6.109) in region IV of Fig.6.4.

## 6.6 Numerical comparisons and recommended formulas

Detailed numerical comparisons among the various approximate formulas listed in the previous section are made here for the Stokes constant $U_1$ as well as for the nonadiabatic transition probability. Since the validity conditions given before are rather qualitative and a bit too strict for practical applications, we relax these conditions based on the numerical calculations here and divide the whole $(a^2, b^2)$−plane ($a^2 > 0$) into five regions I∼V bordered by the solid lines, as is shown in Fig.6.4. The boundaries are, of course, still not exact, but fuzzy. For each region except for region V the best recommended formulas are proposed. In region V, none of the presently available analytical approximations works satisfactorily, and we present

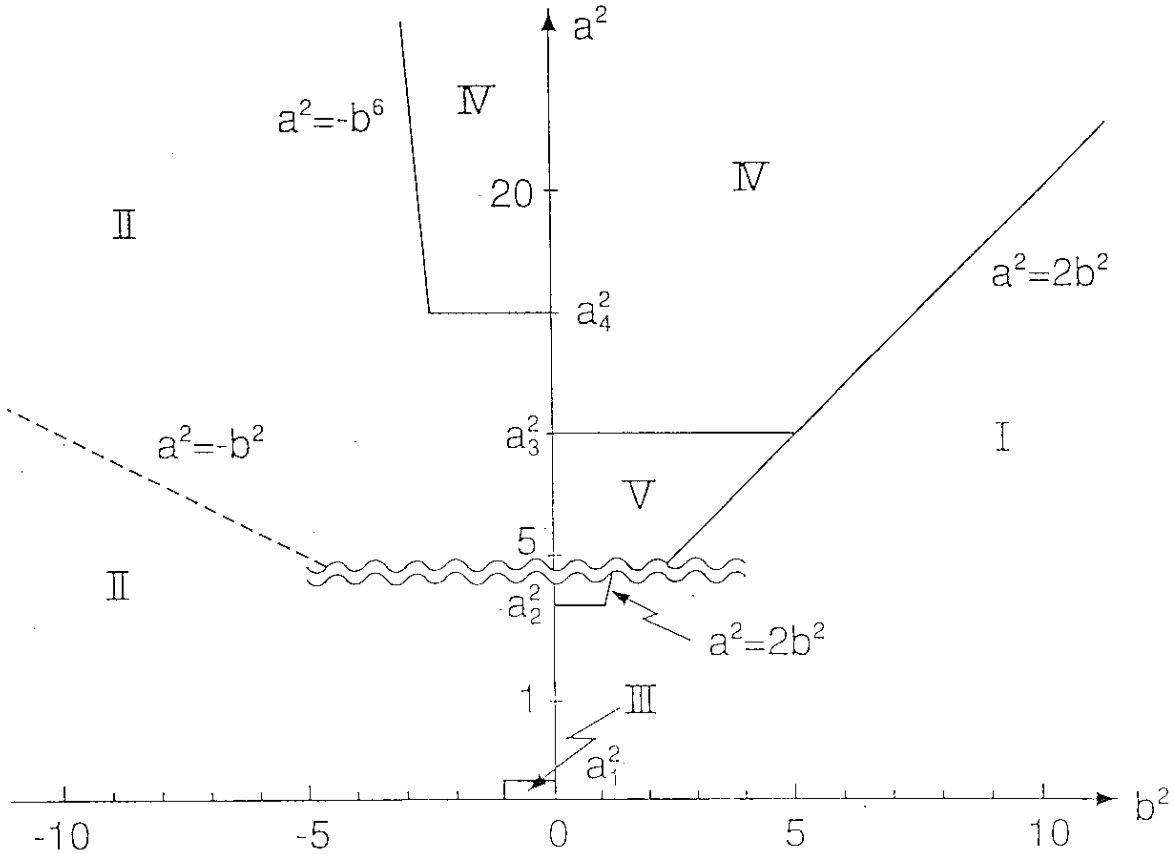



Figure 6.4: Five regions (I—V) in $(a^2, b^2)$ plane. Recommended formulas for the reduced scattering matrix are provided for each region. $a_1^2 = 0.2$, $a_2^2 = 2.0$, $a_3^2 = 10.0$ and $a_4^2 = 15.0$.

good fitting formulas for the Stokes constant $U_1$. The original conditions for the limiting cases (a)-(c) roughly correspond to (a) $b^2 \gg a^2$ and $b^2 \gg 1$, (b) $-b^2 \gg a^2$ and $-b^2 \gg 1$, and (c) $b^2 \ll a^2(b^2 > 0)$ and $-b^2 \ll a^2(b^2 < 0)$ with $a^2 \gg 1$.

Figs.6.5a-e show the Stokes constant $U_1$ for $a^2 = 0.1, 1.0, 5.0, 10.0$ and 15.0 as a function of $b^2$. $\text{Arg}(S_{11}^R)$ is also shown there. Figs.6.6a-e present the results of transition probability $P_{12}$ for the same values of $a^2$. In Figs.6.6c-e, the negative $b^2$ side is magnified. The overall transition probability $P_{12}$ given in the section 4.3A can be rewritten in the ordinary form as

$$P_{12} = \frac{16a^4(\Im U_1)^2}{(|U_1|^2 + 4a^4)^2} = 4p(1-p)\sin^2\Xi, \tag{6.110}$$

where

$$p = (1 + \frac{|U_1|^2}{4a^4})^{-1} \tag{6.111}$$

and

$$\Xi = \arg(U_1). \tag{6.112}$$

Here $p$ has a physical meaning of the nonadiabatic transition probability for one passage of crossing point.

**A. Region I.**

This region is an extension of the limiting case (a). The recommended formulas in this region are (see Figs.6.5a-e and 6.6a-e)

(ZN-I): Zhu-Nakamura given by Eqs. (6.78) and (6.79)

and

(B-I): Bárány given by Eqs. (6.83).

The probability $p$ and the phase $\Xi$ of Eq. (6.110) are given by $p = e^{-2\Gamma}$ and $\Xi = \psi$, respectively. These two approximations work equally well in the region $b^2 \geq 1$ and $b^2/a^2 \geq 1/2$. Furthermore, these approximations can be utilized even for $b^2 \leq 1$ in region I. As is seen from Figs.6.5a-b and 6.6a-b, the ZN-I (B-I) approximation works slightly better at $a^2 \geq 0.2(a^2 \leq 0.2)$.

It should be noted, however, that the ZN-I formulas given by Eqs. (6.78) and (6.79) are explicit simple functions of $a^2$ and $b^2$, while the elliptic type of integral (Eq. (6.84)) should be evaluated in the Bárány's approximation(B-I). Actually, $p_A^{ZN} = e^{-2\Gamma_{ZN}}$ in the ZN-I approximation can be simply expressed as

$$p_A^{ZN} = \exp[-\frac{\pi}{4a^2 x_0}] = \exp[-2\pi\delta_0 \frac{b}{a x_0}] \tag{6.113}$$

with

$$\frac{b}{ax_0} = \left[\frac{2}{1+\sqrt{1+\frac{1}{b^4}}}\right]^{1/2}, \tag{6.114}$$

where $p_{LZ} = e^{-2\pi\delta_0}$ is equal to the conventional Landau-Zener formula. Eq. (6.113) coincides with the latter in the limit $b^2 \gg 1$(see Eq. (6.114) ), but improves it very much at low energies and works well even near the crossing point ($b^2 \sim 0$), as is demonstrated in Fig.6.7. Namely, this formula (Eq. (6.113)) can replace the widely used conventional Landau-Zener formula in practical applications. This is actually one of the significant results obtained in the present thesis.

**B. Region II.**

This region is an extension of the limiting case (b) which roughly corresponds to $b^2 \ll -1$ and $b^2/a^2 \ll -1$. The recommended formulas in this region II are (see Figs.6.5a-e and 6.6a-e)

(ZN-II): Zhu-Nakamura given by Eqs. (6.91) and (6.92).

The Bárány's approximation given by Eqs. (6.96) can not work well in this extended region. This works well equally as the ZN-II only up to $a^2 \leq 2|b^2|$. This is basically because the contributions from the subdominant solutions on the Stokes lines are taken into account in Eqs. (6.91) and (6.92), as was mentioned before. In the same way as in region I, the present ZN-II approximation can be utilized even for $0 > b^2 \geq -1$ but with $a^2 \geq 0.2$. At $a^2 \leq 0.2$ the Bárány's approximation works better (see region III).

**C. Region III.**

This is a small region defined as $a^2 \leq 0.2$ and $-1 \leq b^2 < 0$. The recommended formulas are (see Figs.6.5a and 6.6a)

(B-III):Bárány given by Eqs. (6.96).

In this region the present approximation given by Eqs.(4.29) do not work well compared to the Bárány's. Eqs. (6.74) and (6.92) do not give any significant difference here. Eqs. (6.96) are simple functions of $\rho$ and $\delta$, but these parameters should be evaluated from the elliptic type integral of Eq. (6.84).

**D. Region IV.**

This corresponds to the weak coupling case, i.e., the limiting case (c). The first order perturbation theory first formulated by Bykhovskii, Nikitin and Ovchinnikova [75] and implemented later by others[26, 62, 63] works all right. So the recommended formulas are (see Figs.6.5d-e and 6.6d-e)

(BNO-IV): Bykhovsky, Nikitin and Ovchinnikova given by
Eqs. (6.106) and (6.107).

Asymmetry of this region with respect to the ordinate comes from the properties of the Airy functions. This BNO-IV approximation becomes better for larger $a^2$, but works relatively well also in the regions $b^2/a^2 \geq 1/2(b^2 > 0)$ and $|b^6|/a^2 \geq 1(b^2 < 0)$. Eq. (6.109) works all right at $b^2 < 0$ and $a^2 \geq 10$, but this region can be covered by the ZN-II approximation . Besides, Eq. (6.109) gives only probability.

**E. Region V.**

This region corresponds to the situation that the four transition points are neither well separated, nor very close together. So none of the approximations works well except for the region $b^2 < 0$ which can be covered by the modified ZN-II approximation. Based on the present approximations $U_A^{ZN}$ and $U_B^{ZN}$ (see Eqs. (6.77), (6.73) and (6.74)) for the Stokes constant $U_1$, we have obtained the following fitting formulas for $U_1$:

$$U_1 = U_A^{ZN} + \Delta U_A \qquad \text{for } b^2 \geq 0 \tag{6.115}$$

and

$$U_1 = U_B^{ZN} + \Delta U_B \qquad \text{for } b^2 \leq 0, \tag{6.116}$$

where

$$\begin{aligned}\Delta U_A &= (0.66 + 0.013a^2 + 3.1 \cdot 10^{-3}a^4)\frac{(1.8\frac{a^2-5}{a^2+31} - b^2)(b^2 - 4.6\frac{a^2+5.3}{a^2+10.8})}{b^2 + 3.7 - 0.17a^2 + 6.1 \cdot 10^{-3}a^4} \cdot \\ &\cdot\Theta[\ 4.6 \ \frac{a^2+5.3}{a^2+10.8} - b^2] + i\frac{9.5a^2}{a^2+27}\frac{b^2 - 5.2\frac{a^2+5.4}{a^2+22}}{b^2+2.1}\Theta[5.2\frac{a^2+5.4}{a^2+22} - b^2] \end{aligned} \tag{6.117}$$

and

$$\begin{aligned}\Delta U_B &= 10\frac{|b^2| - 2\frac{a^2-1.13}{a^2+15.5}}{|b^2| + 0.93\frac{a^2+42.7}{a^2+0.94}}\Theta[4.4\frac{a^2-2.1}{a^2+3.5} - |b^2|] + 0.67i\frac{a^2+3}{a^2+15.6}[|b^2| \\ &+ 5.9\frac{a^2+19}{a^2+63}][6.4\frac{a^2+22.6}{a^2+63} - |b^2|]\Theta[6.4\frac{a^2+22.6}{a^2+63} - |b^2|]. \end{aligned} \tag{6.118}$$

Here $\Theta[x]$ is an ordinary step function. These fitting formulas work almost perfectly and can not be distinguished from the exact numbers, if we draw a figure like Figs.6.5 and 6.6. A wider numerical test further confirms that the above equations can be used in practical applications, if necessary, for a very wide range, $50 \geq a^2 \geq 1$ and any $b^2$.

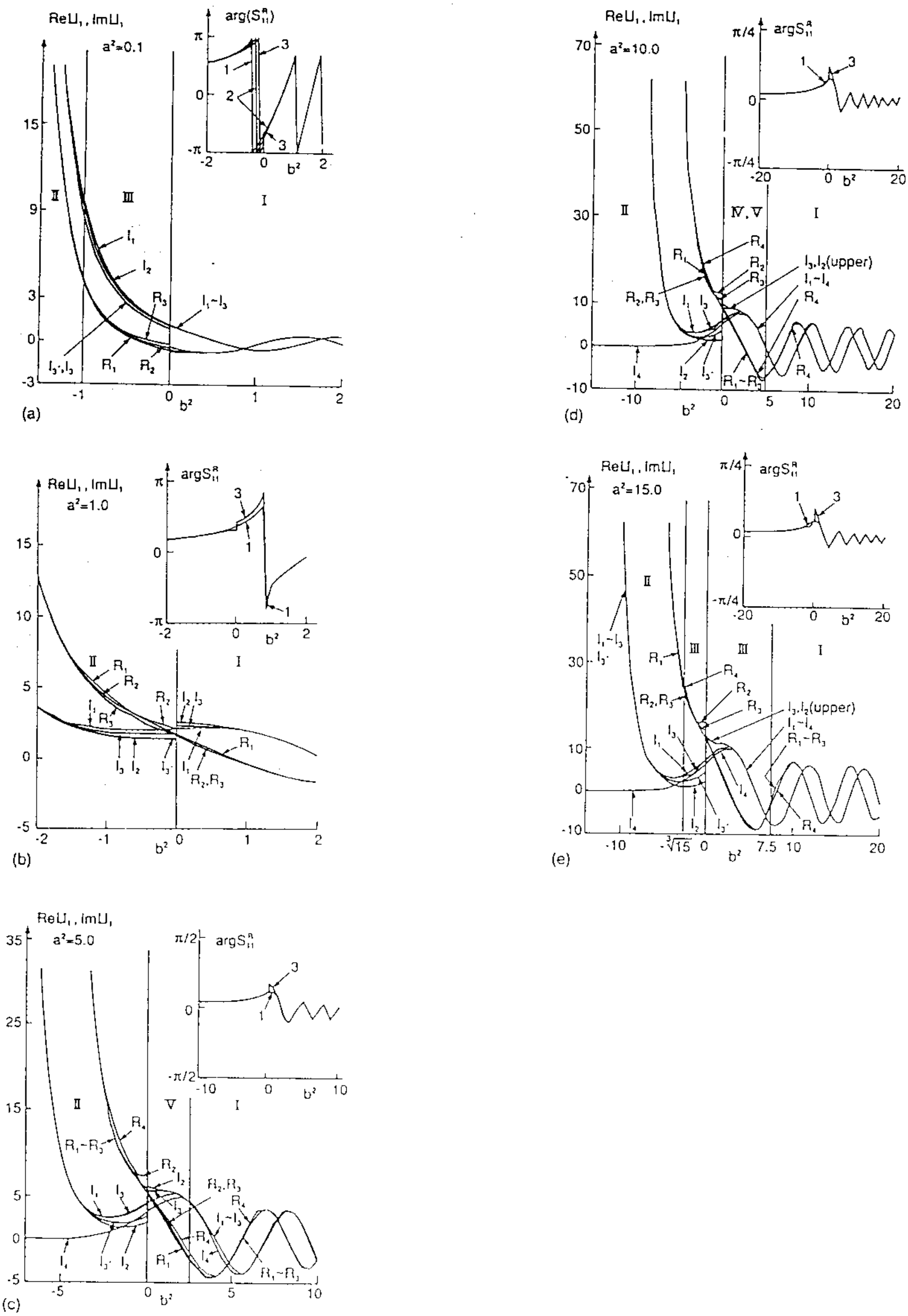



Figure 6.5: Stokes constant $U_1$ and $\arg(S^R_{11})$ as a function of $b^2$. $R(I)$ indicates real(imaginary) part of $U_1$. The number $j$ specifies the approximation as follows: $j=1$, exact; $j=2$, Bárány's approximation; $j=3$, present approximation with modified $\mathrm{Im}(U_1)$ for $b^2<0$; $j=3'$, present approximation; $j=4$, BNO approximation. The formulas of limiting case (a) for $b^2>0$ and limiting case (b) for $b^2<0$. (a) $a^2=0.1$; (b) $a^2=1.0$; (c) $a^2=5.0$; (d) $a^2=10.0$; (e) $a^2=15.0$.

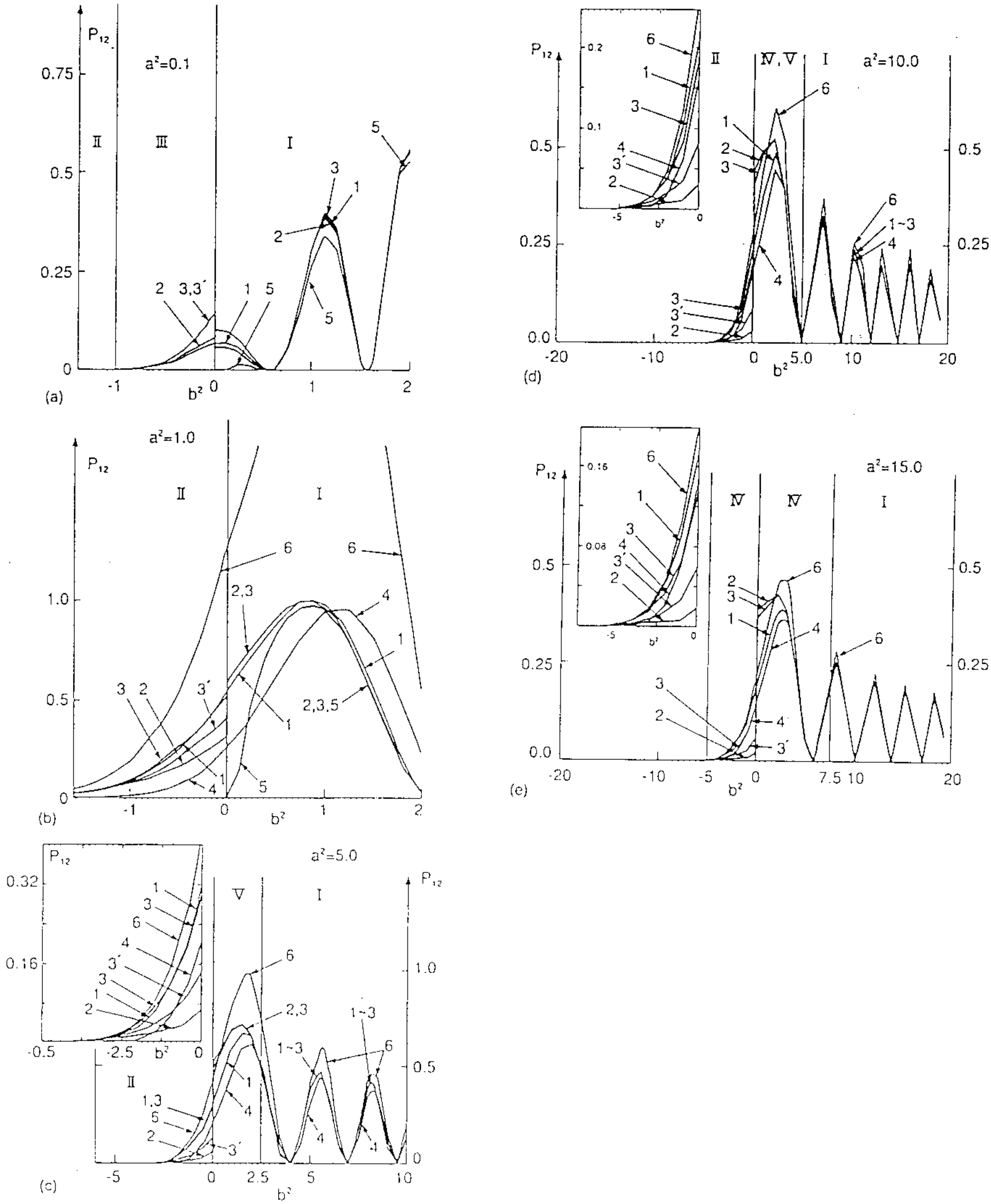


Figure 6.6: Transition probability $P_{12}$ as a function $b^2$. The number attached to each curve specifies the approximation as follows: $j = 1, 2, 3, 4$ is the same as Fig.6.5; $j = 5$, Child's approximation; $j = 6$, Eq.(6.109). The formulas of limiting case (a) for $b^2 > 0$ and limiting case (b) for $b^2 < 0$. (a) $a^2 = 0.1$; (b) $a^2 = 1.0$; (c) $a^2 = 5.0$; (d) $a^2 = 10.0$; (e) $a^2 = 15.0$.

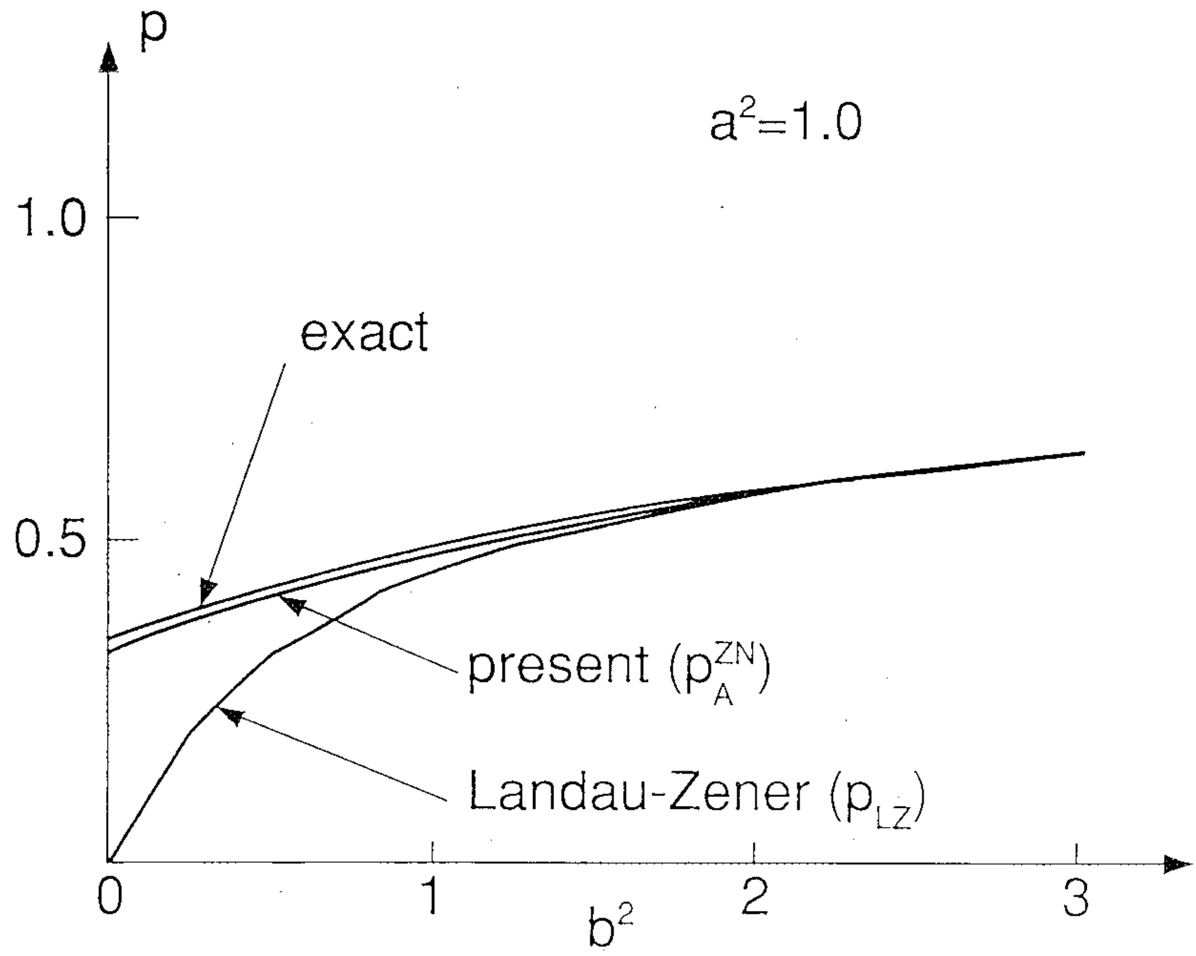



Figure 6.7: Nonadiabatic transition probability $p$ for one passage of crossing point as a function of $b^2$ in the case of $a^2 = 1.0$.

## 6.7 Concluding remarks

In the light of the exact solution obtained in chapter 4 that the reduced scattering matrix can be expressed in a compact form in terms of only one Stokes constant $U_1$, we have discussed analytical approximations to this constant $U_1$ for the Landau-Zener case and proposed two new formulas. We have considered the connections of asymptotic solutions along Stokes lines as well as anti-Stokes lines. Especially, we have properly treated, for the first time, the connection matrix along the Stokes lines to derive the reduced scattering matrix in the limiting case (b) at low energies in which the four transition points are separated into two pairs on the Stokes lines. That is to say, the contribution from the subdominant solutions on the Stokes lines is properly taken into account. The resulting formula was shown to work well in a wider range than that of Bárány.[63]

The formulas proposed in this chapter are simple functions of the two parameters: $a^2$(effective coupling strength) and $b^2$(effective collision energy). Neither sophisticated special functions nor any integrals are necessary to be evaluated. For instance, the nonadiabatic transition probability $p$ for one passage of crossing point valid at high energies has a simple and compact form (see Eq. (6.113) ), and is yet much better than the conventional Landau-Zener formula. This is very useful and can replace the latter in wide range of practical applications.

A thorough numerical comparison was carried out with the best available formulas such as those of Bárány[63], Child[61], and Nikitin and coworkers.[75] The validity region of each formula was clarified, and the two dimensional parameter $(a^2, b^2)$-plane was divided into five regions, in each one of which the best recommended formulas are proposed. In a region near crossing point at an intermediate coupling strength with $b^2 > 0$ no analytical approximation works satisfactorily, and certain (almost perfect) fitting formulas are presented for the Stokes constant $U_1$. If necessary for practical application, these can be used for any values of $a^2$ and $b^2$.

# Appendix

**Derivation of the phase integrals**

In order to evaluate the phase integrals such as Eqs. (6.19), (6.28), (6.51) and (6.58) under the separability condition Eqs. (6.25) or (6.55), we generally have to deal with the following integrals:

$$P_1(N;\alpha^2,\eta^2) \equiv \frac{a^2}{2}\int_X^N \sqrt{[(t-X)^2-\alpha^2][(t+X)^2-\eta^2]}dt \quad \text{for} \quad N\rightarrow\infty \tag{6.119}$$

and

$$P_2(\alpha^2,\eta^2) \equiv \frac{a^2}{2}\int_0^X \sqrt{[(t-X)^2-\alpha^2][(t+X)^2-\eta^2]}dt, \tag{6.120}$$

where $\alpha^2$ and $\eta^2$ are complex, and

$$X^2 \gg |\alpha^2|+|\eta^2|. \tag{6.121}$$

Under this condition, the second factor in the integrand of Eqs. (6.119) and (6.120) can be expanded as

$$\sqrt{(t+X)^2-\eta^2} \simeq (t+X) - \frac{\eta^2}{2(t+X)}. \tag{6.122}$$

Then we can obtain the following explicit expressions:

$$\begin{aligned} P_1(N;\alpha^2,\eta^2) &\simeq \frac{a^2}{2}[\frac{N^3}{3}-(X^2+\frac{\alpha^2}{2}+\frac{\eta^2}{2})N - X(\alpha^2-\eta^2)\ln N] \\ &+ \frac{a^2}{2}[\frac{2X^3}{3}+\frac{X}{2}\eta^2 - X\alpha^2\ln(\frac{2}{\sqrt{-\alpha^2}}) - X\eta^2\ln(2X)] \\ &\text{for} \quad N\rightarrow\infty \end{aligned} \tag{6.123}$$

and

$$P_2(\alpha^2,\eta^2) \simeq \frac{a^2}{2}[\frac{2X^3}{3} - \alpha^2 X\ln\frac{2X}{\sqrt{-\alpha^2}} - \eta^2 X\ln 2 + \frac{\eta^2}{2}X], \tag{6.124}$$

where the first term in Eq. (6.123) exactly cancels the divergent terms in Eqs. (6.19) and (6.51). From Eqs. (6.123) and (6.124), we can easily prove that

$$\begin{aligned} \frac{a^2}{2}(\int_X^N &+ \int_{-X}^{-N})\sqrt{[(t-X)^2-\alpha^2][(t+X)^2-\eta^2]}dt \\ &= P_1(N;\alpha^2,\eta^2) - P_1(N;\eta^2,\alpha^2) \\ &= -2(\beta-\beta')\ln N - (\beta-\beta')\ln 2 - \frac{1}{2}(\beta-\beta') \\ &- \beta'\ln(2X\sqrt{-\eta^2}) + \beta\ln(2X\sqrt{-\alpha^2}) \quad \mathrm{N}\rightarrow\infty \end{aligned} \tag{6.125}$$

and

$$\begin{aligned}
\frac{a^2}{2}\Big(\int_X^N &- \int_{-X}^{-N}\Big)\sqrt{[(t-X)^2-\alpha^2][(t+X)^2-\eta^2]}dt \\
&= \frac{a^2N^3}{3} - [a^2X^2 + (\beta+\beta')/X]N + \Phi \quad \text{for} \quad \mathrm{N} \to \infty, \qquad (6.126)
\end{aligned}$$

where

$$\begin{aligned}
\Phi &\equiv \frac{a^2}{2}\int_{-X}^{X}\sqrt{[(t-X)^2-\alpha^2][(t+X)^2-\eta^2]}dt \\
&= P_2(\alpha^2,\eta^2) + P_2(\eta^2,\alpha^2) \\
&= \frac{2a^2X^3}{3} + \frac{1}{2}(\beta+\beta') + \beta\ln(\frac{\sqrt{-\alpha^2}}{4X}) + \beta'\ln(\frac{\sqrt{-\eta^2}}{4X}) \qquad (6.127)
\end{aligned}$$

with

$$\beta = \frac{1}{2}a^2X\alpha^2 \qquad (6.128)$$

and

$$\beta' = \frac{1}{2}a^2X\eta^2. \qquad (6.129)$$

Directly applying the above formulas, we can obtain phase integrals in the text for the limiting cases (a) and (b).

# Chapter 7

# Analytical approximations for the Stokes constant and scattering matrix: Nonadiabatic tunneling case

Based on the analysis of distributions of the transition points and the Stokes lines in chapter 5, the semiclassical solution of the reduced scattering matrix for the nonadiabatic tunneling case is obtained in this chapter. There are two limiting cases in which the four-transition-point problems can be reduced to two two-transition-point problems. But, there is one case in which the four transition points must be treated as a whole. Again, The new analytical formulas obtained in this chapter are simple and explicit functions of the two parameters $a^2$ and $b^2$.

## 7.1 Introduction

In this chapter we shall deal with the case of the opposite sign of slope of two linear diabatic potential curves with constant coupling. This case is called "nonadiabatic tunneling."[60] This presents a quantum mechanical tunneling accompanied by nonadiabatic transition and represents one of the very basic mechanisms of state or phase change in various fields of physics, chemistry and biology.[28] It should be noted that this nonadiabatic tunneling is quite different from the ordinary tunneling through a single potential.[81]

In chapter 6 we derived analytical approximations for the Stokes constant $U_1$ in very compact forms for the Landau-Zener case (the same sign of slopes of two linear potential curves). The distributions of the four transition points and Stokes lines are generally classified into the following four cases: two limiting cases in which the transition points are well separated into two pairs either along anti-Stokes lines or Stokes lines, and a limiting case that they are located very close together to the origin. In the fourth case, they are neither well separated nor close together. In the former two cases the exact connection matrix was approximately reduced to a product of the two connection matrices of the Weber equation.

In this chapter, we will derive analytical approximations for the Stokes constant $U_1$ in the nonadiabatic tunneling case. As in the Landau-Zener case, there are also four cases, three of which correspond to $|b^2| \geq 1$ and are structurally similar to those in the Landau-Zener case. Approximate solutions of the Stokes constant $U_1$ can be found by using the same treatment as in chapter 6 in these three limiting cases. Based on the complete analysis of the corresponding Stokes phenomenon, we propose practically useful new analytical formulas for the reduced scattering matrix. Employing the phase-integral method of Fröman and Fröman[77] in the adiabatic state representation, Coveney et al.[67] derived certain analytical formulas. Their formula for $b^2 > 1$ works all right (almost equally well as ours), but the one for $b^2 < -1$ does not work at all. For the latter case, they proposed a certain empirical working equation only for nonadiabatic transition probability. Based on this formula and the fact that the reduced scattering matrix is expressed in terms of only one Stokes constant in our exact treatment, we can obtain new analytical formulas for the Stokes constant both in the present framework and in theirs. The former (our formula) is found to work slightly better than the latter; besides ours is a simple function of $a^2$ and $b^2$ compared to theirs which require elliptic type of integral. The fourth case is peculiar to nonadiabatic tunneling, corresponding to $|b^2| \leq 1$, namely, to the collision energy lower than the bottom of the upper adiabatic potential and higher than the top of the lower adiabatic potential. Four transition points are neither separated into any two pairs nor close together to origin. The distribution of transition points and Stokes lines is very different from the other cases. In this case we start with a new comparison equation method based on the exactly solvable special differential equation which can be reduced to Whittaker equation and finally give a good fitting formula for the Stokes constant $U_1$. The two-parameter $(a^2, b^2)$-

plane is divided into five regions and the best recommended formulas of reduced scattering matrix are proposed for each region.

This chapter is organized as follows: The section 7.2 discusses various expressions of the reduced scattering matrix , which facilitate physical interpretation in terms of Stokes constant $U_1$. In the section 7.3 analytical approximation for the Stokes constant $U_1$ is considered for the case $|b^2| \geq 1$ by using the connection matrices along either anti-Stokes lines or Stokes lines. The section 7.4 summarizes the various analytical formulas of reduced scattering matrix and clarifies their mutual relations. An accurate fitting formula for the Stokes constant is provided for the case $|b^2| \leq 1$ based on a new comparison equation method. Elaborate numerical comparison is made in section 7.5 and the best working formulas are recommended for each one of the five regions into which the whole two-parameter plane is divided. The section 7.6 presents concluding remarks.

## 7.2 Various expressions of reduced scattering matrix

As was derived in chapter 4, the quantum mechanically exact reduced scattering matrix $S^R$ in the diabatic representation is given by

$$S^R = \frac{1}{1 + U_1 U_2} \begin{pmatrix} 1 & \frac{U_2}{2a^2} \\ \frac{U_2}{2a^2} & 1 \end{pmatrix} \tag{7.1}$$

with

$$U_2 = \frac{U_1 - U_1^*}{U_1 U_1^* - \frac{1}{4a^4}}, \tag{7.2}$$

and nonadiabatic tunneling probability by

$$P_{12} = |S_{12}^R|^2 = \frac{(\mathrm{Im} U_1/a^2)^2}{[U_1 U_1^* - 1/(4a^4)]^2 + (\mathrm{Im} U_1/a^2)^2}, \tag{7.3}$$

where Stokes constant $U_1$ is, of course, a function of the two basic parameters $a^2$ and $b^2$. In this chapter our central task is to derive approximate solution of $U_1$.

In the following the exact reduced scattering matrix is rewritten in a few different forms so that physical interpretation can be facilitated and also nice comparison with other formulas can be attained. As can be easily seen from Eqs. (7.1) and (7.2), the matrix elements $S_{11}^R$ and $S_{12}^R$ can be rewritten as follows

$$S_{11}^R = \frac{1 - 4a^4|U_1|^2}{1 + 4a^4|U_1|^2 e^{2i\Xi}} = \frac{p}{1 + (1-p)e^{2i\Xi}} \tag{7.4}$$

$$= -\frac{1}{Q-(Q+1)e^{2i(\Xi-\pi/2)}}, \tag{7.5}$$

$$S_{12}^R = -\frac{4ia^2|U_1|\cos\Xi}{1+4a^4|U_1|^2e^{2i\Xi}} = -2i\frac{\sqrt{1-p}\cos\Xi}{1+(1-p)e^{2i\Xi}} \tag{7.6}$$

$$= -2i\frac{\sqrt{Q(Q+1)}\cos\Xi}{Q-(Q+1)e^{2i(\Xi-\pi/2)}}, \tag{7.7}$$

and

$$P_{12} \equiv |S_{12}^R|^2 = \frac{2\cos^2\Xi}{2\cos^2\Xi + p^2/[2(1-p)]} \tag{7.8}$$

$$= \frac{4Q(Q+1)\cos^2\Xi}{1+4Q(Q+1)\cos^2\Xi}, \tag{7.9}$$

where

$$p = 1-4a^4|U_1|^2, \tag{7.10}$$

$$\Xi = \arg U_1 - \pi/2, \tag{7.11}$$

$$Q = 1/(4a^4|U_1|^2-1) \tag{7.12}$$

and

$$U_1 = \frac{1}{2a^2}\sqrt{1-p} \quad e^{i\arg(U_1)}. \tag{7.13}$$

Eqs. (7.4) and (7.6) show a nice correspondence with the semiclassical approximation for[28] and $p$ defined by Eq. (7.10) satisfies $0 < p < 1$ for $b^2 > 1$ and has a clear physical meaning of nonadiabatic transition probability for one passage of crossing point. The $p$ and $\Xi$ exactly correspond to $e^{-2E}$ and $F - \pi/2$ in the treatment by Coveney et al.[67] The present treatment made clear the relations between these physical quantities and the Stokes constant $U_1$. Furthermore, Eq. (7.6) (or (7.8)) gives the quantum mechanical proof that "complete reflection", $P_{12} = 0$, occurs at $\arg(U_1) = n\pi (n = 0, 1, 2, ...)$. This can happen at many energies, since $\arg(U_1)$ increases with $b^2 \to +\infty$. Eqs. (7.5) and (7.7) give the following direct correspondence with the treatment of Coveney et al.[67] for $b^2 < -1$ :

$$Q \longleftrightarrow e^{2E} \quad \text{and} \quad \Xi \longleftrightarrow \phi + \pi/2. \tag{7.14}$$

Furthermore, Eq. (7.9) possesses the same form as that found in the section 4.5 i.e. $P_{12} = |W|^2/(1+|W|^2)$ with $|W|^2 = 4Q(Q+1)\cos^2\Xi$. Since $\arg(U_1) \to 0$ for $b^2 \to -\infty$, $P_{12}$ does not oscillate but monotonically decreases for $b^2 < -1$.

## 7.3 Analytical approximation for $U_1$ in the case $|b^2| \geq 1$

In the case of the opposite sign of slopes , there are also the following two limiting cases: The case that the four transition points are well separated into two pairs on the anti-Stokes lines (real axis) which is called limiting case (a) and the case that they are separated on the Stokes lines which is called limiting case (b). Using the same treatment as in chapter 6, the approximate connection matrix in each case can be obtained and a comparison with the exact one expressed in terms of the Stokes constant $U_1$ can lead to an approximate expression of $U_1$. The separability condition and consistency condition are derived in the process in the same way as in chapter 6.

### A. Limiting case (a)

The exact connection matrix along anti-Stokes lines is defined by the asymptotic solutions of the basic differential equation (4.30) of the section 4.2B,

$$B_1(t) \underset{t\to+\infty}{\longrightarrow} Aq^{-1/4}(t)\exp[i\int_{x_0}^{t} q^{1/2}(t)dt] + Bq^{-1/4}(t)\exp[-i\int_{x_0}^{t} q^{1/2}(t)dt] \tag{7.15}$$

and

$$B_1(t) \underset{t\to-\infty}{\longrightarrow} Cq^{-1/4}(t)\exp[i\int_{-x_0}^{t} q^{1/2}(t)dt] + Dq^{-1/4}(t)\exp[-i\int_{-x_0}^{t} q^{1/2}(t)dt] \tag{7.16}$$

with

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv L \begin{pmatrix} A \\ B \end{pmatrix}, \tag{7.17}$$

where the reference points $x_0$ and $-x_0$ will be specified later (see Fig.7.1) The connection matrix $L$ can be expressed in terms of Stokes constant $U_1$ and phase integrals as (see Eqs. (3.84), (3.79) and (3.80) of chapter 3, and (4.69) of the section 4.3B)

$$L = e^{-i\pi} \begin{pmatrix} (1 - U_1^* U_2)e^{-i\delta_- + i\delta_+} & -\frac{1}{4a^4} U_2 e^{-i\delta_- - i\delta_+} \\ U_2 e^{i\delta_- + i\delta_+} & (1 + U_1 U_2)e^{i\delta_- - i\delta_+} \end{pmatrix}, \tag{7.18}$$

where the Stokes constant $U_2$ is defined in Eq. (7.2), and $\delta_+$ and $\delta_-$ are calculated from

$$i\int_{x_0}^{t} q^{1/2}(t)dt \underset{t\to+\infty}{\longrightarrow} iP(t) - \ln t + i\delta_+$$

and

$$i\int_{-x_0}^{t} q^{1/2}(t)dt \underset{t\to-\infty}{\longrightarrow} iP(t) - \ln t + i\delta_- \tag{7.19}$$

with

$$P(t) = \frac{1}{2}(\frac{a^2t^3}{3} - b^2t). \tag{7.20}$$

In order to find an approximate connection matrix, let us start with the distribution of four transition points which was analyzed in the section 5.2B. Instead of using $x_1$ and $x_2$, here we use $x_0$ and $\Delta x$ defined by

$$x_0 = (x_1 + x_2)/2 \tag{7.21}$$

and

$$\Delta x = (x_2 - x_1)/2. \tag{7.22}$$

Then, from Eqs. (5.16), (5.17) and (5.18) of chapter 5 we have

$$\begin{aligned} x_0^2 + (\Delta x)^2 &= y^2 + \frac{b^2}{a^2}, \\ y(\Delta x)x_0 &= \frac{1}{2a^2} \\ &\text{and} \\ (2x_0^2 - \frac{b^2}{a^2})^2 + \frac{1}{a^4x_0^2} &= (\frac{b^2}{a^2})^2 - \frac{1}{a^4}. \end{aligned} \tag{7.23}$$

In these new notations $q(t)$ in Eq. (4.31) of the section 4.2B can be rewritten as

$$q(t) = \frac{a^4}{4}[(t - x_0)^2 - (\Delta x - iy)^2][(t + x_0)^2 - (\Delta x + iy)^2]. \tag{7.24}$$

The separability condition is now explicitly given by

$$x_0^2 \gg |\Delta x \pm iy|^2, \tag{7.25}$$

under which we can trace the WKB solutions in Eqs. (7.15) and(7.16) on path 2 in Fig.7.1 from $t \to +\infty$ to $t \to -\infty$. Then the whole connection matrix can be decomposed as

$$L^{app} = F_2F_0F_1 = F(\beta_2)F_0F(\beta_1), \tag{7.26}$$

where the matrix $F$ is obtained from the Weber equation given in Eq. (3.35) of the section 3.2A, and the matrix $F_0$ is defined as

$$F_0 = \begin{pmatrix} e^{-i\Phi} & 0 \\ 0 & e^{i\Phi} \end{pmatrix} \tag{7.27}$$

with

$$\Phi = \int_{-x_0}^{x_0} q^{1/2}(t)dt. \tag{7.28}$$

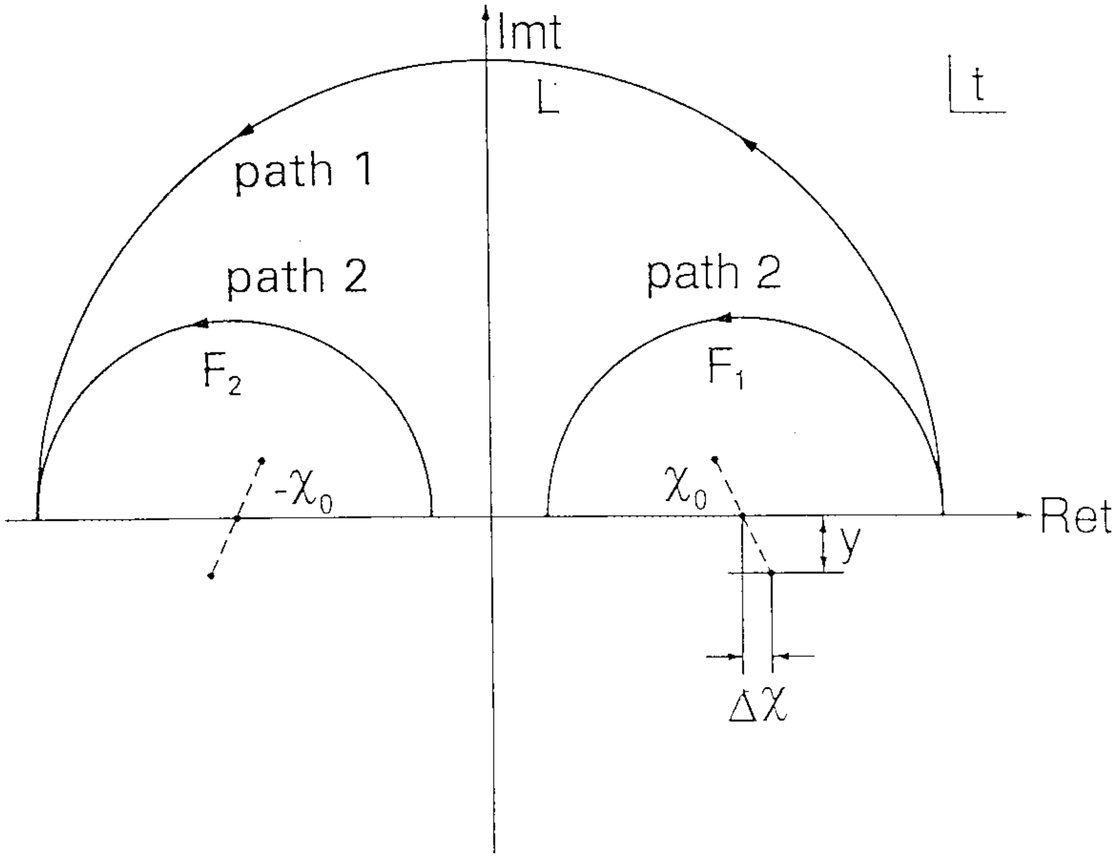



Figure 7.1: Phase-integral paths in the limiting case (a).

By using the same treatment as in chapter 6, the parameters $\beta_1$ and $\beta_2$ in Eq. (7.26) can be obtained as

$$\beta_1 = \frac{1}{2}a^2 x_0(\Delta x - iy)^2 \tag{7.29}$$

and

$$\beta_2 = \frac{1}{2}a^2 x_0(\Delta x + iy)^2. \tag{7.30}$$

A simple manipulation with use of Eqs. (7.23) gives

$$2\beta_0 \equiv \beta_1 + \beta_2 = \frac{1}{4a^2 x_0}(1 + \frac{1}{x_0^2}) \tag{7.31}$$

and

$$\beta_1 - \beta_2 = -i. \tag{7.32}$$

Finally, the connection matrix $L^{app}$ in Eq. (7.26) turns out to be explicitly given by

$$\begin{aligned}
L_{11}^{app} &= \frac{2\pi}{\Gamma(i\beta_0)\Gamma(1+i\beta_0)} e^{\pi\beta_0} e^{-2i\beta_0 + i\phi - i\Phi} + e^{2\pi\beta_0} e^{i\Phi}, \\
L_{12}^{app} &= i\frac{\sqrt{2\pi}}{\Gamma(i\beta_0)} e^{\pi\beta_2/2 + \pi\beta_1} e^{-i\beta_2 + i\beta_2 \ln(e^{i\pi}\beta_2) - i\Phi} \\
&+ i\frac{\sqrt{2\pi}}{\Gamma(-i\beta_0)} e^{\pi\beta_2 + \pi\beta_1/2} e^{i\beta_1 - i\beta_1 \ln(e^{i\pi}\beta_1) + i\Phi}, \\
L_{21}^{app} &= -i\frac{\sqrt{2\pi}}{\Gamma(1+i\beta_0)} e^{\pi\beta_2 + \pi\beta_1/2} e^{-i\beta_1 + i\beta_1 \ln(e^{i\pi}\beta_1) - i\Phi} \\
&- i\frac{\sqrt{2\pi}}{\Gamma(1-i\beta_0)} e^{\pi\beta_1 + \pi\beta_2/2} e^{i\beta_2 - i\beta_2 \ln(e^{i\pi}\beta_2) + i\Phi} \\
&\text{and} \\
L_{22}^{app} &= e^{2\pi\beta_0} e^{-i\Phi} + \frac{2\pi}{\Gamma(1-i\beta_0)\Gamma(-i\beta_0)} e^{\pi\beta_0} e^{2i\beta_0 - i\phi + i\Phi},
\end{aligned} \tag{7.33}$$

where

$$\phi = \beta_1 \ln(e^{i\pi}\beta_1) + \beta_2 \ln(e^{i\pi}\beta_2). \tag{7.34}$$

Next, let us calculate the phase integrals in Eqs. (7.19) and (7.28). By using the integral formulas given in Appendix of chapter 6, we finally obtain

$$\Phi = \frac{2a^2 x_0^3}{3} + \beta_0 + \frac{1}{2}\phi - \beta_0 \ln(8x_0^3 a^2), \tag{7.35}$$

$$\delta_1 \equiv \delta_+ - \delta_- + \pi = \Phi \tag{7.36}$$

and

$$\delta_2 = \delta_+ + \delta_- + \pi = i\ln 2 + \frac{i}{2} + \frac{1}{2}[\beta_1 \ln(e^{i\pi}\beta_1) - \beta_2 \ln(e^{i\pi}\beta_2)] + i\ln\sqrt{a^2/(8x_0)}. \tag{7.37}$$

It should be noted that the first and higher order terms with respect to $|\Delta x \pm iy|^2/x_0^2$ are neglected under the separability condition Eq. (7.25). Since the ratio $L_{12}/L_{21}$ does not depend on the Stokes constants, as is seen from Eq. (7.18), we require

$$\frac{L_{12}^{app}}{L_{21}^{app}} = \frac{L_{12}}{L_{21}} = -\frac{1}{4a^4}e^{-2i\delta_2}. \tag{7.38}$$

From this requirement we find

$$\beta_0 = \frac{1}{8a^2 x_0}, \tag{7.39}$$

which leads to the consistency condition

$$x_0^2 \gg 1 \tag{7.40}$$

in comparison with Eq. (7.31). Furthermore, from Eq. (7.18) we find that the Stokes constant $U_1$ should satisfy

$$U_1 = (L_{22}e^{i\delta_1} - 1)e^{i\delta_2}/L_{21}. \tag{7.41}$$

If we use $L^{app}$ given in Eqs. (7.33), we have

$$U_A^{ZN}(\equiv \text{approximate } U_1) = \frac{i}{2a^2}(1 - e^{-2\pi\beta_0})^{1/2}e^{i\psi} \tag{7.42}$$

with

$$\psi = \frac{2a^2}{3}x_0^3 - \beta_0 \ln x_0^2 + 2\beta_0 + \beta_0 \ln \beta_0 + \arg \Gamma(i\beta_0) + \frac{\pi}{4}, \tag{7.43}$$

where $\beta_0$ is defined by Eq. (7.39) and $x_0^2$ can be solved as

$$x_0^2 = \frac{1}{2}[\frac{b^2}{a^2} + \sqrt{\frac{b^4}{a^4} - \frac{1}{a^4}}] \tag{7.44}$$

from Eqs. (7.23) under the consistency condition Eq. (7.40). Eq.(7.44) implies that $b^2 \geq 1$ is a necessary condition for maintaining the separability in Fig.7.1.

**B. Limiting case (b)**

In the case of $b^2 \ll -1$ the four transition points are well separated into two pairs along Stokes lines (imaginary axis). As in chapter 6, we consider the connection along this line. The exact connection matrix along Stokes lines is defined by the following asymptotic solutions of the basic equation (4.30) of chapter 4 :

$$\phi(t) \underset{t \to e^{i\pi/2}\infty}{\longrightarrow} A(iy,t)_d + B(t,iy)_s \tag{7.45}$$

and

$$\phi(t) \underset{t\to e^{-i\pi/2}\infty}{\longrightarrow} C(-iy,t)_s + D(t,-iy)_d, \tag{7.46}$$

where $y$ will be specified later, the suffices $s$ and $d$ mean subdominant and dominant, respectively, and

$$(t',t'') = q^{-1/4}(t)\exp[i\int_{t'}^{t''} q^{1/2}(t)dt]. \tag{7.47}$$

The connection matrix is given by

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv G \begin{pmatrix} A \\ B \end{pmatrix}. \tag{7.48}$$

Since the connection matrix along Stokes lines for a general four transition point problem was analyzed in chapter 3, we here use Eqs. (3.93)—(3.98) of chapter 3 and Eqs. (4.69) of the section 4.3B. Then we can easily obtain

$$G = e^{-i\pi} \begin{pmatrix} e^{i\Delta_1}[(\mathrm{Re}U_1)^2 - 1/(4a^4)]/[|U_1|^2 - 1/(4a^4)] & -e^{-i\Delta_2}\mathrm{Re}U_1 \\ 4a^4 e^{i\Delta_2}\mathrm{Re}U_1 & e^{-i\Delta_1}(1-4a^4|U_1|^2) \end{pmatrix} \tag{7.49}$$

with

$$\Delta_1 = \Delta_+ - \Delta_- + 2\pi \tag{7.50}$$

and

$$\Delta_2 = \Delta_+ + \Delta_- - 2\pi, \tag{7.51}$$

where $\Delta_+$ and $\Delta_-$ can be estimated from

$$\int_{iy}^{t} q^{1/2}(t)dt \underset{t\to e^{i\pi/2}\infty}{\longrightarrow} P(t) + i\ln t + \Delta_+$$

and

$$\int_{-iy}^{t} q^{1/2}(t)dt \underset{t\to e^{-i\pi/2}\infty}{\longrightarrow} P(t) + i\ln t + \Delta_-. \tag{7.52}$$

Let us next find an approximate connection matrix. It is assumed that the four transition points are well separated on the Stokes lines as in Fig.7.2. The reference points $\pm iy$ in Eqs. (7.52) satisfy (Eq. (5.18) of the section 5.2)

$$(2y^2 + \frac{b^2}{a^2})^2 - \frac{1}{a^4y^2} = (\frac{b^2}{a^2})^2 - \frac{1}{a^4}. \tag{7.53}$$

The $q(t)$ in Eq. (4.31) of the section 4.2B can be rewritten in the present case as

$$q(t) = \frac{1}{4}[(t-iy)^2 - x_1^2][(t+iy)^2 - x_2^2], \tag{7.54}$$

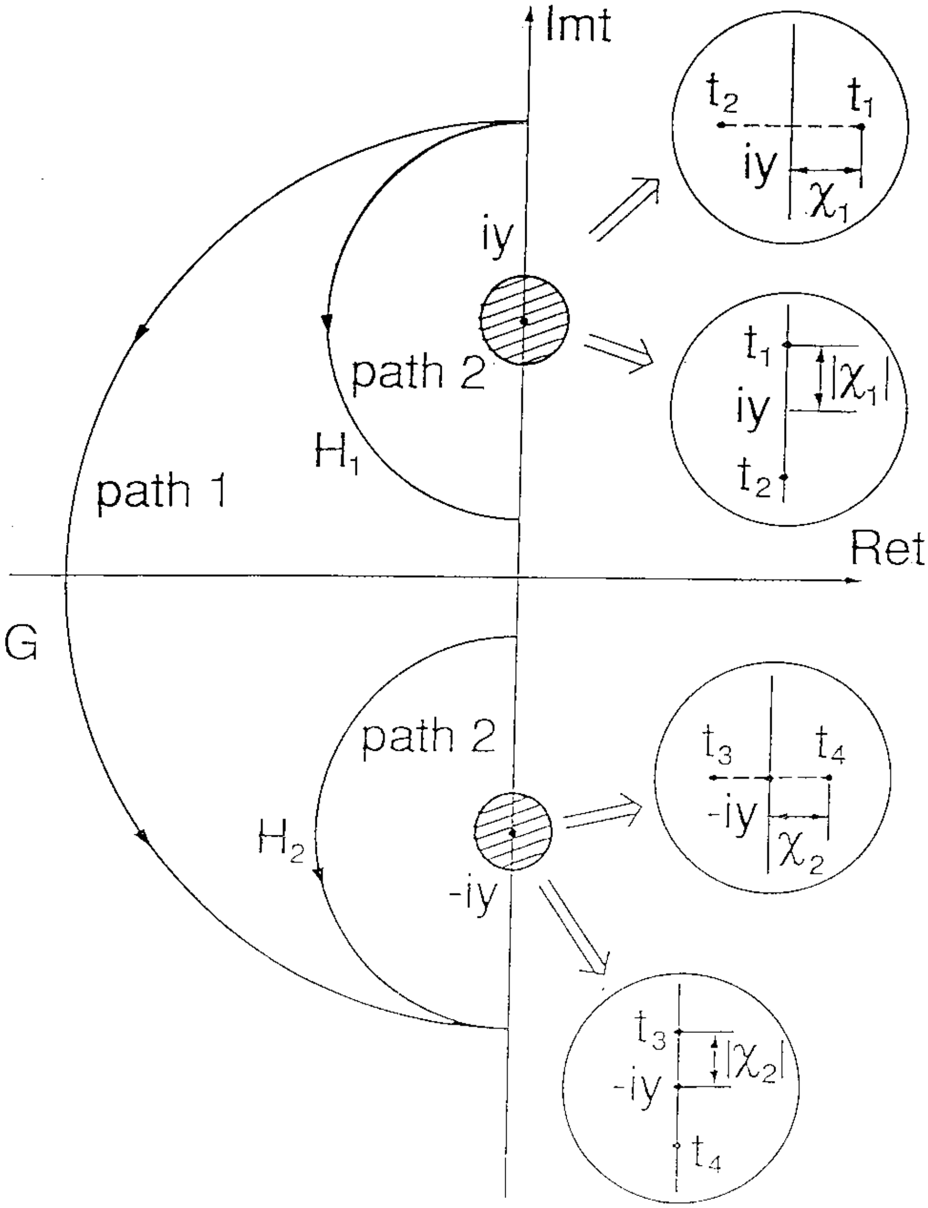



Figure 7.2: Phase-integral paths in the limiting case (b).

where $x_1^2$ and $x_2^2$ are given in Eqs. (5.16) and (5.17) of the section 5.2. The separability condition is defined by

$$y^2 \gg |x_1^2| + |x_2^2|, \tag{7.55}$$

under which we can trace the WKB solutions Eqs. (7.45) and (7.46) on path 2 in Fig.7.2. Then we obtain

$$G^{app} = H_2 H_0 H_1 = H(\alpha_2) H_0 H(-\alpha_1), \tag{7.56}$$

where the matrix $H$ is defined by Eq. (3.58) of the section 3.2B, and $H_0$ is given by

$$H_0 = \begin{pmatrix} e^{-i\tilde{\Phi}} & 0 \\ 0 & e^{i\tilde{\Phi}} \end{pmatrix} \tag{7.57}$$

with

$$\tilde{\Phi} = \int_{-iy}^{iy} q^{1/2}(t)dt. \tag{7.58}$$

The same procedure as in chapter 6 can be utilized to determine the parameters $\alpha_1$ and $\alpha_2$ as

$$\alpha_1 = -\frac{1}{2} a^2 y x_1^2 \tag{7.59}$$

and

$$\alpha_2 = \frac{1}{2} a^2 y x_2^2. \tag{7.60}$$

With help of Eqs. (5.16), (5.17) and (5.18) of the section 5.2, we have

$$2\alpha_0 \equiv \alpha_1 - \alpha_2 = \frac{1}{4a^2 y}(1 - \frac{1}{y^2}), \tag{7.61}$$

and

$$\alpha_1 + \alpha_2 = 1. \tag{7.62}$$

Finally, $G^{app}$ in Eq. (7.56) can be explicitly obtained as

$$\begin{aligned}
G_{11}^{app} &= -\frac{\pi}{2} \sin^2(\pi\alpha_0) \frac{e^{-2\alpha_0 + \tilde{\phi}} e^{-i\tilde{\Phi}}}{\Gamma(\alpha_0)\Gamma(1+\alpha_0)} + \cos^2(\pi\alpha_0) e^{i\tilde{\Phi}}, \\
G_{12}^{app} &= \sqrt{\frac{\pi}{2}} \frac{\sin(2\pi\alpha_0)}{2\Gamma(\alpha_0)} e^{\alpha_2 - \alpha_2 \ln(\alpha_2)} e^{-i\tilde{\Phi}} \\
&- \cos(\pi\alpha_0) \frac{\sqrt{2\pi}}{\Gamma(-\alpha_0)} e^{\alpha_1 - \alpha_1 \ln(e^{-i\pi}\alpha_1)} e^{i\tilde{\Phi}}, \\
G_{21}^{app} &= -\sqrt{\frac{\pi}{2}} \frac{\sin(2\pi\alpha_0)}{2\Gamma(1+\alpha_0)} e^{-\alpha_1 + \alpha_1 \ln(e^{-i\pi}\alpha_1)} e^{-i\tilde{\Phi}}
\end{aligned}$$

$$- \quad \cos(\pi\alpha_0)\frac{\sqrt{2\pi}}{\Gamma(1-\alpha_0)}e^{-\alpha_2+\alpha_2\ln(\alpha_2)}e^{i\tilde{\Phi}}$$

and

$$G_{22}^{app} = \cos^2(\pi\alpha_0)e^{-i\tilde{\Phi}} + \frac{2\pi}{\Gamma(-\alpha_0)\Gamma(1-\alpha_0)}e^{2\alpha_0-\tilde{\phi}}e^{i\tilde{\Phi}}, \tag{7.63}$$

where

$$\tilde{\phi} = \alpha_1\ln(e^{-i\pi}\alpha_1) - \alpha_2\ln(\alpha_2). \tag{7.64}$$

Our next task now is to determine the phase integrals defined in Eqs. (7.52) and (7.58). With help of the integral formulas in Appendix of chapter 6, we obtain the following results:

$$i\tilde{\Phi} = \frac{2a^2y^3}{3} + \alpha_0 - \alpha_0\ln(8a^2y^3) + \frac{\tilde{\phi}}{2}, \tag{7.65}$$

$$\Delta_1 = \tilde{\Phi} + \pi, \tag{7.66}$$

and

$$i\Delta_2 = -\frac{1}{2} - \ln\sqrt{a^2/(2y)} + \frac{1}{2}[\alpha_1\ln(e^{-i\pi}\alpha_1) + \alpha_2\ln(\alpha_2)]. \tag{7.67}$$

From Eq. (7.49) we require

$$\frac{G_{12}^{app}}{G_{21}^{app}} = \frac{G_{12}}{G_{21}} = -\frac{1}{4a^4}e^{-2i\Delta_2}, \tag{7.68}$$

from which we obtain

$$\alpha_0 = \frac{1}{8a^2y}. \tag{7.69}$$

Comparison of Eq. (7.69) with Eq. (7.61) leads to the consistency condition

$$y^2 \gg 1. \tag{7.70}$$

On the other hand, the Stokes constant $U_1$ in Eq. (7.49) satisfies

$$\mathrm{Re}U_1 = G_{12}e^{i\Delta_2} \tag{7.71}$$

and

$$|U_1|^2 = \frac{1}{4a^4}[G_{22}e^{i\Delta_1} + 1]. \tag{7.72}$$

If we insert $G^{app}$ of Eqs. (7.63) into these equations, we can obtain

$$\mathrm{Re}U_B^{ZN} \equiv \mathrm{Re}(\text{approximate } U_1) = \frac{\cos(\pi\alpha_0)}{2a^2\sqrt{\alpha_0}}[\sqrt{\frac{\pi}{2}}\sin(\pi\alpha_0)\frac{e^{-\tilde{\psi}}}{\Gamma(\alpha_0)} - \frac{\sqrt{2\pi}e^{\tilde{\psi}}}{\Gamma(-\alpha_0)}], \tag{7.73}$$

and

$$\mathrm{Im}U_B^{ZN} = \frac{\sin(\pi\alpha_0)}{2a^2\sqrt{\alpha_0}}[-\frac{\pi\cos^2(\pi\alpha_0)}{2\Gamma(\alpha_0)^2}e^{-2\tilde{\psi}} + \frac{2\pi}{\Gamma(-\alpha_0)^2}e^{2\tilde{\psi}} - \alpha_0\cos(2\pi\alpha_0)]^{1/2}, \quad (7.74)$$

where $\alpha_0$ is given in Eq. (7.69) and

$$\tilde{\psi} = \frac{2a^2y^3}{3} + 2\alpha_0 - \alpha_0\ln(\frac{y^2}{\alpha_0}). \quad (7.75)$$

Under the consistency condition of Eq. (7.70), $y^2$ can be approximately solved as

$$y^2 = \frac{1}{2}[-\frac{b^2}{a^2} + \sqrt{\frac{b^4}{a^4} - \frac{1}{a^4}}]. \quad (7.76)$$

This implies that $b^2 \leq -1$ is a necessary condition for the validity of the Stokes constant $U_1$ given by Eqs. (7.73) and (7.74).

## 7.4 Mutual relations among analytical formulas

Now it is time for us to make clear the mutual relations among the presently derived formulas and other available analytical approximations for reduced scattering matrix. The comparison is made by reformulating the other formulas in terms of the Stokes constant $U_1$. The reduced scattering matrix is, of course, given by Eqs. (7.1) and (7.2). Discussions are given for the following four cases separately: (A) $b^2 \geq 1$, in which limiting case (a) is included, (B) $b^2 \leq -1$, in which limiting case (b) is included, (C) $|b^2| \leq 1$ and (D) $a^2 \gg 1$. It should be noted that the separability condition and the consistency condition given in chapter 7.3 are very important in order to make validity of each formula clear.

**A.** $b^2 \geq 1$

In this case analytical approximation for the Stokes constant $U_1$ can be generally expressed in a unified form as

$$U_A = \frac{i}{2a^2}(1 - e^{-2\Gamma})^{1/2}e^{i\psi}. \quad (7.77)$$

The following three approximations are considered:

1. **Present formula:** $U_A = U_A^{ZN}$ **(Eq.(7.42))**

$$\Gamma = \Gamma_{ZN} = \pi\beta_0$$

and

$$\psi = \psi_{ZN} \;=\; \frac{2a^2}{3}x_0^3 - \beta_0 \ln x_0^2 + 2\beta_0 + \beta_0 \ln \beta_0 + \arg\Gamma(i\beta_0) + \frac{\pi}{4}, \qquad (7.78)$$

where

$$\beta_0 = \frac{1}{8a^2 x_0} \qquad (7.79)$$

and

$$x_0^2 = \frac{1}{2}\Big[\frac{b^2}{a^2} + \sqrt{\frac{b^4}{a^4} - \frac{1}{a^4}}\Big]. \qquad (7.80)$$

**2. Formula of Coveney, Child and Bárány:[67]** $U_A = U_A^{CCB}$

$$\Gamma = \Gamma_{CCB} = \delta$$

and

$$\psi = \psi_{CCB} \;=\; \sigma + \frac{\delta}{\pi} - \frac{\delta}{\pi}\ln\frac{\delta}{\pi} + \arg\Gamma\Big(i\frac{\delta}{\pi}\Big) + \frac{\pi}{4}, \qquad (7.81)$$

where $\sigma$ and $\delta$ are defined by

$$\frac{1}{2}\sigma - i\delta = \frac{1}{4\sqrt{a^2}}\int_{-b^2}^{1}\Big(\frac{t^2-1}{t+b^2}\Big)^{1/2} dt \quad \text{for } b^2 > 1. \qquad (7.82)$$

**3. Formula of Child:[61]** $U_A = U_A^C$

$$\Gamma = \Gamma_C = \pi\delta_0 \qquad (7.83)$$

and

$$\psi = \psi_C = \frac{2b^3}{3a} - \delta_0 \ln\Big(\frac{b^2}{a^2}\Big) + \delta_0 \ln \delta_0 + \arg\Gamma(i\delta_0) + \frac{\pi}{4}, \qquad (7.84)$$

where

$$\delta_0 = \frac{1}{8ab}. \qquad (7.85)$$

As is seen from the above three formulas, there holds the following correspondence among the parameters:

$$\beta_0 \iff \frac{\delta}{\pi} \xrightarrow[b^2 \gg 1]{} \delta_0, \qquad (7.86)$$

$$\frac{2a^2}{3}x_0^3 + \beta_0 - \beta_0 \ln\Big(\frac{x_0^2}{\beta_0^2}\Big) \iff \sigma \xrightarrow[b^2 \gg 1]{} \frac{2b^3}{3a} - \delta_0 \ln\Big(\frac{b^2}{a^2\delta_0^2}\Big) \qquad (7.87)$$

and

$$\psi_{ZN} \iff \psi_{CCB} \xrightarrow[b^2 \gg 1]{} \psi_C. \tag{7.88}$$

Numerical comparisons indicate that $U_A^{ZN}$ and $U_A^{CCB}$ are better than $U_A^C$ and that all three coincide in the limit $b^2 \gg 1$.

**B.** $b^2 \leq -1$

Following the representation of Eqs. (7.73) and (7.74), we will give here approximate analytical expressions of $\mathrm{Re}U_1$ and $\mathrm{Im}U_1$.

**1. Present formula:** $U_B = U_B^{ZN}$ **(see Eqs.(7.73) and (7.74) )**

$$\mathrm{Re}U_B^{ZN} = \frac{\cos(\pi\alpha_0)}{2a^2\sqrt{\alpha_0}}[\sqrt{\frac{\pi}{2}}\frac{\sin(\pi\alpha_0)e^{-\tilde{\psi}}}{\Gamma(\alpha_0)} - \frac{\sqrt{2\pi}}{\Gamma(-\alpha_0)}e^{\tilde{\psi}}] \tag{7.89}$$

and

$$\mathrm{Im}U_B^{ZN} = \frac{1}{4a^2}\{\cos(2\pi\alpha_0)[\frac{d}{\sin^2(\pi\alpha_0)} + \frac{4}{\cos^2(2\pi\alpha_0)}]^{1/2} - \frac{\sqrt{d}}{\sin(\pi\alpha_0)}\}, \tag{7.90}$$

where

$$d = 4a^4(\mathrm{Re}U_B^{ZN})^2/\cos^2(\pi\alpha_0), \tag{7.91}$$

$$\tilde{\psi} = \frac{2a^2y^3}{3} + 2\alpha_0 - \alpha_0\ln(\frac{y^2}{\alpha_0}), \tag{7.92}$$

$$\alpha_0 = \frac{1}{8a^2y} \tag{7.93}$$

and

$$y^2 = \frac{1}{2}[-\frac{b^2}{a^2} + \sqrt{\frac{b^4}{a^4} - \frac{1}{a^4}}]. \tag{7.94}$$

The imaginary part of Stokes constant $U_B^{ZN}$ here is modified from Eq. (7.74). Eq. (7.74) was found not to work well for $y^2 < 1$ which corresponds to a region $a^2 \geq |b^2|$ with $b^2 \leq -1$. Since the real part (Eq. (7.89)) remains good in this region, the imaginary part (apart from sign) was determined first by using the working formula for nonadiabatic transition probability of Coveney et al.[67] and the exact formula obtained in chapter 4. Then Eq. (7.90) was finally obtained with a slight modification from this expression by a numerical comparison with the exact phase of the Stokes constant $U_1$. The nonadiabatic transition probability in this approximation is thus given by

$$P_B^{ZN} = \frac{4\sin^2(\pi\alpha_0)}{d + 4\sin^2(\pi\alpha_0)} \simeq \frac{2\pi e^{-2\tilde{\psi}}}{\alpha_0\Gamma(\alpha_0)^2 + 2\pi e^{-2\tilde{\psi}}}. \tag{7.95}$$

**2. Formula of modified Coveney, Child and Bárány: $U_B = U_B^{MCCB}$**

$$\mathrm{Re}U_B^{MCCB} = -\sqrt{\frac{\pi}{2\rho}\frac{\cos(\pi\rho)}{a^2\Gamma(-\rho)}}e^{\delta+\rho-\rho\ln\rho} \tag{7.96}$$

and

$$\mathrm{Im}U_B^{MCCB} = \frac{1}{4a^2}\left\{\cos(2\pi\rho)\left[\frac{d'}{\sin^2(\pi\rho)} + \frac{4}{\cos^2(2\pi\rho)}\right]^{1/2} - \frac{\sqrt{d'}}{\sin(\pi\rho)}\right\}, \tag{7.97}$$

where

$$d' = 4a^4(\mathrm{Re}U_B^{MCCB})^2/\cos^2(\pi\rho) \tag{7.98}$$

and

$$2\pi\rho - i\delta = \frac{1}{2\sqrt{a^2}}\int_{-b^2}^{-1}\left(\frac{t^2-1}{t+b^2}\right)^{1/2}dt \quad \text{for } b^2 < -1. \tag{7.99}$$

The real part Eq. (7.96) was obtained by comparing the approximate expression for reduced scattering matrix of Coveney et al.[67] and the exact one obtained in chapter 4. Then, the imaginary part Eq. (7.97) was determined in the same way as before, namely, by using the working formula for nonadiabatic transition probability of Coveney et al (Eq. (7.100) below) and Eq. (7.96). The nonadiabatic transition probability is thus given by[67]

$$P_B^{CCB} = \frac{4\sin^2(\pi\rho)}{d' + 4\sin^2(\pi\rho)} = \frac{B(\rho)e^{-2\delta}}{1 + B(\rho)e^{-2\delta}} \tag{7.100}$$

with

$$B(\rho) = \frac{2\pi\rho^{2\rho}e^{-2\rho}}{\rho\Gamma(\rho)^2}. \tag{7.101}$$

**3. Formula of Ovchinnikova[61, 66]**

In this approximation only one pair of transition points in $\mathrm{Im}t > 0$ are taken into account and the results are not very correct. Furthermore, it is not possible to derive an expression for the Stokes constant $U_1$, and only the nonadiabatic transition probability is given as,

$$P_B^O = \frac{2\pi}{\delta_0\Gamma(\delta_0)^2}\delta_0^{2\delta_0}e^{-2\delta_0}e^{-|4b^3/3a|} \tag{7.102}$$

where

$$\delta_0 = \frac{1}{8a|b|}. \tag{7.103}$$

Correspondence among the parameters in the above three approximations is found to be as follows:

$$\alpha_0 \Longleftrightarrow \rho \xrightarrow[b^2 \ll -1]{} \delta_0\Big(= \frac{1}{8a|b|}\Big) \tag{7.104}$$

and

$$\frac{2a^2y^3}{3} + \alpha_0 - \alpha_0 \ln(\frac{y^2}{\alpha_0^2}) \Longleftrightarrow \delta. \tag{7.105}$$

It should be noted that compared to Eqs. (7.96) and (7.97), Eqs. (7.89) and (7.90) contain extra terms corresponding to the first term of Eq. (7.89). These represent a contribution from the subdominant solutions on Stokes lines and make the present approximation better than Eqs. (7.96) and (7.97) at $b^2 \to -1$. More details are given later.

C. $|b^2| \le 1$

As is described in Appendix, based on the exactly solvable special differential equation in the section 3.4C, we have derived the approximate solution for the Stokes constant $U_1$. However, since the phase part of this approximate solution is valid only for $a^2 \gg 1$ and the amplitude $f$ should be numerically fitted, we have tried to relax the condition $a^2 \gg 1$ and to find explicit expressions for both $\beta$ and $f$ by a numerical fitting. By a comparison with the exact $U_1$ we finally obtained the following expressions:

$$U_C^{ZN} = \frac{i}{2a^2} f e^{-i\pi\beta}, \tag{7.106}$$

where

$$\beta = \begin{cases} \frac{1}{3}\big[(1+\frac{1.9+b^2}{a^2})^{1/3} - \frac{(0.13b^2+0.87)b^2}{(2a^2)^{1/3}}\big] & \text{for } a^2 \ge 4 \\ \frac{1}{3}\Big\{(1.11+\frac{1.352}{a^2})^{1/3} - \big[\frac{0.087(a^{2.8}+9.9)b^2}{a^{2.8}+2.17} + 0.78\big]\frac{b^2}{(2a^2)^{1/3}}\Big\} & \\ \text{for } 0.25 \le a^2 \le 4 & \end{cases} \tag{7.107}$$

and

$$f = \begin{cases} \frac{8.33b^4}{(\ln a^2+1.74)^{4.28}} + 0.054\frac{\ln a^2-6.9}{\ln a^2+0.6}b^2 + 0.021\frac{a^{0.72}+55.8}{a^{0.72}+0.19} & \text{for } a^2 \ge 4 \\ -0.00444\frac{a^{3.24}+21.25}{a^{3.24}+0.116}b^6 + 0.0641\frac{a^{4.9}+3.72}{a^{4.9}+0.614}b^4 - 0.334\big[\frac{1}{a^2+0.524}\big]^{0.523}b^2 & \\ +1.066\big[\frac{1}{a^2+0.63}\big]^{0.322} \text{ for } 0.25 \le a^2 \le 4. & \end{cases} \tag{7.108}$$

In the limit $a^2 \gg 1$, Eq. (7.107) does not exactly coincide with approximate solution of $\beta$ in appendix, but the difference is not significant there. These formulas can not go beyond $a^2 \le 0.25$, because the distribution of four transition points in this region becomes like Fig.5.3d of chapter 5, which can not be taken care of by the differential equation of the section 3.4C.

The working formula by Coveney et al.[67] can not give an expression for the Stokes constant $U_1$ and only the nonadiabatic transition probability is given as

$$P_C^{CCB} = \frac{e^{-2\delta}}{1+e^{-2\delta}}, \tag{7.109}$$

where

$$i\delta = \frac{1}{2\sqrt{a^2}} \int_{-b^2}^{1} \Big(\frac{t^2-1}{t+b^2}\Big)^{1/2} dt \quad \text{for } |b^2| < 1. \tag{7.110}$$

This formula works well in the region $a^2 \leq 0.25$.

**D. $a^2 \gg 1$(Perturbative formulas[61, 86] )**

When the diabatic coupling is very weak ($a^2 \gg 1$), the perturbation formula for the Stokes constant $U_1$ can be given also in the form of Eq. (7.77), in which the parameters $\psi$ and $\Gamma$ now become

$$\begin{aligned}
\Gamma = \Gamma_D &= -\frac{1}{2}\ln[1 - \frac{\pi^2}{4a^{4/3}}(B_i^2(-\nu) + A_i^2(-\nu))] \\
&\text{and} \\
\psi = \psi_D &= \arctan\Big[\frac{A_i(-\nu)}{B_i(-\nu)}\Big] - \frac{\pi}{2},
\end{aligned} \tag{7.111}$$

where

$$\nu = \frac{b^2}{a^{2/3}}, \tag{7.112}$$

and $A_i(X)$ and $B_i(X)$ are the Airy functions.[80]

Since the Airy functions should be small enough in this approximation, $|b^3/a| \ll 1$ is required. Considering this condition, the following simplified formula for transition probability is often utilized.[67]

$$P_D = \pi^2 a^{-4/3} A_i^2(-b^2 a^{-2/3}). \tag{7.113}$$

However, we recommend here the formula,

$$\bar{P}_D = \frac{P_D}{1+P_D}, \tag{7.114}$$

because it can be shown that the exact expression for nonadiabatic transition probability is given in the fractional form like Eq. (7.114) as proved in the section 4.5. Numerical results also confirm that $\bar{P}_D$ is much better than $P_D$.

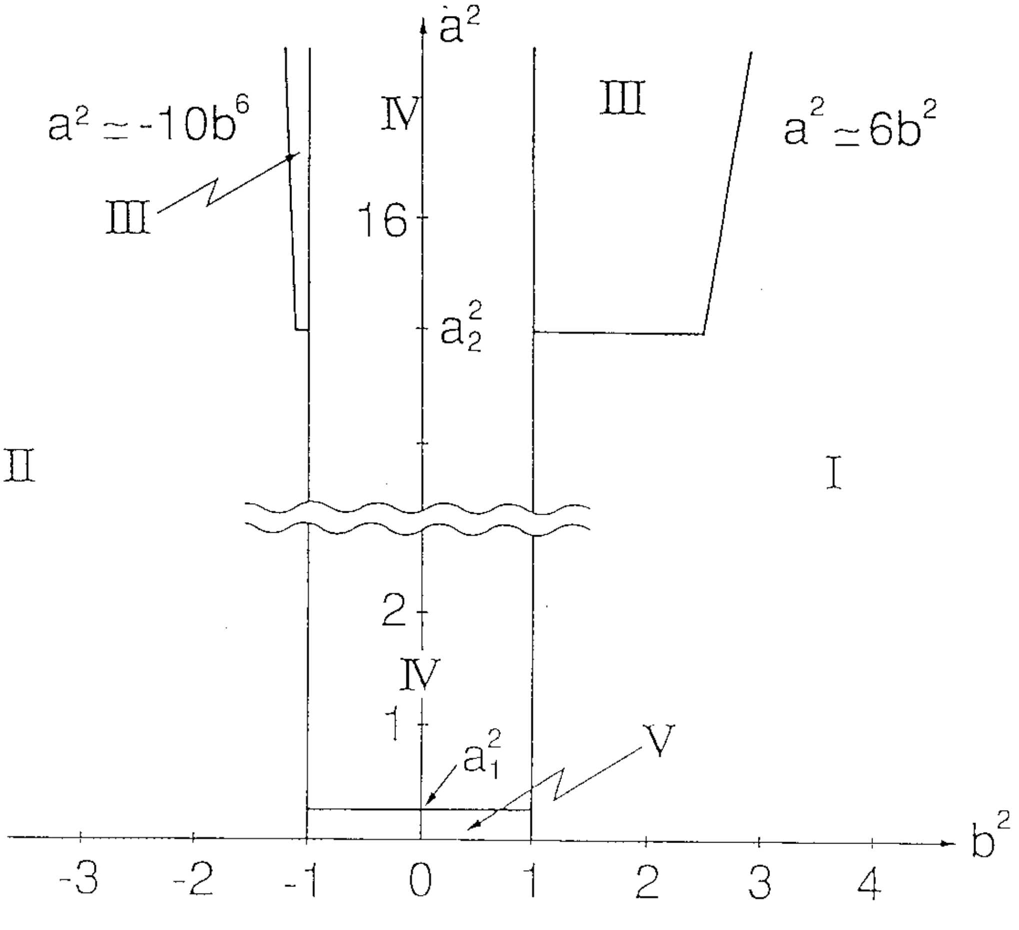



Figure 7.3: Five regions (I–V) in $(a^2, b^2)$ plane. Recommended formulas for reduced scattering matrix are provided for each region. $a_1^2 = 0.25$ and $a_2^2 = 15.0$.

## 7.5 Numerical comparisons and recommended formulas

The separability condition given by Eq. (7.25) for limiting case (a) or Eq. (7.55) for limiting case(b) and the consistency condition of Eq. (7.40) for limiting case (a) or Eq. (7.70) for limiting case (b) provide a qualitative and clear definition of validity condition for each approximate formula. Numerical results indicate, however, that each approximation can work well in a wider region than predicted by these conditions. In this section, detailed numerical comparisons among the various formulas listed in the previous section are made for the Stokes constant $U_1$ as well as for the nonadiabatic transition probability $P_{12}$. From these numerical comparisons it turned out that we can divide the whole $(a^2, b^2)$-plane $(a^2 > 0)$ into five regions I-V, as is shown in Fig.7.3. For each region, the best recommended formulas are proposed for the Stokes constant $U_1$. The reduced scattering matrix is given by Eqs. (7.1) and (7.2). See also the expressions in Eqs. (7.4)-(7.9). It should be noted that the boundary lines in Fig.7.3 are not exact, but fuzzy.

Figs.7.4a-d show the Stokes constant $U_1$ for $a^2 = 0.1, 1.0, 10.0$, and $20.0$ as a function of $b^2$. $\mathrm{Arg}(S^R_{11})$ is also shown there. Figs.7.5 present the results of nonadiabatic transition probability for the same values of $a^2$.

**A. Region I**

This region corresponds to the case in which the four transition points are separated along the anti-Stokes lines (see Fig.7.1). The recommended formulas in this region are

(ZN-I): Zhu-Nakamura given by Eqs. (7.78).

and

(CCB-I): Coveney, Child and Bárány given by Eqs. (7.81).

The probability $p$ and phase $\Xi$ in Eqs. (7.10) are equal to $p = e^{-2\Gamma}$ and $\Xi = \psi$, respectively. The above two approximations work equally well.

It should be noted, however, that the ZN-I formulas are explicit simple functions of $a^2$ and $b^2$, while the elliptic type of integral (Eq. (7.82)) should be evaluated in the CCB-I approximation. Actually, $p_A^{ZN} = e^{-2\Gamma_{ZN}}$ in the ZN-I approximation can be simply expressed as

$$p_A^{ZN} = \exp[-\frac{\pi}{4a^2 x_0}] = \exp[-2\pi\delta_0 \frac{b}{a x_0}]. \tag{7.115}$$

with

$$\frac{b}{a x_0} = \Big[\frac{2}{1+\sqrt{1-b^{-4}}}\Big]^{1/2}, \tag{7.116}$$

where $p_{LZ} = e^{-2\pi\delta_0}$ is nothing but the conventional Landau-Zener formula which coincides with Eq. (7.115) in the limit $b^2 \gg 1$. As is seen in Fig.7.6, Eq. (7.115) works better than the conventional Landau-Zener formula at large $b^2$; but the latter works acceptably well for the whole range of $b^2 > 1$, although the Stokes constant (or reduced scattering matrix) is not very good with this formula. In contrast to the case of the same sign of slopes (Landau-Zener case), the region $|b^2| \leq 1$ can not be covered by the formulas here and should be treated separately.

### B. Region II

This region corresponds to the case in which the four transition points are separated along the Stokes lines (see Fig.7.1). The recommended formulas in this region are

(ZN-II): Zhu-Nakamura given by Eqs. (7.89) and (7.90).

The MCCB formulas given by Eqs. (7.96) and(7.97) can work equally well for transition probability, but they become slightly worse for the Stokes constant $U_1$ when $b^2$ approaches -1. The reason for this is as follows. The extra terms in ZN-II which represent a contribution from the subdominant solutions on the Stokes lines make the ZN-II formula work slightly better. This situation is the same as in chapter 6. Besides the ZN-II formula is a simple function of $a^2$ and $b^2$; and thus we recommend only the ZN-II here.

### C. Region III

This corresponds to the weak coupling case. The recommended formulas are

(N-III): Perturbation formula given by Eqs. (7.111).

Asymmetry of this region seen in Fig.7.3 for $b^2 > 1$ and $b^2 < -1$ comes from the properties of Airy functions. At relatively small $a^2$, the formula with one Airy function (especially Eq. (7.114)) works much better (see Fig.7.5c). As is seen from Eqs. (7.111), this formula breaks down when the argument of the logarithmic function becomes negative, which happens at $b^2$ smaller than a certain negative value (see Figs.7.4c, 7.4d, 7.5c, and 7.5d). Although this formula works all right at $a^2 \geq a_2^2$ (see Fig.7.3) for any $b^2 > 1$ (see Figs.7.4d and 7.4d), we put a boundary line as in Fig.7.3. This is because the formulas (ZN-I) and (CCB-I) work equally well there; besides the (ZN-I) is simpler than the others and more useful.

### D. Region IV

In this region, the recommended formulas are

(ZN-IV): Zhu-Nakamura given by Eq. (7.106) with Eqs. (7.107) and (7.108).

The perturbation formula mentioned above can work acceptably well for $a^2 \gg 1$, but not as well as this.

### E. Region V

In this region, good approximation for the Stokes constant $U_1$ could not be found, unfortunately. For nonadiabatic transition probability, however, we can recommend

(CCB-V): Coveney, Child and Bárány given by Eq. (7.109).

## 7.6 Concluding remarks

In chapter 4 of this thesis, we have obtained the exact solutions of reduced scattering matrix for the two cases: Landau-Zener and nonadiabatic tunneling. These are expressed in terms of the only one Stokes constant $U_1$, which is solved in the form of infinite series as a function of the basic parameters $a^2$ and $b^2$. Furthermore, in chapter 6 we have derived new compact approximate analytical solutions for the Landau-Zener case by decomposing the connection matrix along either anti-Stokes lines or Stokes lines into a product of two matrices based on the Weber equation. The new method of connection along Stokes lines led us to a new formula in the region $b^2 < -1$ which works better than the other available ones.

In this chapter we considered analytical approximation for the nonadiabatic tunneling case. It was demonstrated that the methods employed in chapter 6 can be directly applied to the case $|b^2| > 1$. Two new compact approximate analytical solutions were again derived, and the one for $b^2 < -1$ was found to be better than the other. These new formulas obtained here are simple functions of $a^2$ and $b^2$, namely, neither any special functions nor any integrals are required. A new simple expres-

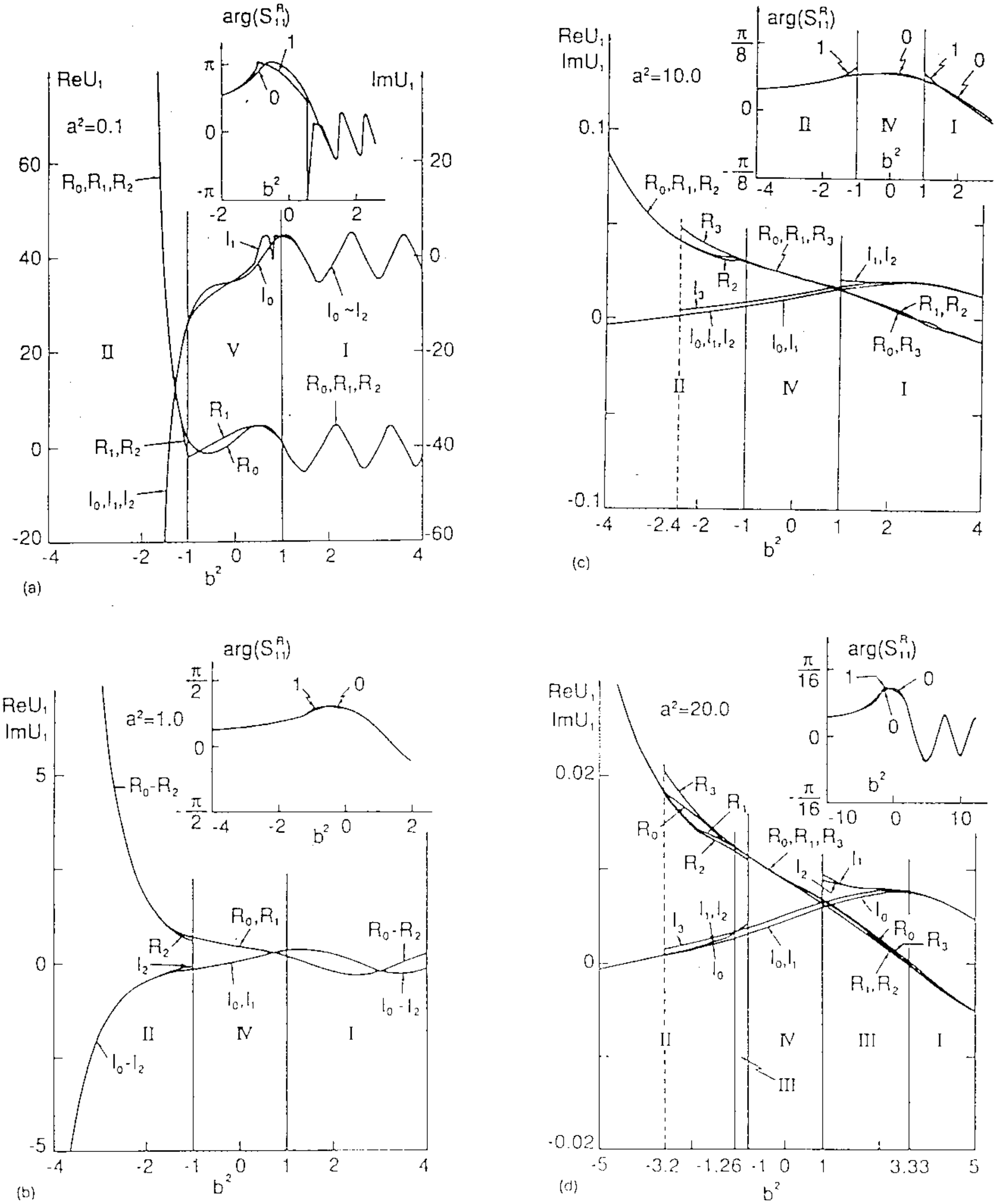



Figure 7.4: Stokes constant $U_1$ and $\arg(S_{11}^R)$ as a function of $b^2$. $R(I)$ indicates real(imaginary) part of $U_1$. The number $j$ specifies approximation as follows: $j = 0$, exact; $j = 1$, present approximation; $j = 2$, Coveney et al's approximation; $j = 3$, Nikitin's approximation. Results from formulas of the limiting case (a) for $b^2 > 1$ and the limiting case (b) for $b^2 < -1$, but only present formula available for $-1 < b^2 < 1$. (a) $a^2 = 0.1$, (b) $a^2 = 1.0$, (c) $a^2 = 10$, and (d) $a^2 = 20.0$.

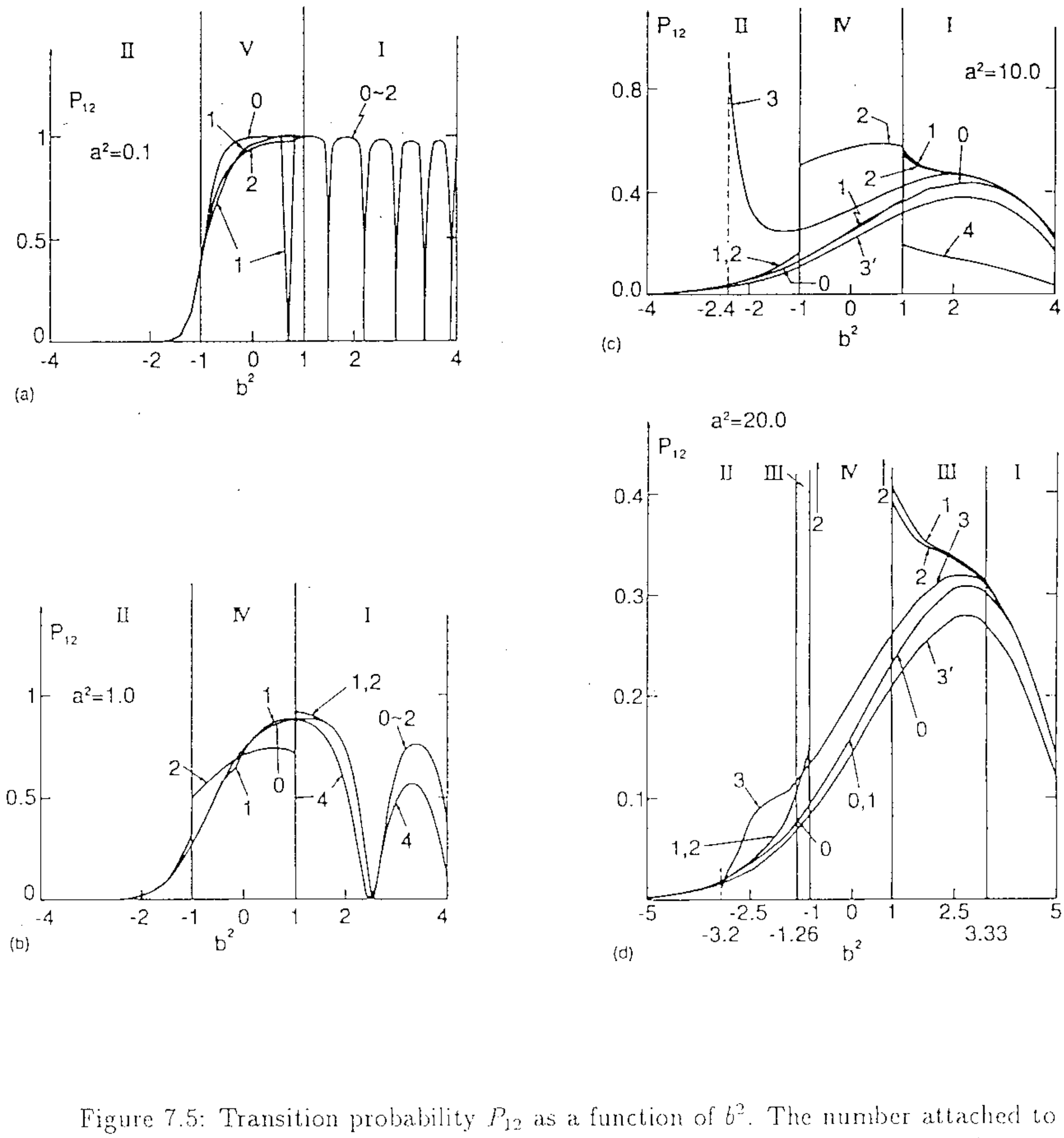



Figure 7.5: Transition probability $P_{12}$ as a function of $b^2$. The number attached to each curve specifies approximation as follows: $j = 1, 2, 3$: the same as in Fig.7.4; $j = 3'$, Eq.(7.114); $j = 4$, Child's approximation. Note in $j = 2$ Eq.(7.109) is used for $-1 < b^2 < 1$. (a) $a^2 = 0.1$, (b) $a^2 = 1.0$, (c) $a^2 = 10$, and (d) $a^2 = 20.0$.

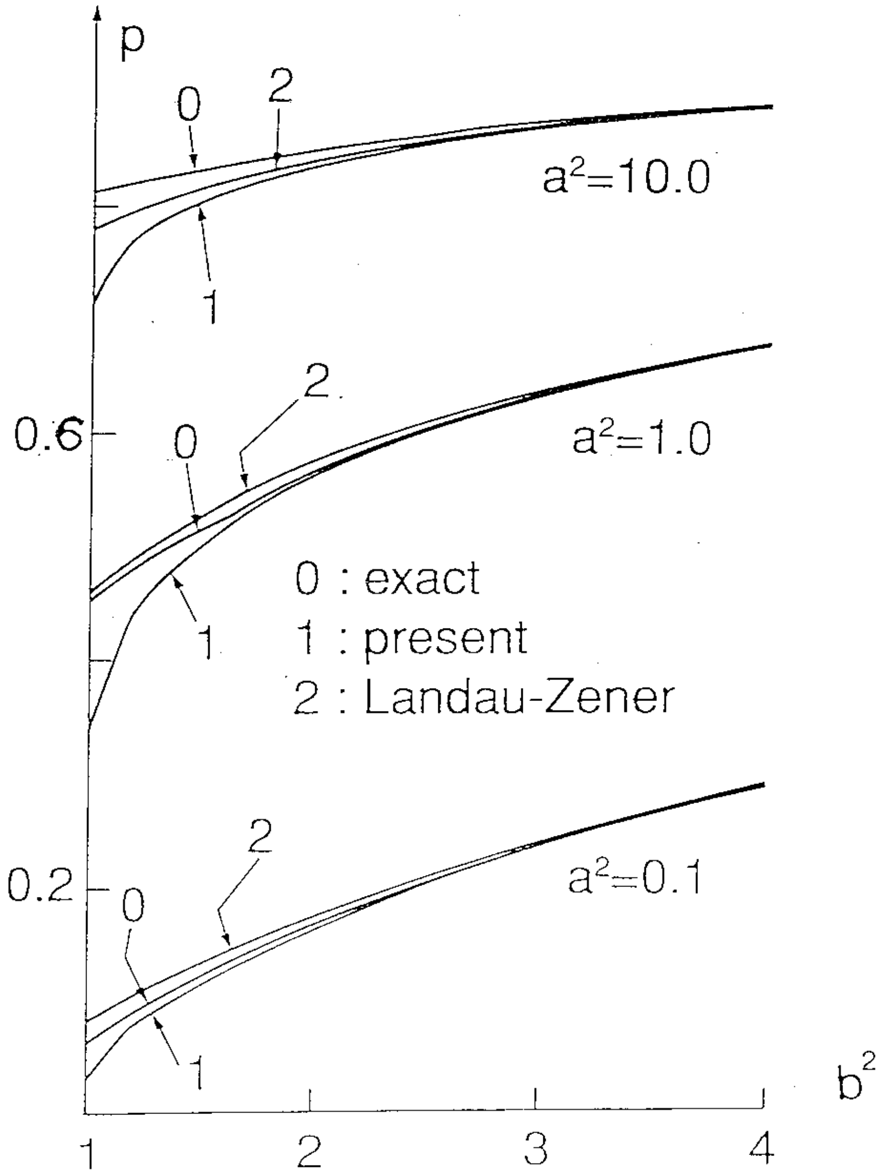



Figure 7.6: Nonadiabatic transition probability for one passage of crossing point as a function of $b^2$ for $a^2 = 0.1, 1.0$, and $10.0$. It should be noted that $p$ loses physical meaning when $b^2 < 1$.

sion for nonadiabatic transition probability $p$ for one passage of crossing point was obtained for $b^2 > 1$, but it turned out that the conventional Landau-Zener formula works acceptably well in this region as far as $p$ is concerned. Furthermore, in this region the exact reduced scattering matrix was found to have a nice correspondence with the semiclassical approximation.

The case $|b^2| < 1$ is very difficult to deal with analytically. There is no analogy in the Landau-Zener case. We started with a comparison equation method based on the exactly solvable case of $q(t) = a_4 t^4 + a_1 t$ (see chapter 3) which can be reduced to the well known Whittaker equation. Because of the asymmetry of our problem, this method did not work quantitatively well, unfortunately. With use of the knowledge obtained from this comparison equation method, however, we could finally propose good fitting formulas for the phase and the amplitude of the Stokes constant $U_1$.

A thorough numerical comparison was carried out with the formula of Coveney et al.,[67] the one modified from theirs and the perturbative one.[86] The whole range of the two parameter $(a^2, b^2)$-plane was divided into five regions, and the best recommended formulas were proposed in each region.

# Appendix

**Comparison equation method in the case $|b^2| \leq 1$.**

In this special case, the distributions of transition points and Stokes lines have two subcases as is shown in Figs.5.3c and 5.3d of chapter 5. In neither of them the transition points can not be considered to be well separated and should be taken into account as a whole. The case of Fig.5.3c of chapter 5, however, has a topologically similar distribution of transition points to the case of $q(z) = a_4 z^4 + a_1 z$ in chapter 3(see Fig.3.8), in which one of the zeros $z_0$ is located at origin and the others are symmetrically distributed on a circle.

Next, let us consider the distribution of four transition points in Fig.7.7 (see Fig.5.3c of chapter 5). If Figs.3.8 and 7.7 are assumed to has topologically the same distribution of Stokes lines, we can consider Eq. (3.101) in chapter 3 as a comparison equation of Eq. (4.30) in chapter 4. Thus, the connection matrix $L$ in Eq. (7.18) may be approximately put equal to the connection matrix $L_0$ in Eq. (3.112) of chapter 3. If we set

$$L_{22} \simeq (L_0)_{22} \tag{7.117}$$

and assume that the phase relation $\delta_+^0 = \delta_-^0$ in $L_0$ approximately holds for $\delta_+$ and $\delta_-$ defined by Eqs. (7.19),

$$\delta_+ \simeq \delta_- \quad \text{with } x_0 = 0, \tag{7.118}$$

then from Eqs. (7.2) and (7.18) we have

$$L_{22} + 1 = -U_1 \frac{U_1 - U_1^*}{|U_1|^2 - 1/(4a^4)} \simeq -e^{-2\pi i Q_1}[1 + 2\cos(2\pi Q_1)]. \tag{7.119}$$

The approximate solution for $U_1$ is thus obtained as

$$U_1^{app} \simeq \frac{i}{2a^2}\sqrt{1 + 2\cos(2\pi Q_1)}e^{-2\pi i Q_1}. \tag{7.120}$$

It should be noted that we obtain the same results when we set up equality of the other matrix elements between $L$ and $L_0$.

Now, our next task is to relate the quantity $Q_1$ in terms of the basic parameters $a^2$ and $b^2$ in Eq. (4.10) of chapter 4. This can be done by comparing the phase integrals of the two equations (3.101) and (4.30). These phase integrals are given by

$$-\pi Q_1 = \int_{z_0=0}^{z_1} \sqrt{a_4 z^4 + a_1 z}dz = \sqrt{a_4}\int_0^{il} \sqrt{z(z-il)[(z+il/2)^2 - 3l^2/4]}dz \quad (7.121)$$

with

$$(-il)^3 = \frac{a_1}{a_4} \quad (7.122)$$

and

$$\begin{aligned} -\psi &\equiv \int_{t_2}^{t_1} \sqrt{(t-t_1)(t-t_2)(t-t_3)(t-t_4)}dt \\ &= \frac{a^2}{2}\int_0^{2i|x_1|} \sqrt{t(t-2i|x_1|)\{[t+i(2y-|x_1|)]^2 - x_2^2\}}dt, \end{aligned} \quad (7.123)$$

where $y, x_1$ and $x_2$ are defined in Eqs.(5.16)-(5.18) of chapter 5. We have chosen these phase integrals because of the symmetry. In comparison of these two integrals, the following relations may be required:

$$\begin{aligned} l &= 2|x_1|, \\ \sqrt{a_4} &= \frac{a^2}{2}, \\ \frac{il}{2} &= i(2y-|x_1|), \\ \text{and} & \\ \frac{3l^2}{4} &= x_2^2. \end{aligned} \quad (7.124)$$

These conditions can not be satisfied simultaneously, because that would correspond to the exact coincidence of Figs.3.8 and 7.7.

If we use the first three equations of Eqs. (7.124) with help of Eq. (7.122) and the definition $Q_1$ of the section 3.4C, then we obtain

$$Q_1 = \frac{2a^2}{3}|x_1|^3. \quad (7.125)$$

and

$$|x_1| = y, \quad (7.126)$$

which leads to (see Eqs. (5.16)-(5.18) of chapter 5)

$$|x_1|^3 = \frac{1}{2a^2}(1 - b^2|x_1|) \simeq \frac{1}{2a^2}[1 - \frac{b^2}{(2a^2)^{1/3}}], \quad (7.127)$$

where the condition $a^2 \gg 1$ is used in the second equality. Finally, $Q_1$ can be expressed explicitly in terms of $a^2$ and $b^2$ as

$$Q_1 = \frac{1}{3}[1 - \frac{b^2}{(2a^2)^{1/3}}] \quad \text{for } a^2 \gg 1. \tag{7.128}$$

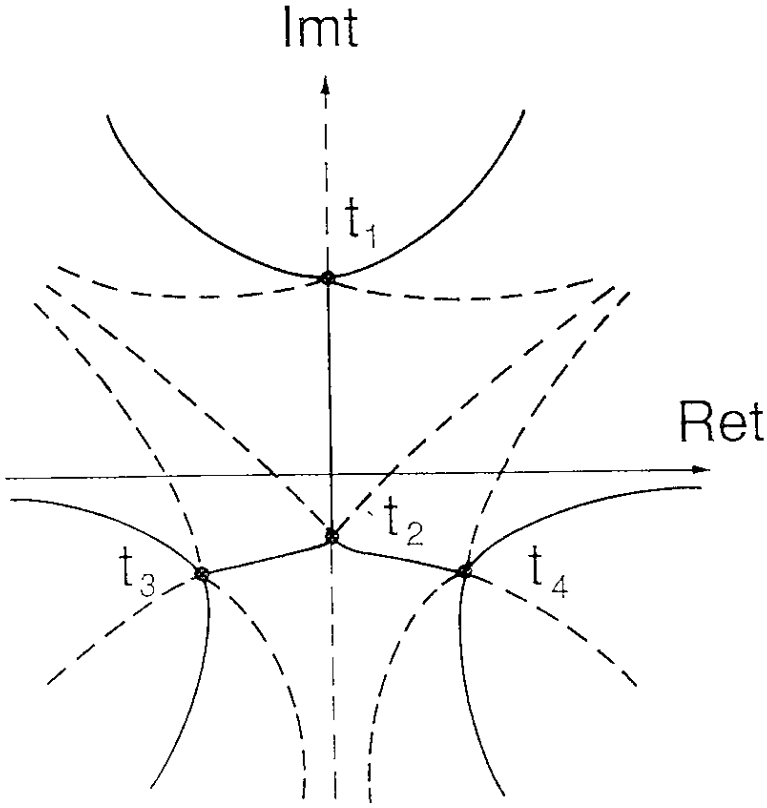
Unfortunately, numerical comparison with the exact Stokes constant $U_1$ shows that Eq. (7.120) with (7.128) is not accurate enough and should be modified as

$$U_1^{app} = \frac{i}{2a^2} f e^{-\pi i \beta}, \tag{7.129}$$

where

$$\beta \equiv Q_1 = \frac{1}{3}[1 - \frac{b^2}{(2a^2)^{1/3}}] \quad \text{for } a^2 \gg 1. \tag{7.130}$$

Here the function $f$ is to be determined only by numerical fitting, unfortunately. Since numerical fitting turned out to be unavoidable for $f$, we have decided to give a fitting formula also for the phase $\beta$ so that we can cover much wider range than $a^2 \gg 1$ for $|b^2| \leq 1$. The results are given in the text. This unfortunate result of the present comparison equation method would probably be due to the symmetry of the problem, because our problem (Fig.7.7) never becomes totally symmetric like Fig.3.8.




$$|t_1 - t_2| > |t_3 - t_2| = |t_4 - t_2|$$

Figure 7.7.

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