

Semiclassical Phase Integrals

2.1 Approximation

2.1.1 JWKB Approximation

The semiclassical approximation is also known as the JWKB (or WKB) approximation because it was first developed in quantum mechanics by H. Jeffreys [342], G. Wentzel [595], H.A. Kramers [366], and L. Brillouin [87]. Prior to the advent of quantum mechanics, it was also known as the Green–Liouville method [324]. This approximation corresponds to an expansion in powers of \hbar . Consider the one-dimensional time-independent Schrödinger equation (TISE)

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u}{dx^2} + V(x)u = Eu \quad (2.1)$$

$$\Rightarrow \frac{d^2 u}{dx^2} + k^2(x)u = 0 \quad (2.2)$$

where

$$k(x) \equiv \frac{1}{\hbar} [2\mu (E - V(x))]^{1/2} \quad (V(x) < E) \quad (2.3)$$

or

$$\frac{d^2 u}{dx^2} - k_1^2(x)u = 0 \quad (2.4)$$

where

$$k_1(x) \equiv \frac{1}{\hbar} [2\mu (V(x) - E)]^{1/2} \quad (V(x) > E) \quad (2.5)$$

With S as action and A as amplitude we put

$$u(x) = Ae^{iS(x)/\hbar} \quad (2.6)$$

Then

$$\begin{aligned}
\frac{d^2 u}{dx^2} &= A \frac{d}{dx} \left[\frac{i}{\hbar} S' e^{iS(x)/\hbar} \right] \\
&= \frac{iA}{\hbar} \left\{ S'' + \frac{i}{\hbar} (S')^2 \right\} e^{iS(x)/\hbar}
\end{aligned} \tag{2.7}$$

Substituting into (2.1) \Rightarrow

$$i\hbar \frac{d^2 S}{dx^2} - \left(\frac{dS}{dx} \right)^2 + 2\mu[E - V(x)] = 0 \tag{2.8}$$

Expand S in powers of \hbar :

$$S = S_0 + \hbar S_1 + \dots \quad (\text{Maclaurin expansion in } \hbar \text{ but note } 1/\hbar \text{ in exponential}) \tag{2.9}$$

The terms independent of \hbar give

$$-\left(\frac{dS_0}{dx} \right)^2 + 2\mu[E - V(x)] = 0 \tag{2.10}$$

while the terms of first order in \hbar give

$$i \frac{d^2 S_0}{dx^2} - 2 \frac{dS_0}{dx} \cdot \frac{dS_1}{dx} = 0 \tag{2.11}$$

Integrating (2.10) gives

$$\begin{aligned}
S_0(x) &= \pm \int_{x_0}^x \{2\mu(E - V(s))\}^{1/2} ds \\
&\equiv \pm \hbar \int_{x_0}^x k(s) ds
\end{aligned} \tag{2.12}$$

and integrating (2.11) \Rightarrow

$$\begin{aligned}
S_1(x) &= \frac{1}{2} i \ln \left(\frac{dS_0}{dx} \right) \\
&= \frac{1}{2} i \ln k(x)
\end{aligned} \tag{2.13}$$

including the arbitrary constant of integration in A of (2.6). Neglecting higher-order terms, it follows from (2.6), (2.9) that

$$\begin{aligned}
u(x) &\approx A e^{i/\hbar (S_0(x) + \hbar S_1(x))} \\
&= A e^{\pm i \int_{x_0}^x k(s) ds - \frac{1}{2} \ln k(x)} \\
&= A [k(x)]^{-\frac{1}{2}} e^{\pm i \int_{x_0}^x k(s) ds} \quad (V(x) < E)
\end{aligned} \tag{2.14}$$

Similarly

$$u(x) = B [k_1(x)]^{-\frac{1}{2}} e^{\pm \int_{x_0}^x k_1(s) ds} \quad (V(x) > E) \tag{2.15}$$

where $k^2(x_0) = 0 = k_1^2(x_0) \Rightarrow x_0$ is a turning point. We expect these equations to be valid if $\hbar S_1/S_0$ is small. Equation (2.13) \Rightarrow

$$\hbar S_1(x) = \frac{i\hbar}{2} \ln k(x) = \int_c^x \frac{i\hbar}{2} \frac{dk(s)}{k(s)} ds \quad (2.16)$$

where $k(c) = 1$.

Equations (2.12) and (2.16) \Rightarrow

$$\frac{1}{\hbar} |S_0| \gg |S_1|$$

if

$$\left| \frac{dk(x)/dx}{2k^2(x)} \right| \ll 1 \quad (2.17)$$

The local de Broglie wavelength λ is $2\pi/k$; thus we may write this condition as

$$\frac{\lambda}{4\pi} \frac{1}{k} \left| \frac{dk}{dx} \right| \ll 1 \quad (2.18)$$

Hence the fractional change in k over the distance $\lambda/4\pi$ should be small. This is a small-wavelength or *high-frequency* approximation. In reality this is the inverse of perturbation theory, that is, the basic quantity is large rather than small.

At the turning point(s) of the classical motion where

$$V(x_0) = E \quad (2.19)$$

we see that k (and k_1) vanishes and so condition (2.18) is violated, to the extent that the left-hand side $= +\infty$ ($k'(x_0) \neq 0$). Thus the approximation is valid only several wave-lengths away from the turning point and so is termed an *asymptotic approximation*. Because this approximation is based on the assumption that the higher-order terms in \hbar are negligible, it is a *semiclassical* approximation ($\hbar \rightarrow 0$ in classical limit).

We now consider the solution near a linear turning point as indicated in Figure 2.1.

With $V(x_0) = E$,

$$\begin{aligned} V(x) &< E & (x > 0) \\ V(x) &> E & (x < 0) \\ V(x) &= E - Fx & (F > 0) \end{aligned}$$

Define

$$\begin{aligned} \xi_1(x) &= \int_x^0 k_1(s) ds, & \xi(x) &= \int_0^x k(s) ds \\ (x < 0) &\Rightarrow ds > 0 & (x > 0) &\Rightarrow ds > 0 \\ \text{Region 1} & & \text{Region 2} & \end{aligned} \quad (2.20)$$

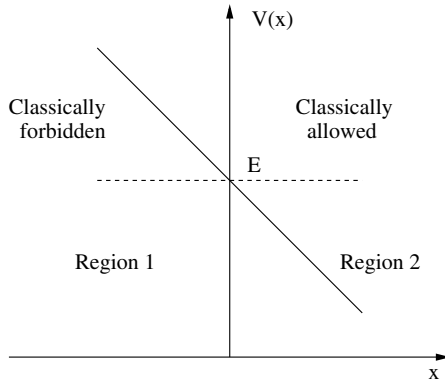


Fig. 2.1. Classical turning point

Both $\xi_1(x)$ and $\xi(x)$ increase as we move away from the turning point. The time independent Schrödinger equations (2.2) and (2.4) can then be solved in each of the two regions, namely

$$u^\pm(x) = A_\pm \xi^{1/2}(x) k^{-1/2}(x) J_{\pm 1/3}(\xi) \quad (x > 0) \quad (2.21)$$

$$u_1^\pm(x) = B_\pm \xi_1^{1/2}(x) k_1^{-1/2}(x) I_{\pm 1/3}(\xi_1) \quad (x < 0) \quad (2.22)$$

where $J_n(z)$ is a regular Bessel function ([1], Chapter 11) (of the first kind), satisfying

$$\frac{d^2 y}{dz^2} + \frac{1}{z} \frac{dy}{dz} + \left(1 - \frac{n^2}{z^2}\right) y = 0 \quad (2.23)$$

and $I_n(z)$ is a modified Bessel function, given by

$$I_n(z) = i^{-n} J_n(iz) \quad (2.24)$$

2.1.2 Gans–Jeffreys Asymptotic Connection Formula

By using the known behaviour of $J_{\pm 1/3}(x)$ and $I_{\pm 1/3}(x)$ as $|x| \rightarrow 0$ and as $|x| \rightarrow \infty$ ([1], Chapter 10) we may obtain the following connection formulae as follows: consistent with Figure 2.1, with $\gamma = \sqrt{2\mu F}$ we have

$$\frac{d^2 u}{dx^2} + \gamma^2 x u = 0 \quad (-\infty < x < +\infty) \quad (2.25)$$

Using a Fourier transform, we deduce that

$$u(+\infty) = (2\pi)^{-1} \gamma^{-2/3} \int_{-\infty}^{+\infty} dp \exp \left[i \left(\frac{p^3}{3\gamma^2} - px \right) \right] \quad (2.26)$$

$$\equiv \text{Ai}(-\gamma^{2/3}x) \quad (2.27)$$

$$= \begin{cases} \frac{1}{3} \gamma^{1/3} x^{1/2} \left[J_{1/3} \left(\frac{2}{3} \gamma x^{3/2} \right) + J_{-1/3} \left(\frac{2}{3} \gamma x^{3/2} \right) \right] & (x \geq 0) \\ \frac{1}{3} \gamma^{1/3} (-x)^{1/2} \left[I_{-1/3} \left(\frac{2}{3} \gamma (-x)^{3/2} \right) - I_{+1/3} \left(\frac{2}{3} \gamma (-x)^{3/2} \right) \right] & (x \leq 0) \end{cases} \quad (2.28)$$

$$\simeq \begin{cases} \pi^{-1/2} \gamma^{-1/6} x^{-1/4} \sin \left(\frac{2}{3} \gamma x^{3/2} + \frac{\pi}{4} \right) & (x \gg 1) \\ \frac{1}{2} \pi^{-1/2} \gamma^{-1/6} (-x)^{-1/4} \exp \left(-\frac{2\gamma}{3} (-x)^{3/2} \right) & (x \ll -1) \end{cases} \quad (2.29)$$

$$\frac{1}{2} k_1^{-1/2} e^{-\xi_1} \xrightarrow{(x < 0)} k^{-1/2} \sin \left(\xi + \frac{\pi}{4} \right) \quad (x > 0) \quad (2.30)$$

and similarly

$$k_1^{-1/2} e^{\xi_1} \xleftarrow{(x < 0)} k^{-1/2} \sin \left(\xi - \frac{\pi}{4} \right) \quad (x > 0) \quad (2.31)$$

We note in (2.30) that the arrow must point from $x < 0$ to $x > 0$ and *not* from $x > 0$ to $x < 0$, since a small error in the phase of the sine will introduce an e^{ξ_1} component in the solution for $x < 0$, which “blows up,” i.e., tends to infinity as $x \rightarrow -\infty$. In a similar way in (2.31) the arrow must point in the other direction since a small unobservable component of $e^{-\xi_1}$, as $x \rightarrow -\infty$, will modify the phase of the sine by a significant amount.

One problem with the derivation of (2.26) is that as $x \rightarrow +\infty$, $u(x)$ suffers an infinite oscillatory divergence, which is assumed to average out at zero. Also by our choice of Figure 2.1, the quantally allowed region lies to the right and the classically forbidden region to the left. In [324] for instance, the reverse is true. Our choice is more natural because, for the radial coordinate $r \in [0, +\infty]$, the classically forbidden region will always lie to the left for continuum states where two aggregate particles will separate infinitely (r is the positive distance between two particles, by definition of spherical polar coordinates).

A more convincing¹ treatment, tracing the solutions around the complex x -plane, across Stokes lines and avoiding the turning point, is given later. The critical aspect of the Stokes phenomenon is that the coefficient of the exponentially subdominant solution suffers an abrupt change in crossing a Stokes line, that is, in the presence of a nonzero exponentially dominant solution.

2.2 Phase Integrals

2.2.1 Stokes Phenomenon: One Transition Point

From (2.14) and (2.15), we have

¹ After all, it appears, perhaps incorrectly, that the Gans–Jeffreys derivation relates only to the linear potential of Figure 2.1. In fact, as we shall see, the only necessary condition is the existence of a simple transition/turning point.

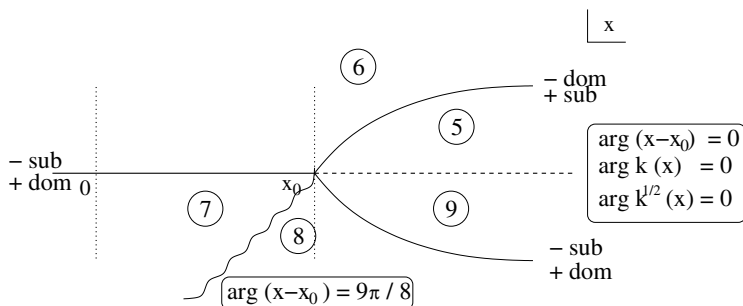


Fig. 2.2. Complex x -plane for the one-transition-point problem

$$u(x) \underset{x \gtrsim x_0}{\simeq} k^{-1/2}(x) \left[A e^{i \int_{x_0}^x k(s) ds} + B e^{-i \int_{x_0}^x k(s) ds} \right] \quad (2.32)$$

Similarly

$$u(x) \underset{x \lesssim x_0}{\simeq} k_1^{-1/2}(x) \left[C e^{\int_x^{x_0} k_1(s) ds} + D e^{-\int_x^{x_0} k_1(s) ds} \right] \quad (2.33)$$

These asymptotic formulae have branch-point singularities at x_0 at which u becomes infinite. Of course $x = \infty$ is an essential singularity in all collision problems ($E > 0$).

Expressions on the right-hand side of (2.32) and (2.33) may be termed phase integrals because they are of the form $\exp(i\theta)$ where θ is expressed as an integral and ‘phase’ is another word for “angle in radians”.

Heavy lines are Stokes lines on which phase integrals are exponentially dominant or subdominant. They emanate from a simple zero at $\pi/3$, π , $-\pi/3 (= 5\pi/3)$. The Stokes phenomenon may be described as follows. As a Stokes line is crossed, the coefficient of the subdominant solution suffers an abrupt change in order to emerge on the next anti-Stokes line with the appropriate coefficient, required for the next domain in which it is again dominant. The abrupt change is parameterized by the Stokes constant times the coefficient of the dominant term. Thus, we have, with b the unique (by symmetry) positive-direction Stokes constant: in Figure 2.2

$$\text{Region 5 : } u \simeq k^{-1/2} \left[A \exp(i \int_{x_0}^x k \, ds) + B \exp(-i \int_{x_0}^x k \, ds) \right] \quad (2.34)$$

$$\text{Region 6 : } u \simeq k^{-1/2} \left[(A + bB) \exp(i \int_{x_0}^x k \, ds) + B \exp(-i \int_{x_0}^x k \, ds) \right] \quad (2.35)$$

$$\text{Region 7 : } u \simeq k^{-1/2} \left[(A + bB) \exp(i \int_{x_0}^x k \, ds) + \{b(A + bB) + B\} \exp(-i \int_{x_0}^x k \, ds) \right] \quad (2.36)$$

$$\begin{aligned} \text{Region 8 : } u \simeq -ik^{-1/2} & \left[\{b(A + bB) + B\} \exp(i \int_{x_0}^x k \, ds) \right. \\ & \left. + (A + bB) \exp(-i \int_{x_0}^x k \, ds) \right] \end{aligned} \quad (2.37)$$

$$\begin{aligned} \text{Region 9 : } u \simeq -ik^{-1/2} & \left[\{bA + (1 + b^2)B\} \exp(i \int_{x_0}^x k \, ds) \right. \\ & \left. + \{A + bB + b\{bA + (1 + b^2)B\}\} \exp(-i \int_{x_0}^x k \, ds) \right] \end{aligned} \quad (2.38)$$

Analyticity (which follows from ascending Frobenius series solutions to equation (2.2) in powers of $(x - x_0)$), (2.34) and (2.38) imply

$$b = i \quad (2.39)$$

A purely subdominant solution on the π Stokes line requires

$$A + bB = 0 \quad (2.40)$$

Setting

$$A = \frac{c}{2} \exp\left(-\frac{\pi i}{4}\right), \quad B = \frac{c}{2} \exp\left(\frac{\pi i}{4}\right) \quad (2.41)$$

gives the Jeffreys' connection formula

$$\frac{c}{2} |\nu|^{-1/2} \exp\left(-\int_x^{x_0} |\nu| \, ds\right) \longrightarrow c \nu^{-1/2} \sin\left[\int_{x_0}^x \nu \, ds + \frac{\pi}{4}\right] \quad (2.42)$$

where we have avoided the no-go area around/near x_0 . The ubiquitous $\pi/4$ is thus half the phase of b , the positive Stokes constant.

As stated in [160], it appeared to Budden [100], [101] that Furry [287] was the first author to have treated the idea of the Stokes phenomenon seriously and to have derived the Stokes constants and hence the Jeffreys' connection formula for the one-transition-point problem, by analyticity arguments. However, Stueckelberg [574] not only preceded Furry in this respect by fifteen years but also made an outstanding contribution to the solution of what is essentially a four-transition-point problem. It may be noted that, in particular, Furry's treatment is blurred because he does not specify the location of the branch cut for $k^{1/2}(x)$.

Bohr–Sommerfeld Quantization Rule

Two turning points are given by

$$V(x_1) = E = V(x_2) \quad (2.43)$$

$$\Rightarrow \quad V(x) > E \quad (x < x_1 \text{ and } x > x_2) \quad (2.44)$$

$$V(x) < E \quad (x_1 < x < x_2) \quad (2.45)$$

Concerning the x_1 turning point

$$x > x_1 \Rightarrow (\text{ see (2.35)}) \quad u(x) = Ak^{-1/2} \sin \left(\int_{x_1}^x k(s) ds + \frac{\pi}{4} \right) \quad (2.46)$$

where

$$k(s) \equiv \frac{1}{\hbar} [2\mu(E - V(s))]^{1/2} \quad (2.47)$$

Concerning the x_2 turning point

$$x < x_2 \Rightarrow \quad u(x) = A'k^{-1/2} \sin \left(\int_x^{x_2} k(s) ds + \frac{\pi}{4} \right) \quad (2.48)$$

such that as x decreases, the integral term increases. It follows from (2.46), (2.48) that the wave function has the following form:

$$\begin{aligned} u(x) &= -A'k^{-1/2} \sin \left[\int_{x_2}^x k(s) ds - \frac{\pi}{4} \right] \\ &= -A'k^{-1/2} \sin \left[\int_{x_1}^x k(s) ds - \frac{\pi}{4} - \eta \right] \end{aligned} \quad (2.49)$$

where

$$\eta \equiv \int_{x_1}^{x_2} k(x) dx \quad (2.50)$$

The solutions given by (2.46), (2.49) connect smoothly if $A' = (-1)^{n+1}A$ and $\eta = n\pi + \pi/2$ where $n = 0, 1, 2, \dots$. Thus we obtain

$$\int_{x_1}^{x_2} k(x) dx = (n + \frac{1}{2})\pi \quad (2.51)$$

which can be written as ($p = \hbar k$)

$$\int_{x_1}^{x_2} [2\mu(E - V(x))]^{1/2} dx = (n + \frac{1}{2})\hbar\pi \quad (2.52)$$

($\hbar = h/2\pi = 1$ in atomic units), and determines the energy eigenvalue E_n . Since the linear momentum is given by

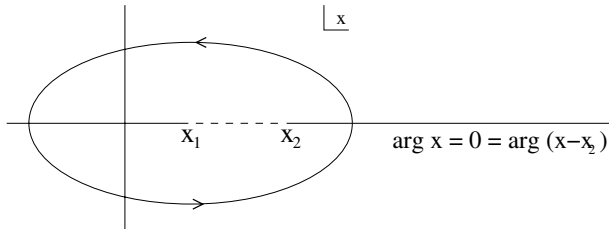


Fig. 2.3. Path of phase integral of (2.54) in complex x -plane

$$p = [2\mu(E - V(x))]^{1/2} \quad (2.53)$$

a classical expression, (2.52) can be written as

$$\begin{aligned} \frac{1}{2} \oint^{(x_1+, x_2+)} p \, dx &= \frac{1}{2} \left[\int_{x_1}^{x_2} p \, dx + \int_{x_2}^{x_1} e^{i\pi} p \, dx \right] \\ &= \int_{x_1}^{x_2} p \, dx = \left(n + \frac{1}{2}\right) \hbar \pi \quad (n = 0, 1, 2, \dots) \end{aligned} \quad (2.54)$$

where the left-hand side is an integral over the complete cycle $x_1 \rightarrow x_2 \rightarrow x_1$. Equation (2.54) is known as the *Bohr–Sommerfeld quantization rule*. Wide-ranging discussions of one-dimensional semiclassical elastic scattering are given by Mott and Massey [443], Brink [88], and Flannery [271].

The cases that arise when (2.41) is not fulfilled are considered by Nakamura [447] and by Coveney et al. [152].

2.2.2 Application of JWKB to Coupled Wave Equations

Introduction

The semiclassical treatment of atom-atom collisions involving electronic transitions is discussed in [40]. As is well known, difficulties occur if the classical trajectories associated with the various states of importance in a collision process differ significantly. A method designed to overcome these is described. It will be referred to as the *forced-common-turning-point method*. The four coupled first-order differential equations that describe the new version of the semiclassical two-state treatment for an atom-atom collision may be reduced to a pair of generalized impact parameter equations.

The first Born approximation to the cross section obtained from the straightforward semiclassical treatment differs from the corresponding cross section obtained from the full quantal treatment mainly in that it contains an anomalous multiplying factor equal to the ratio of the initial to the final velocity of relative motion. This anomaly does not come up with the forced-common-turning-point method.

A model collision process that provides a very searching test is considered. Only two states are included. The initial interaction is zero, the final interaction is Coulombic, and the transition matrix element is exponential. Curve-crossing may occur. The

distorted-wave approximation to the excitation cross section may be found exactly and may also be computed using the forced-common-turning-point method. There is remarkable accord between the results. Thus, in a case where the reduced mass of the colliding systems is 2 on the chemical scale, where the excitation energy is 3.4 eV, and where the incident kinetic energy of relative motion is only 0.85 eV above this, the excitation cross sections obtained differ by as little as 0.01%; moreover, the patterns of the contributions to the cross sections from the separate partial waves are similar.

As was first pointed out by Mott [442] the theory of collisions between atomic systems is greatly simplified by the assumption that the nuclei move like classical particles. This assumption leads immediately to the impact parameter treatment. It was made by Landau [376] and by Zener [611] in their research on the effect of pseudo-crossings of potential energy surfaces. Stueckelberg [574] carried through a much more elaborate analysis in which he described the motion of the nuclei by an expansion in powers of Planck's constant, that is semiclassically (cf. [443] p.351). The semiclassical treatment based on the JWKB or eikonal approximation has received much attention [42], [307], [156], [601], [111]. It is more powerful than the closely related impact parameter treatment.

There remains a general collision problem that has not yet been satisfactorily solved by either treatment: the problem of how to carry out calculations if the classical trajectories in the initial and final states differ markedly.

A possible approach in the distorted-wave approximation is to use semiclassical wave functions in the transition matrix element occurring in the formula for the cross section ([43] [443] p. 354). The behaviour near the classical turning points in the initial and final states, at r_0 and r_1 respectively, causes difficulty. Since the amplitude of a wave function diminishes rapidly as the penetration into the classically forbidden region is increased, it has been suggested that the region within r_m , the greater of r_0 and r_1 , contributes little to the transition matrix element and may be neglected. Because of the highly oscillatory nature of the integrand, such neglect is in fact unjustified and, as we have verified by detailed computations, may give rise to serious error. A less crude procedure is needed. Preferably it should not be limited to the distorted-wave approximation but should be widely applicable.

With this in mind we consider the equations arising in the quantal partial-wave cross section analysis. In order to avoid irrelevant complications, we shall take explicit account of only the initial and final states. Allowance may readily be made for other states, provided the associated classical trajectories are effectively the same as either the initial- or final-state classical trajectories. The restriction is of little practical importance since the classical trajectories do not differ significantly except at very low velocities of relative motion, unless the Coulomb parts of the interaction between the colliding systems for the states concerned differ.

We proceed by modifying the pair of coupled equations so that the classical turning points coincide. Using the one-dimensional JWKB approximation, as Bates and Holt [42] used the three-dimensional JWKB approximation we solve the modified equations accurately both by an elementary method and with the aid of the Green function. As a check we consider a problem that is exactly solvable in the distorted-

wave approximation and demonstrate that in this case the artifice of forcing a common turning point is remarkably successful.

Two-State Approximation in Wave Treatment

For reference purposes we briefly recall the wave treatment (cf. [443] p. 347).

Denoting the reduced mass of the colliding systems by M and the interaction between them by V , write

$$U \equiv 2MV/\hbar^2 \quad (2.55)$$

and represent the matrix elements of this with respect to the electronic wave functions by the same symbol with subscripts affixed to indicate the states. On the two-state approximation the l th partial cross section Q_l^{01} for transitions from the initial state 0 to the final state 1 is determined by the proper solution to the coupled equations

$$\left(\frac{d^2}{dr^2} + K_{0l}^2(r) + \frac{1}{4r^2} \right) G_{0l} = U_{01} G_{1l} \quad (2.56)$$

$$\text{and} \quad \left(\frac{d^2}{dr^2} + K_{1l}^2(r) + \frac{1}{4r^2} \right) G_{1l} = U_{10} G_{0l} \quad (2.57)$$

where $k(r)$ of Section 2.1 is generalized to $K_{jl}(r)$ ($j = 0, 1$) given by

$$K_{jl}^2(r) = k_j^2(\infty) - U_{jj}(r) - \frac{(l + \frac{1}{2})^2}{r^2} \equiv k_j^2(r) - \frac{(l + \frac{1}{2})^2}{r^2} \quad (j \equiv 0, 1) \quad (2.58)$$

in which

$$k_j(r) = Mv_j(r)/\hbar \quad (2.59)$$

$v_j(r)$ being the magnitude of the classical speed of relative motion at separation r in state j . The boundary conditions to be satisfied are

$$\left. \begin{aligned} G_{0l}(0) &= G_{1l}(0) = 0 \\ G_{0l}(r) &\underset{r \rightarrow \infty}{\simeq} i^l \sin\{k_0(\infty)r - \tfrac{1}{2}l\pi\} + \alpha_l \exp\{ik_0(\infty)r\} \\ G_{1l}(r) &\underset{r \rightarrow \infty}{\simeq} \beta_l \exp\{ik_1(\infty)r\} \end{aligned} \right\} \quad (2.60)$$

where α_l and β_l are constants. The partial elastic and inelastic cross sections are related to the values of these constants: in particular

$$Q_l^{01} = \frac{4\pi k_1(\infty)(2l+1)|\beta_l|^2}{k_0^3(\infty)} \quad (2.61)$$

Semiclassical Treatment

Following Langer [378] we replace $l(l+1)$ in (2.56) and (2.57) by $(l + 1/2)^2$ to get

$$\left(\frac{d^2}{dr^2} + K_{0l}^2(r) \right) G_{0l} = U_{0l} G_{0l} \quad (2.62)$$

$$\left(\frac{d^2}{dr^2} + K_{1l}^2(r) \right) G_{1l} = U_{10} G_{0l} \quad (2.63)$$

To force a common turning point we take

$$K_{jl}^2(r) = k_j^2(r) \left\{ 1 - \frac{(l + \frac{1}{2})^2}{r^2 k_0(r) k_1(r)} \right\} \quad (2.64)$$

except that where the difference, $K_{0l}^2(r) - K_{1l}^2(r)$, occurs we use the exact value, the results being very sensitive to the magnitude of this difference.

We seek solutions to (2.62) and (2.63) in the form

$$G_{jl} = \alpha_{jl}^+ S_{jl}^+ + \alpha_{jl}^- S_{jl}^- \quad (j = 0, 1) \quad (2.65)$$

where α_{jl}^\pm are slowly varying functions of r and where

$$S_{jl}^\pm \equiv K_{jl}^{-\frac{1}{2}} \exp \pm i \left\{ \frac{1}{4} \pi + \int_R^r K_{jl}(s) ds \right\} \quad (2.66)$$

are JWKB approximations to the solutions of the equations

$$\left(\frac{d^2}{dr^2} + K_{jl}^2(r) \right) F_{jl} = 0 \quad (2.67)$$

which describe the motion in the absence of transitions. The separation R at the turning point is, of course, the greatest positive root of

$$x^2 k_0(x) k_1(x) = (l + \frac{1}{2})^2 \quad (2.68)$$

Substituting (2.65) into (2.62) and (2.63) and ignoring the small terms $\alpha_{jl}^{\pm\prime\prime} S_{jl}^\pm$ in which the primes indicate differentiation with respect to r , we obtain

$$2\{\alpha_{0l}^{+\prime} S_{0l}^{+\prime} + \alpha_{0l}^{-\prime} S_{0l}^{-\prime}\} = U_{01} \{\alpha_{1l}^+ S_{1l}^+ + \alpha_{1l}^- S_{1l}^-\} \quad (2.69)$$

$$\text{and} \quad 2\{\alpha_{1l}^{+\prime} S_{1l}^{+\prime} + \alpha_{1l}^{-\prime} S_{1l}^{-\prime}\} = U_{10} \{\alpha_{0l}^+ S_{0l}^+ + \alpha_{0l}^- S_{0l}^-\} \quad (2.70)$$

Solutions to these that meet the requirement of being slowly varying functions of r may be derived from

$$2\alpha_{0l}^{\pm\prime} S_{0l}^{\pm\prime} = U_{01} \alpha_{1l}^+ S_{1l}^+ + \alpha_{1l}^\pm S_{1l}^\pm \quad (2.71)$$

$$\text{and} \quad 2\alpha_{1l}^{\pm\prime} S_{1l}^{\pm\prime} = U_{10} \alpha_{0l}^+ S_{0l}^+ + \alpha_{0l}^\pm S_{0l}^\pm \quad (2.72)$$

Taking

$$S_{jl}^{\pm\prime} S_{jl}^\mp \simeq \pm i \quad (2.73)$$

we reduce (2.71) and (2.72) to

$$\pm 2iK_{0l}^{\frac{1}{2}}K_{1l}^{\frac{1}{2}}\alpha_{0l}^{\pm'} = U_{01}\alpha_{1l}^{\pm} \exp\{\mp i\mu_l\} \quad (2.74)$$

$$\text{and} \quad \pm 2iK_{0l}^{\frac{1}{2}}K_{1l}^{\frac{1}{2}}\alpha_{1l}^{\pm'} = U_{10}\alpha_{0l}^{\pm} \exp\{\pm i\mu_l\} \quad (2.75)$$

where

$$\mu_l = \int_R^r (K_{0l}(s) - K_{1l}(s)) ds \quad (2.76)$$

The boundary conditions are

$$\alpha_{0l}^-(\infty) = \frac{1}{2}k_0^{\frac{1}{2}}(\infty), \quad \alpha_{1l}^-(\infty) = 0 \quad (2.77)$$

and from the JWKB connection formula

$$\alpha_{jl}^+(R) + \alpha_{jl}^-(R) = 0 \quad (j = 0, 1) \quad (2.78)$$

Referring to equation (2.61) we see that the partial cross sections are

$$Q_l^{01} = \frac{4\pi(2l+1)}{k_0^3(\infty)} |\alpha_{1l}^+(\infty)|^2 \quad (2.79)$$

The total excitation cross section is

$$Q^{01} = \sum_{l=0}^{\infty} Q_l^{01} \quad (2.80)$$

Great simplification may be effected in (2.74) and (2.75) without further approximation. Changing the independent and dummy variables from r and s to

$$|z| = \int_R^r \left\{ 1 - \frac{(l + \frac{1}{2})^2}{t^2 k_0(t) k_1(t)} \right\}^{-\frac{1}{2}} dt, \quad |\zeta| = \int_R^s \left\{ 1 - \frac{(l + \frac{1}{2})^2}{t^2 k_0(t) k_1(t)} \right\}^{-\frac{1}{2}} dt \quad (2.81)$$

we obtain

$$\pm 2ik_0^{\frac{1}{2}}(r)k_1^{\frac{1}{2}}(r) \frac{d\alpha_{0l}^{\pm}}{d|z|} = U_{01}\alpha_{1l}^{\pm} \exp\{\mp i\mu_l\} \quad (2.82)$$

$$\pm 2ik_0^{\frac{1}{2}}(r)k_1^{\frac{1}{2}}(r) \frac{d\alpha_{1l}^{\pm}}{d|z|} = U_{10}\alpha_{0l}^{\pm} \exp\{\pm i\mu_l\} \quad (2.83)$$

$$\mu_l = \int_0^{|z|} \{k_0(s) - k_1(s)\} d|\zeta| \quad (2.84)$$

Introducing coefficients $c_{jl}(z)$ and functions $v_l(z)$ that are defined over the complete range of z by

$$\left. \begin{aligned} c_{jl}(z) &\equiv \alpha_{jl}^+(|z|), & v_l(z) &\equiv \mu_l(|z|), & (z \geq 0) \\ &\equiv -\alpha_{jl}^-(|z|), & &\equiv -\mu_l(|z|), & (z \leq 0) \end{aligned} \right\} \quad (2.85)$$

we reduce the four equations of (2.82) and (2.83) to the two impact-parameter-type equations

$$i \frac{dc_{0l}}{dz} = \frac{U_{01}(r)}{2k_0^{\frac{1}{2}}(r)k_1^{\frac{1}{2}}(r)} c_{1l} \exp(-iv_l(z)) \quad (2.86)$$

$$\text{and} \quad i \frac{dc_{1l}}{dz} = \frac{U_{10}(r)}{2k_0^{\frac{1}{2}}(r)k_1^{\frac{1}{2}}(r)} c_{0l} \exp(iv_l(z)) \quad (2.87)$$

If we take the boundary conditions to be

$$c_{0l}(-\infty) = 1, \quad c_{1l}(-\infty) = 0 \quad (2.88)$$

we see that formula (2.79) for the partial cross section is replaced by

$$Q_l^{01} = \frac{(2l+1)\pi}{k_0^2(\infty)} |c_{1l}(+\infty)|^2 \quad (2.89)$$

It may be noted in parentheses that the variable z has a simple interpretation in the special case where

$$k_0^2(\infty) = k_1^2(\infty) \quad \text{and} \quad U_{00}(r) = U_{11}(r) \quad (2.90)$$

so that the initial and final classical trajectories are identical. Omitting the subscripts as unnecessary and introducing the impact parameter

$$\rho = (l + \frac{1}{2})/k(\infty) \quad (2.91)$$

we see from (2.81) that

$$dz = dr \left/ \left(1 - \frac{\rho^2 k^2(\infty)}{r^2 k^2(r)} \right) \right|^{\frac{1}{2}} \quad (2.92)$$

which is just an element of length along the common trajectory. The difference between equations (2.86) and (2.87) and the corresponding pair of equations for the case of a common rectilinear trajectory (cf. Bates [35]) is therefore as would be expected physically.

Semiclassical Treatment by Green Function Formalism

In general, if

$$U_{jj}(r) \underset{r \rightarrow \infty}{\simeq} -2\lambda_j M/r \quad (2.93)$$

then the boundary conditions on the radial wave functions must be generalized to

$$\begin{aligned}
G_{0l}(r) \underset{r \rightarrow \infty}{\simeq} & \ i^l \sin \left[k_0(\infty)r - \frac{l\pi}{2} + \arg \Gamma \left(l+1 - \frac{i\lambda_0}{v_0(\infty)} \right) \right. \\
& + \frac{\lambda_0}{v_0(\infty)} \ln(2k_0(\infty)r) \left. \right] e^{i \arg \Gamma(l+1-i\lambda_0/v_0(\infty))} \\
& + \alpha_l \exp \left[ik_0(\infty)r + 2i \arg \Gamma \left(l+1 - \frac{i\lambda_0}{v_0(\infty)} \right) \right. \\
& + \frac{i\lambda_0}{v_0(\infty)} \ln(2k_0(\infty)r) \left. \right] \quad (2.94)
\end{aligned}$$

$$\begin{aligned}
G_{1l}(r) \underset{r \rightarrow \infty}{\simeq} & \ \beta_l \exp \left[ik_0(\infty)r + i \arg \Gamma \left(l+1 - \frac{i\lambda_1}{v_1(\infty)} \right) \right. \\
& + i \arg \Gamma \left(l+1 - \frac{i\lambda_0}{v_1(\infty)} \right) + \frac{i\lambda_1}{v_1(\infty)} \ln(2k_1(\infty)r) \left. \right] \quad (2.95)
\end{aligned}$$

We introduce outgoing Green functions \mathcal{G}_{jl} defined by

$$\mathcal{G}_{jl}(r, r') \equiv \frac{1}{2} i S_{jl}^+(r_>)[S_{jl}^+(r_<) - S_{jl}^-(r_<)] \quad (2.96)$$

where

$$\left(\frac{d^2}{dr^2} + K_{jl}^2(r) + \frac{1}{4r^2} \right) S_{jl}^\pm(r) = 0 \quad (2.97)$$

$$\begin{aligned}
S_{jl}^\pm(r) \underset{r \rightarrow \infty}{\simeq} & \ k_j^{-\frac{1}{2}}(\infty) \exp \left[\pm i \left\{ k_j(\infty)r + \eta_{jl} - \frac{1}{2} l\pi + \arg \Gamma \left(l+1 - \frac{i\lambda_j}{v_j(\infty)} \right) \right. \right. \\
& + \frac{\lambda_j}{v_j(\infty)} \ln(2k_j(\infty)r) \left. \left. \right\} \right] \quad (2.98)
\end{aligned}$$

and

$$r_{\leq} = \min_{\max} (r, r')$$

It is easy to show that

$$\begin{aligned}
\sin \eta_{jl} = & \int_0^\infty \left[U_{jj}(r) + \frac{2\lambda_j}{r} M \right] (S_{jl}^+ - S_{jl}^-) i \exp(-ik_j(\infty)r) \\
& \times \frac{(2k_j(\infty)r)^{l+1}}{k_j^{\frac{1}{2}}(\infty)(2l+1)!} \Gamma \left(l+1 + \frac{i\lambda_j}{v_j(\infty)} \right) \exp \left(\frac{\pi\lambda_j}{2v_j(\infty)} \right) \\
& \times {}_1F_1 \left(l+1 + \frac{i\lambda_j}{v_j(\infty)}; 2l+2; 2ik_j(\infty)r \right) dr \quad (2.99)
\end{aligned}$$

However, it is not normally necessary to calculate η_{jl} explicitly. It follows that

$$\left(\frac{d^2}{dr^2} + K_{jl}^2(r) + \frac{1}{4r^2} \right) \mathcal{G}_{jl}(r, r') = \delta(r - r') \quad (2.100)$$

where δ is the Dirac delta function. Integration by parts of (2.56), (2.57), and (2.100) suitably premultiplied yields the coupled integral equations:

$$G_{0l}(r) = \frac{i^{l-1} k_0^{\frac{1}{2}}(\infty) \exp(i\eta_{0l})}{2i} (S_{0l}^+(r) - S_{0l}^-(r)) + \int_0^\infty U_{01}(r') G_{1l}(r') \mathcal{G}_{0l}(r, r') dr' \quad (2.101)$$

$$G_{1l}(r) = + \int_0^\infty U_{10}(r') G_{0l}(r') \mathcal{G}_{1l}(r, r') dr' \quad (2.102)$$

Substitution of (2.96) into (2.101) and (2.102), together with definition (2.65), leads without loss of generality to the four coupled integral equations:

$$\begin{aligned} \alpha_{0l}^+(r) &= \frac{1}{2} i^{l-1} k_0^{\frac{1}{2}}(\infty) \exp(i\eta_{0l}) + \frac{1}{2} i \int_0^\infty U_{01}(r') G_{1l}(r') S_{0l}^+(r') dr' \\ &\quad - \frac{1}{2} i \int_0^r U_{01}(r') G_{1l}(r') S_{0l}^-(r') dr' \end{aligned} \quad (2.103)$$

$$-\alpha_{0l}^-(r) = \frac{1}{2} i^{l-1} k_0^{\frac{1}{2}}(\infty) \exp(i\eta_{0l}) + \frac{1}{2} i \int_r^\infty U_{01}(r') G_{1l}(r') S_{0l}^+(r') dr' \quad (2.104)$$

$$\alpha_{1l}^+(r) = \frac{1}{2} i \int_0^\infty U_{10}(r') G_{0l}(r') S_{1l}^+(r') dr' - \frac{1}{2} i \int_0^r U_{10}(r') G_{0l}(r') S_{1l}^-(r') dr' \quad (2.105)$$

$$-\alpha_{1l}^-(r) = \frac{1}{2} i \int_r^\infty U_{10}(r') G_{0l}(r') S_{1l}^+(r') dr' \quad (2.106)$$

Differentiation with respect to r gives four exact first-order coupled differential equations:

$$\alpha_{0l}^{+'} = -\frac{1}{2} i U_{01} S_{0l}^- (\alpha_{1l}^+ S_{1l}^+ + \alpha_{1l}^- S_{1l}^-) \quad (2.107)$$

$$\alpha_{0l}^{-'} = \frac{1}{2} i U_{01} S_{0l}^+ (\alpha_{1l}^+ S_{1l}^+ + \alpha_{1l}^- S_{1l}^-) \quad (2.108)$$

$$\alpha_{1l}^{+'} = -\frac{1}{2} i U_{10} S_{1l}^- (\alpha_{0l}^+ S_{0l}^+ + \alpha_{0l}^- S_{0l}^-) \quad (2.109)$$

$$\alpha_{1l}^{-'} = \frac{1}{2} i U_{10} S_{1l}^+ (\alpha_{0l}^+ S_{0l}^+ + \alpha_{0l}^- S_{0l}^-) \quad (2.110)$$

with

$$\alpha_{0l}^-(\infty) = \frac{1}{2} k_0^{\frac{1}{2}}, \quad \alpha_{1l}^-(\infty) = 0, \quad \alpha_{jl}^+(0) + \alpha_{jl}^-(0) = 0 \quad (j = 0, 1) \quad (2.111)$$

Thus far no approximation has been made and we have reduced two coupled second-order differential equations to four coupled first-order equations by a method that is essentially equivalent to the well-known variation-of-parameters method. We now assume that α_{jl}^\pm are slowly varying functions compared with S_{jl}^\pm and neglect such

terms as $S_{jl}^- S_{kl}^-$ and $S_{jl}^+ S_{kl}^+$ in comparison with $S_{jl}^+ S_{kl}^-$ on the grounds that oscillatory integrands lead to negligible integrals. This condition will be relaxed in Section 4.5. We thus obtain

$$\alpha_{0l}^{\pm'} = \mp \frac{1}{2} i U_{01} S_{0l}^{\mp} S_{1l}^{\pm} \alpha_{1l}^{\pm} \quad (2.112)$$

$$\alpha_{1l}^{\pm'} = \mp \frac{1}{2} i U_{01} S_{1l}^{\mp} S_{0l}^{\pm} \alpha_{0l}^{\pm} \quad (2.113)$$

where S_{jl}^{\pm} are still the exact functions defined by (2.97) and (2.98). If, however, we now make the semiclassical approximations to S_{jl}^{\pm} given in (2.66) and maintain the exact difference $K_{0l}^2(r) - K_{1l}^2(r)$ as in Section 2.2.2, then we obtain precisely equations (2.74) to (2.78).

Distorted-Wave and Born Approximations

Assuming that the coupling between the initial and final states is weak we may take $c_{0l}(z)$ on the right of (2.87) to be unity. This corresponds to the distorted-wave approximation and leads to

$$i c_{1l}(+\infty) = \int_{-\infty}^{+\infty} \frac{U_{01}(r)}{2k_0^{\frac{1}{2}}(r)k_1^{\frac{1}{2}}(r)} \exp\{i v_l(z)\} dz \quad (2.114)$$

$$= \frac{2}{\hbar v_0^{\frac{1}{2}}(\infty) v_1^{\frac{1}{2}}(\infty)} \int_0^{\infty} f(r) V_{10}(r) \cos\{v_l(z)\} dz \quad (2.115)$$

where

$$f(r) = \left[\frac{k_0(\infty)k_1(\infty)}{k_0(r)k_1(r)} \right]^{\frac{1}{2}} \quad (2.116)$$

In the Born approximation $f(r)$ is unity. If ρ_0 and ρ_1 are the impact parameters in the initial and final states then

$$l + \frac{1}{2} = \rho_0 k_0(\infty) = \rho_1 k_1(\infty) \quad (2.117)$$

It is convenient to put

$$\rho_0 \rho_1 = \rho^2 \quad (2.118)$$

so that

$$z = \int_{\rho}^r \left(1 - \frac{\rho^2}{t^2} \right)^{-\frac{1}{2}} dt = (r^2 - \rho^2)^{\frac{1}{2}} \quad (2.119)$$

Formula (2.115) becomes

$$i c_{1l}(+\infty) = \frac{2}{\hbar v_0^{\frac{1}{2}}(\infty) v_1^{\frac{1}{2}}(\infty)} \int_0^{\infty} V_{10}(r) \cos \left[\frac{2\epsilon_{01} z}{\hbar(v_0(\infty) + v_1(\infty))} \right] dz \quad (2.120)$$

where ϵ_{01} is the excitation energy. Using (2.89) and replacing the summation over l in (2.80) by an integration we find

$$Q^{01} = \frac{8\pi}{\hbar^2 v_0^2(\infty)} \int_0^\infty \rho \left\{ \int_0^\infty V_{10}(r) \cos \left[\frac{2\epsilon_{01}z}{\hbar(v_0(\infty) + v_1(\infty))} \right] dz \right\}^2 d\rho \quad (2.121)$$

This may be rearranged to give

$$Q^{01} = \frac{1}{2\pi\hbar^2 v_0^2(\infty)} \int_{|k_0(\infty) - k_1(\infty)|}^\infty |g(\mathbf{q})|^2 q dq \quad (2.122)$$

where the modulus on the lower limit includes the possibility of deexcitation and where

$$g(\mathbf{q}) = \int \exp(-i\mathbf{q} \cdot \mathbf{r}) V_{10}(r) d^3\mathbf{r} \quad (2.123)$$

a summation or average over states differing only in magnetic quantum number being assumed [158]. The corresponding formula obtained from the straightforward semiclassical treatment [42] differs from (2.122) by the factor $v_0(\infty)/v_1(\infty)$, while that obtained from the full quantal treatment differs from (2.122) only in that the upper limit to the integration is $k_0(\infty) + k_1(\infty)$ instead of being infinite. The effect of the latter difference is minute unless extremely close to the threshold. This represents a remarkable success for the forced-common-turning-point version of the semiclassical treatment. Indeed it leads to the possibility that the treatment is useful even for electron-atom collisions [47].

An Exact Distorted-Wave Calculation

It is essential to test the efficacy of (2.86) and (2.87) as a general approximation to equations (2.56) and (2.57) when U_{00} and U_{11} are unequal. From a practical point of view this is most easily achieved by investigating the weak-coupling limit, since its application to (2.86) and (2.87) does not obviate the basic underlying assumption of a forced common turning point. In this same limit, equations (2.56) and (2.57) yield the exact distorted-wave formula:

$$|\beta_l|^2 = \frac{k_0(\infty)}{k_1(\infty)} \left| \frac{1}{2} \int_0^\infty U_{10}(S_{0l}^+ - S_{0l}^-)(S_{1l}^+ - S_{1l}^-) dr \right|^2 \quad (2.124)$$

which is most easily obtained by substituting the first term of (2.101) into (2.102).

To be specific we take

$$U_{00}(r) \equiv 0 \quad (2.125)$$

and

$$U_{11}(r) \equiv -2\lambda M/r \quad (2.126)$$

where all quantities are now in atomic units. Except where otherwise specified we shall use these units throughout the remainder of the section.

We have that η_{0l} and η_{1l} are zero,

$$S_{0l}^+ - S_{0l}^- = \mathcal{F}_0(0) \equiv 2ik_0^{\frac{1}{2}}(\infty)rj_l(k_0(\infty)r) \quad (2.127)$$

$$\text{and} \quad S_{1l}^+ - S_{1l}^- = \mathcal{F}_1(\lambda) \quad (2.128)$$

where

$$\begin{aligned} \mathcal{F}_j(\mu) &\equiv \frac{i \exp\{-ik_j(\infty)r\}(2k_j(\infty)r)^{l+1}}{k_j^{\frac{1}{2}}(\infty)(2l+1)!} \left| \Gamma\left(l+1 + \frac{i\mu}{v_j(\infty)}\right) \right| \exp\left\{\frac{\pi\mu}{2v_j(\infty)}\right\} \\ &\times {}_1F_1\left(l+1 + \frac{i\mu}{v_j(\infty)}; 2l+2; 2ik_j(\infty)r\right) \end{aligned} \quad (2.129)$$

In order to obtain an analytical result in closed form, we must first consider the case

$$U_{10}(r) \equiv (2M/r)e^{-\alpha r} \quad (2.130)$$

so that

$$\begin{aligned} \beta_l &= \frac{2(4k_0(\infty)k_1(\infty))^{l+1}l! \left| \Gamma\left(l+1 + \frac{i\lambda}{v_1(\infty)}\right) \right| \exp\left\{\frac{\pi\lambda}{2v_1(\infty)}\right\}}{v_1(\infty)[2(2l+1)!]^2} \\ &\times \int_0^\infty \exp\{-(\alpha + ik_0(\infty) + ik_1(\infty))r\} r^{2l+1} {}_1F_1(l+1; 2l+2; 2ik_0(\infty)r) \\ &\times {}_1F_1\left(l+1 + \frac{i\lambda}{v_1(\infty)}; 2l+2; 2ik_1(\infty)r\right) dr \end{aligned} \quad (2.131)$$

$$\begin{aligned} &= \frac{2(4k_0(\infty)k_1(\infty))^{l+1}l! \left| \Gamma\left(l+1 + \frac{i\lambda}{v_1(\infty)}\right) \right| \exp\left\{\frac{\pi\lambda}{2v_1(\infty)}\right\} (2l+1)!}{v_1(\infty)[2(2l+1)!]^2 [\alpha^2 + (k_0(\infty) - k_1(\infty))^2]^{l+1}} \\ &\times \left[\frac{\alpha + ik_0(\infty) + ik_1(\infty)}{\alpha + ik_0(\infty) - ik_1(\infty)} \right]^{i\lambda/v_1(\infty)} \\ &\times {}_2F_1\left[l+1, l+1 + \frac{i\lambda}{v_1(\infty)}; 2l+2; \frac{-4k_0(\infty)k_1(\infty)}{\alpha^2 + (k_0(\infty) - k_1(\infty))^2}\right] \end{aligned} \quad (2.132)$$

$$\begin{aligned} &= \frac{l! \exp\{\theta(\frac{1}{2}\pi - \phi)\} |\Gamma(l+1 + i\theta)| \left\{ \frac{x+1}{x-1} \right\}^{\pm \frac{1}{2}i\theta}}{2v_1(\infty)(2l+1)!(-v)^{l+1}} \\ &\times {}_2F_1\left(l+1, l+1 \pm i\theta; 2l+1; \frac{1}{v}\right) \end{aligned} \quad (2.133)$$

$$= \frac{l! \exp\{\theta(\frac{1}{2}\pi - \phi)\}}{v_1(\infty) |\Gamma(l+1 + i\theta)|} \left\{ \frac{x+1}{x-1} \right\}^{\frac{1}{2}i\theta} Q_l^{(-i\theta, +i\theta)}(x) \quad (2.134)$$

where

$$v = \frac{\alpha^2 + (k_0(\infty) - k_1(\infty))^2}{-4k_0(\infty)k_1(\infty)} \quad (2.135)$$

$$\theta = \lambda/v_1(\infty) \quad (2.136)$$

$$x = \frac{\alpha^2 + k_0^2(\infty) + k_1^2(\infty)}{2k_0(\infty)k_1(\infty)} \quad (2.137)$$

$$\phi = \begin{cases} \tan^{-1} \left(\frac{2\alpha k_1(\infty)}{\alpha^2 + 2M\epsilon_{01}} \right) & \text{if } \alpha^2 + 2M\epsilon_{01} \geq 0 \\ \pi - \tan^{-1} \left(\frac{2\alpha k_1(\infty)}{-\alpha^2 - 2M\epsilon_{01}} \right) & \text{if } \alpha^2 + 2M\epsilon_{01} \leq 0 \end{cases} \quad (2.138)$$

and where $Q_l^{(\alpha, \beta)}$ is a Jacobi function of the second kind. Recurrence relations for the latter function [32] lead to

$$(l^2 + \theta^2)^{\frac{1}{2}} \beta_{l-1} = (2l+1)x\beta_l - \{(l+1)^2 + \theta^2\}^{\frac{1}{2}} \beta_{l+1} \quad (2.139)$$

Since x is greater than unity, upward recurrence would rapidly involve numerical instability. Thus downward recurrence is necessary. The method, essentially due to J. C. P. Miller (cf. [14, 429]), requires setting $\beta_{L+1} = 0$ and $\beta_L = 1$ for some sufficiently large L .

However, it is numerically more convenient to consider the case:

$$U_{10}(r) \equiv 2Me^{-\alpha r} \quad (2.140)$$

The computer program is then amenable to testing in the limit as $\lambda \rightarrow 0$, corresponding to the exact first Born case. Use of (2.130) in this limit involves a Cauchy principal value and a transition probability that behaves like $(\ln \rho)^2$ as ρ tends to zero, a circumstance to be expected within the weak-coupling limit. Equations (2.122), (2.123), and (2.140) yield the first Born approximation:

$$Q^{01} = \frac{16\pi\alpha^2}{3v_0^2(\infty)} \{\alpha^2 + (k_0(\infty) - k_1(\infty))^2\}^{-3} \quad (2.141)$$

This provides a simple check on calculations in the zero-distortion limit. The adoption of (2.140) requires that β_l be replaced by

$$\tilde{\beta}_l \equiv \frac{\partial \beta_l}{\partial \alpha} = -\theta \frac{\partial \phi}{\partial \alpha} \beta_l + \frac{\alpha (lx\beta_l - \sqrt{(l^2 + \theta^2)}\beta_{l-1})}{k_0(\infty)k_1(\infty)(x^2 - 1)} \quad (2.142)$$

In obtaining this, we have used

$$l(x^2 - 1) \frac{\partial}{\partial x} Q_l^{(-i\theta, +i\theta)}(x) = l(lx + i\theta) Q_l^{(-i\theta, +i\theta)}(x) - (l^2 + \theta^2) Q_{l-1}^{(-i\theta, +i\theta)}(x) \quad (2.143)$$

Substituting from (2.139) and replacing l by $l-1$ gives $\tilde{\beta}_{l-1}$ in terms of β_l and β_{l-1} :

$$\tilde{\beta}_{l-1} = -\theta \frac{\partial \phi}{\partial \alpha} \beta_{l-1} + \frac{\alpha (\sqrt{(l^2 + \theta^2)}\beta_l - lx\beta_{l-1})}{k_0(\infty)k_1(\infty)(x^2 - 1)} \quad (2.144)$$

where, of course,

$$\frac{\partial \phi}{\partial \alpha} = \frac{2k_1(\infty)(2M\epsilon_{01} - \alpha^2)}{(\alpha^2 + 2M\epsilon_{01})^2 + 4\alpha^2 k_1^2(\infty)} \quad (2.145)$$

The β_l were calculated from (2.139) and then the $\tilde{\beta}_l$ were calculated from (2.144). The sequence $\{\tilde{\beta}_l\}$ was normalized by setting

$$\tilde{\beta}_0 = \frac{\exp(-\theta\phi)}{v_1(\infty)} \left[\frac{2\pi\theta}{1-\exp(-2\pi\theta)} \right]^{1/2} \times \left[\frac{2k_1(\infty)(2M\epsilon_{10}-\alpha^2)\sin z}{(\alpha^2+2M\epsilon_{01})^2+4k_1^2(\infty)\alpha^2} + \frac{\alpha\cos z}{k_0(\infty)k_1(\infty)(x^2-1)} \right] \quad (2.146)$$

where

$$z = \frac{1}{2}\theta \ln \left(\frac{x+1}{x-1} \right) \quad (2.147)$$

The total cross section was calculated from

$$Q^{01} = \sum_{l=0}^{\infty} \frac{4\pi k_1(\infty)(2l+1)}{k_0^3(\infty)} |\tilde{\beta}_l|^2 \quad (2.148)$$

Comparison of Results of Exact and Approximate Distorted-Wave Calculations

For potentials (2.125), (2.126), and (2.140) equations (2.89) and (2.115) yield the approximate distorted-wave cross section:

$$Q^{01} = \pi \sum_{l=0}^{\infty} \frac{32(l+\frac{1}{2})}{k_0(\infty)k_1(\infty)v_0^2(\infty)} \left\{ \int_0^{\infty} g_l(x) \cos \theta_l(x) dx \right\}^2 \quad (2.149)$$

with

$$g_l(x) = \frac{r\{r^2k_1(r) + \rho^2k_1(\infty)\}^{\frac{1}{2}} \exp(-\alpha r)}{k_1^{\frac{1}{2}}(\infty)\{r^3 + (\rho^4/R^3)(r^2 + rR + R^2)\}^{\frac{1}{2}}} \quad (2.150)$$

and

$$\theta_l(x) = 2 \int_0^x \frac{\{k_1(s) - k_0(\infty)\}}{k_1(\infty)} \left\{ \frac{s^2k_1(s)[s^2k_1(s) + \rho^2k_1(\infty)]}{s^3 + (\rho^4/R^3)(s^2 + sR + R^2)} \right\}^{\frac{1}{2}} dy \quad (2.151)$$

in which $R(\rho)$ is the greatest positive root of

$$t^4 + \frac{2\lambda M}{k_1^2(\infty)} t^3 - \rho^4 = 0 \quad (2.152)$$

and in which

$$r = x^2 + R \quad (2.153)$$

$$s = y^2 + R \quad (2.154)$$

$$k_1^2(r) = k_1^2(\infty) + 2\lambda M/r \quad (2.155)$$

At low energies, where distortion becomes important, the summation over l in (2.149) is easier to carry out numerically than an integration over ρ , which is in turn much easier to use at higher energies, where in fact a check was made that (2.149) tends to (2.141). For each l , interpolation in the cosine argument was found to be expedient, except for the higher values of α , which required such fine grids that direct integration for each value of x was probably equally efficient. Newton's

method was used to obtain $R(\rho)$, while the integrations over x and y were effected by splitting the interval and applying a 7-point Curtis–Clenshaw quadrature, checked by a double 5-point Lobatto quadrature. The latter method is due to O’Hara and Smith (private communication) and is closely related to the methods reported in their paper [463]. However, since rapid oscillations in the sign of the r -integrand occur, a local relative error accuracy was employed. One advantage of the particular choice of integration variables in (2.149) and (2.151), namely x and y , is that the integrands are well behaved at $\rho = 0$.

Of major interest are transitions involving one pseudo-crossing point r_c given by the only real positive root of

$$k_0^2(s) = k_1^2(s) \quad (2.156)$$

On the assumption that $v_0(\infty)$ is very much less than unity, $k_0(s) - k_1(s)$ is very large and the method of steepest descent (or stationary phase) may be tentatively applied to (2.115). Integration over ρ , with averaging over the rapidly varying phase, yields

$$Q^{01} = \frac{8\pi^2 r_c^2 V_{10}^2(r_c)}{v_0^2(\infty) |k'_0(r_c) - k'_1(r_c)|} \quad (2.157)$$

which is just the weak-coupling limit of the Landau-Zener formula and which for the test case reduces to

$$Q^{01} = \frac{8\pi^2 r_c^4 \exp\{-2\alpha r_c\}}{|\lambda| v_0(\infty)} \quad (2.158)$$

where $r_c = \lambda/\epsilon_{01}$ is the crossing point, assuming $\lambda\epsilon_{01} > 0$. In particular, we consider results for $\lambda = +1$ and $\epsilon_{01} = 0.125$ atomic units (a.u.), which correspond to an attractive Coulomb potential in the final state and to excitation, respectively. We take $M = 2 \times 1837$ a.u. and $k_0^2(\infty) = M\epsilon_{01}p$ a.u. with $p = 2.5$, corresponding to an initial relative velocity of 9.223×10^{-3} a.u. and an incident relative kinetic energy of 4.25 eV which is only 0.85 eV above threshold. We confirmed that for $\alpha = 1/2$, the exact formula (2.148) and the forced-common-turning-point formula (2.149) agreed, giving $3747.4(\pi a_0^2)$, while the steepest-descent formula (2.157) gave $3744(\pi a_0^2)$. To obtain a more sensitive test we therefore proceeded to higher values of α , until (2.148) and (2.157) substantially differed, that is, until the individual transition probabilities depended on significant contributions from other than the crossing point. Of course, the evaluation of (2.149) becomes more difficult as α increases. For $\alpha = 2$, we obtained 1635.3, 1635.3, and 1414 (all in units of $10^{-10}\pi a_0^2$) for (2.148), (2.149), and (2.157) respectively, thus showing that the common-turning-point method predicts the wave distortion very accurately for all internuclear separations. Moreover, allowance for deviation from a straight-line trajectory is clearly successful, because although an impact-parameter-type formula, with $\lambda = 0$ except in $k_0(\infty) - k_1(s)$, gives $1677(10^{-10}\pi a_0^2)$, the maximum value of l for which Q_l^{01} contributes to Q^{01} is 200, whereas for (2.148) and (2.149) it is 285. Of course, even the exact Q_l^{01} and the forced-common-turning-point Q_l^{01} , contributing to (2.148) and (2.149) respectively, are somewhat out of phase for all l , but this is not too surprising in view of the very rapid oscillations of Q_l^{01} as a function of l (cf. Table 2.1).

Table 2.1. Oscillation of Q_l^{01} with respect to l

l	Exact Q_l^{01} (πa_0^2)	Approximate Q_l^{01} (πa_0^2)	l	Exact Q_l^{01} (πa_0^2)	Approximate Q_l^{01} (πa_0^2)
100	2.8^{-10}	4.4^{-11}	108	1.2^{-10}	5.2^{-10}
101	4.5^{-10}	4.5^{-10}	109	1.2^{-10}	3.2^{-10}
102	2.8^{-11}	3.4^{-10}	110	5.5^{-10}	7.0^{-14}
103	2.5^{-10}	1.1^{-12}	111	2.3^{-10}	3.4^{-10}
104	4.9^{-10}	3.0^{-10}	112	4.3^{-11}	5.4^{-10}
105	6.0^{-11}	5.0^{-10}	113	5.1^{-10}	1.2^{-10}
106	2.0^{-10}	9.7^{-11}	114	3.7^{-10}	8.3^{-11}
107	5.3^{-10}	1.1^{-10}	115	2.6^{-13}	5.3^{-10}

Note: The exact Q_l^{01} and the approximate (forced-common-turning-point) Q_l^{01} were calculated from (2.148) and (2.149) respectively; the indices give the power of 10 by which the entries must be multiplied.

The evaluation of (2.149) for a low relative velocity is a difficult task due to the severity of the cancellation occurring within each complete cosine wave if α is small or between the different cosine waves if α is large. Some auxiliary computations were carried out to illustrate this cancellation and to demonstrate the extent to which the contribution from the region well away from the crossing is important.

Let the crossing occur at x_c (which of course depends on l and exists only if $l + 1/2 < r_c k_0(\infty)$) and put

$$\theta_l(x_c) \equiv 2n\pi + \delta \quad (2.159)$$

in which n is a positive integer and

$$0 \leq \delta < 2\pi \quad (2.160)$$

Consider

$$q_l(m) \equiv \frac{32\pi(l + \frac{1}{2})}{k_0(\infty)k_1(\infty)v_0^2(\infty)} \left\{ \int_{x_m^-}^{x_m^+} g_l(x) \cos \theta_l(x) dx \right\}^2 \quad (2.161)$$

where m is another positive integer and the sequences x_m^\pm are such that

$$\theta_l(x_m^\pm) = 2(n - m)\pi \quad (2.162)$$

and

$$0 \leq x_m^- \leq x_c, \quad x_m^+ \geq x_c \quad (2.163)$$

It may be seen that in going from m to $m + 1$ two extra complete cosine waves, one on either side of the crossing, are included in the integral in (2.161); and it may readily be verified that the difference between $q_l(n)$ and the partial cross section Q_l^{01} is insignificant.

The parameters involved in the model were assigned the values used earlier. Computations were carried out for a number of different l 's, but it is sufficient to

Table 2.2. Approach of $q_{33}(m)$ to Q_{33}^{01}

m	$q_{33}(m)$ (πa_0^2)	m	$q_{33}(m)$ (πa_0^2)	m	$q_{33}(m)$ (πa_0^2)	m	$q_{33}(m)$ (πa_0^2)
0	8.4^{-9}	7	4.2^{-6}	14	1.5^{-5}	21	1.7^{-6}
1	1.1^{-8}	8	6.4^{-6}	15	1.4^{-5}	22	8.6^{-7}
2	6.1^{-8}	9	8.9^{-6}	16	1.2^{-5}	23	3.9^{-7}
3	2.2^{-7}	10	1.1^{-5}	17	9.2^{-6}	24	1.6^{-7}
4	5.9^{-7}	11	1.3^{-5}	18	6.8^{-6}	25	5.1^{-8}
5	1.3^{-6}	12	1.5^{-5}	19	4.6^{-6}	26	1.1^{-8}
6	2.5^{-6}	13	1.5^{-5}	20	2.9^{-6}	27	5.2^{-11}

Note: $n = 27$, $Q_{33}^{01} = 5.2 \times 10^{-11} \pi a_0^2$; the indices give the power of 10 by which the entries must be multiplied.

give results for the 33rd partial wave as they are quite representative. The values of ρ and n in this case are 1.48 a.u. and 27 respectively. If $\alpha = 0.5$ then

$$q_{33}(0) = 1.3 \times 10^1, \quad q_{33}(m) = 2.2 \times 10^1, \quad m = 1 \rightarrow 27$$

(in units of πa_0^2). The asymptotic value here is reached very close to the crossing because of the cancellation within each complete cosine wave. However, if $\alpha = 2$ the values of $q_{33}(m)$ are as in Table 2.2, from which it is apparent that there is severe cancellation between the different complete cosine waves and that an important contribution to the integral comes even from the complete cosine wave next to the x origin. This emphasizes the severity of the test on the forced-common-turning-point model.

This semiclassical approach has been applied to cold atomic collisions by Bichoutskaia et al. [77] (see Section 4.5).

2.3 Two and Four Transition Points: Crossing and Noncrossing

2.3.1 Introduction

Concerning low-energy heavy-particle collisions embracing excitation and/or charge transfer, much work has been done in the last forty years, not least on the composite Nikitin [453] and generalized Demkov [221] models using both the comparison equation and strong-coupling asymptotics method [167, 193, 467] and the phase-integral method [28]. In principle, a simpler model would appear to be the parabolic model (which has no pole) developed by Crothers [160], using both the phase-integral and comparison equation method, with special reference to strong-coupling asymptotic expansions [161, 476] of parabolic cylinder functions, for both crossing and noncrossing and in the context of the Stokes phenomenon. The asymptotic parameter is the inverse impact velocity (see (2.258)).

We have traced the two solutions of the parabolic differential equation

$$\left(\frac{d^2}{dz^2} + p + \frac{1}{2} - \frac{z^2}{4} \right) D_p(z) = 0 \quad (2.164)$$

for the *noncrossing* case, around the T_0 plane, namely $AD_{-i\gamma}(2e^{\pi i/4}T_0\sqrt{\gamma})$ and $BD_{-1+i\gamma}(2e^{-\pi i/4}T_0\sqrt{\gamma})$ in the lower T_0 half-plane clockwise [161] where A and B are arbitrary constants and γ is a reasonably large, positive parameter. The Stokes lines emanate from two transition points $\pm i$; those in the upper T_0 plane have initial directions $\pi/6$, $-7\pi/6$ and $-\pi/2$. The Stokes lines in the lower T_0 plane are the mirror images of those in the upper plane, reflected in the real T_0 -axis, so that we have a double Stokes line running from i to $-i$ along the imaginary T_0 -axis, and our branch cuts are chosen such that they run from $\pm i$ to $\pm i\infty$ respectively; since our $D_p(z)$'s, appropriate to collisions, are analytic functions of the positive Stueckelberg variable T_0 , we avoid Stueckelberg's choice of nonphysical branch cuts [160, 574]. Thus, there is no simple correspondence between our results and the results of Fröman et al. [284] or Nakamura [447], both of whom use weak-coupling expansions.

We obtain the four parabolic-model Stokes constants (which we name a , b , α , and β), using analyticity and the fact that solutions must connect along the real T_0 -axis,

$$a = \beta = -1 + e^{-2\pi\gamma} \quad (2.165)$$

$$b = \alpha = -1 - e^{-2\pi\gamma} \quad (2.166)$$

Equations (2.165) and (2.166) agree with Crothers [160], [161] regarding both phase (mod π) and magnitude.

Moreover, in a procedure similar to the one in which Berry [71] shows that the abrupt change in the subdominant solution is continuous across a Stokes line for the one-transition-point problem, we succeed in a similar procedure for our two-transition-point problem using Stirling numbers of the first kind to parameterize our original strong-coupling expansions. We will also consider the crossing case [163], [165] by tracing $D_{-1-i\gamma}(2e^{-3\pi i/4}T_0\sqrt{\gamma})$ anticlockwise in the lower T_0 half-plane.

2.3.2 Exact Resumming of Asymptotic Relations for Parabolic Cylinder Functions of Large Order and Argument

The Weak-Coupling Case

We may take as our definition for the parabolic cylinder function:

$$D_p(z) \equiv \frac{\Gamma(1+p)}{2\pi i} e^{-\frac{z^2}{4}} \int_{(-\infty)}^{(0+)} e^{zs - \frac{s^2}{2}} s^{-1-p} ds \quad (2.167)$$

where p is not an integer. The principal branch of s^{-p} is assumed.

Putting $t = e^{\pi i}zs$ and assuming $\arg(z) \in (-\pi/2, +\pi/2)$ we may rewrite (2.167) as

$$D_p(z) = \frac{-\Gamma(1+p)}{2\pi i} e^{-\frac{z^2}{4}} z^p \int_{\infty \exp(i \arg z)}^{(0+)} e^{-t - \frac{t^2}{2z^2}} (te^{-i\pi})^{-1-p} dt \quad (2.168)$$

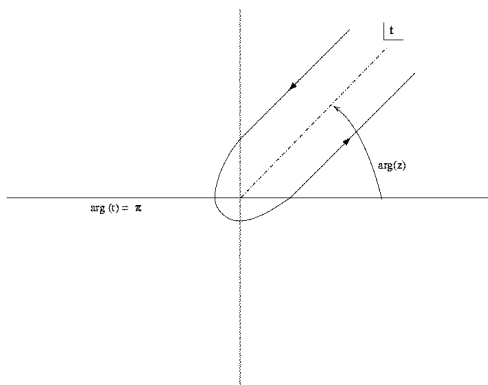


Fig. 2.4. Contour and branch cut for (2.168)

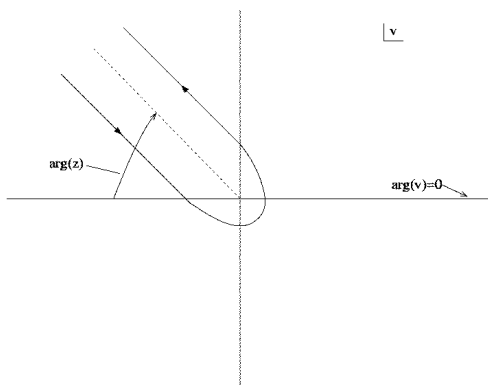


Fig. 2.5. Contour and branch cut for (2.170)

where the contour and branch of t^{-p} are indicated in Figure 2.4. Expanding $e^{(-t-t^2/2z^2)}$ we obtain the usual asymptotic expansion

$$D_p(z) \cong e^{-\frac{z^2}{2}} z^p {}_2F_0\left(-\frac{p}{2}, \frac{1-p}{2}; -\frac{2}{z^2}\right) \quad (2.169)$$

the first term of which is a good approximation if $|z| \gg \max(1, |p|)$.

The $D_p(z)$ in equation 2.169 is only useful in the weak-coupling case (cf. [506] section 3.2); when $|z|$ is not very much greater than $|p|$, then the expression is poorly determined. Instead we put $v = z^{-1}s$ with $\arg(z) \in (-\pi, +\pi)$ so that

$$D_p(z) \equiv \frac{\Gamma(1+p)}{2\pi i} e^{-\frac{z^2}{2}} z \int_{\infty \exp\{i(\pi-\arg z)\}}^{(0+)} \exp\left(z^2\left(v - \frac{v^2}{2}\right) - (1+p)\ln(zv)\right) dv \quad (2.170)$$

where the contour and the branch of $\ln(v)$ are indicated in Figure 2.5 [161], [476].

The Strong-Coupling Case

We assume that $|z|^2$ and $|p|$ are both large so that the method of steepest descent may be applied. This involves expanding the exponential in the integral about its saddle points. They are calculated by finding the zeros of the differential of the argument of the exponential in question. So, in this case, our argument $f(v)$ is

$$f(v) = z^2 \left(v - \frac{v^2}{2} \right) - (1 + p) \ln(zv)$$

and from $f'(v_j) = 0$, the two distinct saddle points are given by

$$2zv_0 = z \pm \sqrt{z^2 - 4(1 + p)} \quad (2.171)$$

provided that $z^2 \neq 4(1 + p)$ and the square root branch is chosen so that $\arg(zv_j) \in (-\pi, +\pi)$.

Finally we expand about the saddle points (looking only at the integral)

$$I = \int \exp \left(f(v_j) + \frac{1}{2} f''(v_j)(v - v_j)^2 + \sum_{n=3}^{\infty} \frac{f^n(v_j)}{n!} (v - v_j)^n \right) dv \quad (2.172)$$

This expression is simplified by making the substitution

$$t^2 = e^{-i\pi} (v - v_j)^2 f''(v_j)$$

which allows us to rewrite I as

$$I = \frac{e^{(i\alpha_j + f(v_j))}}{\sqrt{|f''(v_j)|}} \int_{-\infty}^{\infty} dt \exp \left(-\frac{t^2}{2} + \sum_{n=3}^{\infty} \frac{(-1)^n e^{in\alpha_j} t^n (1 + p)}{n v_j^n |f''(v_j)|^{n/2}} \right) \quad (2.173)$$

and by using the properties of partition functions the result is that

$$\begin{aligned} D_p(z) &\cong \frac{\Gamma(1 + p)}{i \sqrt{2\pi}} e^{-\frac{z^2}{4}} z \sum_{j=0}^1 \frac{e^{i\alpha_j + f(v_j)}}{\sqrt{|f''(v_j)|}} \\ &\times \left(1 + \sum_{l=2}^{\infty} \frac{(2l-1)!! e^{2il\alpha_j}}{v_j^{2l} |f''(v_j)|^l} \sum_{\{\lambda_n\}} \prod_{n=3}^{2l} \left(\frac{\left(\frac{1+p}{n}\right)^{\lambda_n}}{\lambda_n!} \right) \right) \end{aligned} \quad (2.174)$$

where

$$f(v) \equiv z^2 \left(v - \frac{v^2}{2} \right) - (1 + p) \ln(zv) \quad (2.175)$$

$$\alpha_j = \frac{\pi}{2} - \frac{1}{2} \arg(f''(v_j)) \quad (2.176)$$

and where the innermost sum is over all distinct partitions of $2l$ given by the non-negative integer solutions $\{\lambda_n\}$ such that

$$\sum_{n=3}^{2l} n\lambda_n = 2l \quad (2.177)$$

The phases α_0 and α_1 that give the directions of the lines of steepest descent are formally ambiguous by an additive factor of π and must be determined absolutely by reference to the prevailing global geometry.

Resumming the Divergent Tail

We again use the method of steepest descent, i.e., we expand the argument of the exponential (in the integral), but we rewrite as follows:

$$I = \int_{-\infty}^{+\infty} \exp\left(-\frac{t^2}{2} + \sum_{k=1}^{\infty} \frac{x_k t^k}{k} - x_1 t - \frac{x_2 t^2}{2}\right) dt \quad (2.178)$$

where

$$x_k \equiv \left(-\frac{e^{i\alpha_j}}{\nu_j \sqrt{|f''(\nu_j)|}}\right)^k (1+p) \equiv (\beta_j)^k (1+p) \quad (2.179)$$

By using a Maclaurin expansion for the power series in the exponential we have

$$I = \int_{-\infty}^{+\infty} dt \exp\left(-x_1 t - \frac{t^2}{2}(1+x_2)\right) \sum_{m=0}^{\infty} \frac{\left(\sum_{k=1}^{\infty} \frac{x_k t^k}{k}\right)^m}{m!} \quad (2.180)$$

Considering the sum only, we see that the innermost sum is the generating function for the multinomial coefficients [1] such that the sum is now

$$1 + \sum_{m=1}^{\infty} \sum_{n=m}^{\infty} \frac{t^n}{n!} \sum (n; \lambda_1, \lambda_2, \dots, \lambda_n)^* x_1^{\lambda_1} x_2^{\lambda_2} \dots x_n^{\lambda_n} \quad (2.181)$$

where the innermost sum is over $\{\lambda_1, \lambda_2, \dots, \lambda_n\}$ subject to $\lambda_1 + 2\lambda_2 + \dots + n\lambda_n = n$ and $\lambda_1 + \lambda_2 + \dots + \lambda_n = m$. Now,

$$x_1^{\lambda_1} x_2^{\lambda_2} \dots x_n^{\lambda_n} = (1+p)^m \beta_j^n$$

and

$$\sum (n; \lambda_1, \lambda_2, \dots, \lambda_n)^* = (-1)^{n-m} S_n^{(m)}$$

where the $S_n^{(m)}$ are the Stirling numbers of the first kind ([1], 24.1.3, page 824).

So, after reversing the order of the summation and replacing x_k by $\beta_j^k (1+p)$ we have

$$I = \int_{-\infty}^{+\infty} dt e^{-\beta_j(1+p)t - \frac{t^2}{2}(1+\beta_j^2(1+p))} \times \sum_{n=0}^{\infty} \frac{(-t\beta_j)^n}{n!} \sum_{m=0}^n (-1-p)^m S_n^{(m)} \quad (2.182)$$

which simplifies to

$$I = \int_{-\infty}^{+\infty} dt e^{-\beta_j(1+p)t - \frac{t^2}{2}(1+\beta_j^2(1+p))} \times \sum_{n=0}^{\infty} \frac{(t\beta_j)^n}{n!} (1+p)_n \quad (2.183)$$

Changing the Variable

If we make the substitution

$$T = t + \frac{\beta_j(1+p)}{1 + \beta_j^2(1+p)}$$

(which completes the square in the exponential) and use the following integral result

$$\int_{-\infty}^{+\infty} dT e^{-\mu T^2} T^j = \frac{\Gamma\left(\frac{j+1}{2}\right)}{\mu^{(j+1)/2}}$$

we get

$$\begin{aligned} I = & \sqrt{2\pi} \exp\left[\frac{\beta_j^2(1+p)^2}{2(1 + \beta_j^2(1+p))}\right] \sum_{j \text{ even}} \frac{2^{j/2} \left(\frac{1}{2}\right)_{j/2}}{j! (1 + \beta_j^2(1+p))^{(j+1)/2}} \\ & \times \left(\frac{1 + \beta_j^2(1+p)}{-\beta_j(1+p)}\right)^j \sum_{n=j}^{\infty} \frac{\left(\frac{-\beta_j^2(1+p)}{1 + \beta_j^2(1+p)}\right)^n}{(n-j)!} (1+p)_n \end{aligned} \quad (2.184)$$

after reversing the order of summation.

Now using the substitution $n = N + j$ allows us to write the innermost sum as

$$\sum_{N=0}^{\infty} \frac{\left(\frac{-\beta_j^2(1+p)}{1 + \beta_j^2(1+p)}\right)^N}{N!} (1+p+j)_N$$

that is the hypergeometric function

$${}_1F_0\left(1+p+j; -\frac{\beta_j^2(1+p)}{1 + \beta_j^2(1+p)}\right)$$

which in turn can be written as

$$\left[1 + \frac{\beta_j^2(1+p)}{1 + \beta_j^2(1+p)}\right]^{-1-p-j}$$

which means that I can now be written as

$$\begin{aligned} I = & \sqrt{2\pi} \left(\frac{(1 + \beta_j^2(1+p))^{\left(\frac{1}{2}+p\right)}}{(1 + 2\beta_j^2(1+p))^{(1+p)}}\right) \exp\left[\frac{\beta_j^2(1+p)^2}{2(1 + \beta_j^2(1+p))}\right] \\ & \times {}_2F_0\left(\frac{1+p}{2}, 1 + \frac{p}{2}; \frac{2\beta_j^2(1 + \beta_j^2(1+p))}{(1 + 2\beta_j^2(1+p))^2}\right) \end{aligned} \quad (2.185)$$

But the ${}_2F_0$ can be written [562] in terms of Kummer's confluent hypergeometric function thus ([1], 13.1.10, page 504)

$${}_2F_0\left(a, 1+a-b; ; -\frac{1}{z}\right) = z^a U(a, b, z)$$

and through this relation ([1], 13.6.36, page 510)

$$U\left(\frac{\tilde{a}}{2} + \frac{1}{4}, \frac{1}{2}, \frac{z^2}{2}\right) = 2^{\frac{\tilde{a}}{2} + \frac{1}{4}} e^{\frac{z^2}{4}} D_{-\tilde{a}-1/2}(z)$$

can be connected to the parabolic cylinder function, where $\tilde{a} = 2a - \frac{1}{2}$.

After simplification and summing over both branches of the square root we have

$$\begin{aligned} D_p(z) &= \frac{\Gamma(1+p)}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{4} - \frac{(1+p)}{2}\right) z \sum_{j=0}^1 \frac{\exp(i\alpha_j + f(\nu_j))}{\sqrt{|f''(\nu_j)|}} \\ &\times \left(\frac{(1 + \beta_j^2(1+p))^{p/2}}{\beta_j^{1+p}} \exp\left(\frac{i\pi p}{2} - \frac{1}{4\beta_j^2} - \frac{1+p}{4(1 + \beta_j^2(1+p))}\right) \right) \\ &\times D_{-(1+p)}\left[\frac{i(1 + 2\beta_j^2(1+p))}{\beta_j \sqrt{1 + \beta_j^2(1+p)}}\right] \end{aligned} \quad (2.186)$$

where

$$\beta_j \equiv -\frac{e^{i\alpha_j}}{\nu_j \sqrt{|f''(\nu_j)|}}$$

so that we have

$$D_p(z) = \frac{\Gamma(1+p)}{\sqrt{2\pi}} \left[e^{i\pi p/2} D_{-1-p}(iz) + e^{-i\pi p/2} D_{-1-p}(-iz) \right] \quad (2.187)$$

which agrees with the *exact* recurrence relation of Magnus and Oberhettinger [399]. Notice that, from Figure 2.5, strictly $\arg z \in (-\pi/2, +\pi/2)$. However this condition may be relaxed by analytic continuation. Notice also that we have completely re-summed the JWKB asymptotic divergent expansions about the saddle points, not just the tails as in Berry [71]. Thus, not surprisingly, the connection formula between (16), (18), and (13)* of Crothers [161] is exact.

The Noncrossing Parabolic Model

Of course, in retrospect, the perhaps surprising result of the previous section should not be too much so, for the following reasons. A solution of the second-order ordinary differential equation

$$\left(\frac{d^2}{dz^2} + p + \frac{1}{2} - \frac{z^2}{4} \right) u = 0 \quad (2.188)$$

is given by the parabolic-cylinder function

$$u = D_p(z)$$

where the parabolic potential is given by

$$V(z) = p + \frac{1}{2} - \frac{z^2}{4} \quad (2.189)$$

and the d^2/dz^2 operator is the scaled (by -2) kinetic energy operator. The complete operator in (2.188) is even in z and invariant under the mappings $p \rightarrow -1 - p$ and $z \rightarrow iz$, so that we have four solutions:

$$I(16) \quad D_p(z) \quad (2.190)$$

$$I(17^*) \quad D_p(-z) \quad (2.191)$$

$$I(18) \quad D_{-1-p}(iz) \quad (2.192)$$

$$I(13^*) \quad D_{-1-p}(-iz) \quad (2.193)$$

where $*$ means conjugate (of argument and order, since $D_p(z)$ is a real function of complex variables p and z) and where the left-hand labels refer to Crothers [161], to be referred to hereafter as I . Thus, from ordinary-differential-equation theory, there must be a linear (with respect to z) relationship between any three of the four solutions. These are given by Magnus and Oberhettinger [399] as:

$$I(16) = \frac{\Gamma(1+p)}{\sqrt{2\pi}} \left[e^{\frac{ip\pi}{2}} I(18) + e^{-\frac{ip\pi}{2}} I(13^*) \right] \quad (2.194)$$

$$= e^{-p\pi i} I(17^*) + \frac{\sqrt{2\pi}}{\Gamma(-p)} e^{-i(p+1)\frac{\pi}{2}} I(18) \quad (2.195)$$

$$= e^{p\pi i} I(17^*) + \frac{\sqrt{2\pi}}{\Gamma(-p)} e^{i(p+1)\frac{\pi}{2}} I(13^*) \quad (2.196)$$

By symmetry and rearrangement, any one can be given in terms of any two of the other three. We now set:

$$p = -i\gamma \quad (2.197)$$

$$z = 2 \exp\left(\frac{\pi i}{4}\right) T_0 \sqrt{\gamma} \quad (2.198)$$

so that, corresponding to (2.190) to (2.193), we have

$$I(16) \quad D_{-i\gamma} \left(2e^{\pi i/4} T_0 \sqrt{\gamma} \right)$$

$$I(17^*) \quad D_{-i\gamma} \left(2e^{-3\pi i/4} T_0 \sqrt{\gamma} \right)$$

$$I(18) \quad D_{-1+i\gamma} \left(2e^{3\pi i/4} T_0 \sqrt{\gamma} \right)$$

$$I(13^*) \quad D_{-1+i\gamma} \left(2e^{-\pi i/4} T_0 \sqrt{\gamma} \right)$$

We have from $I(14)$ and $I(15)$:

$$\tilde{\theta} = \frac{\gamma}{2} - \frac{\gamma}{2} \ln \gamma + \gamma \ln \left(T_0 + \sqrt{1 + T_0^2} \right) + \gamma T_0 \sqrt{1 + T_0^2} \quad (2.199)$$

$$= \frac{\gamma}{2} - \frac{\gamma}{2} \ln \gamma - i \frac{\pi \gamma}{2} - 2\gamma \int_{T_0}^{-i} (1 + T^2)^{\frac{1}{2}} dT \quad (2.200)$$

where the tilde on the theta is to distinguish it from the parameter θ in the $T - \tau$ model of Nikitin, the phase integral is outgoing (flip the limits),

$$g = \tan^{-1} \left\{ \sqrt{1 + T_0^2} - T_0 \right\} \quad (2.201)$$

and we assume for noncrossing (otherwise known as perturbed symmetric resonance [160], [162]) that $T_0 > 0$ and of order unity, and $\gamma \gg 1$. Using the method of the second paragraph of Section 2.3.2, we may write the leading asymptotic expansions as

$$I(16) \quad D_{-i\gamma} \left(2e^{\frac{\pi i}{4}} T_0 \sqrt{\gamma} \right) \cong e^{\frac{\pi \gamma}{4} + i\gamma \ln \gamma - i\tilde{\theta}} \cos g + e^{-\frac{3\pi \gamma}{4} + i\tilde{\theta}} \sin g \quad (2.202)$$

$$I(17^*) \quad D_{-i\gamma} \left(2e^{-\frac{3\pi i}{4}} T_0 \sqrt{\gamma} \right) \cong e^{\frac{\pi \gamma}{4} + i\tilde{\theta}} \sin g + e^{-\frac{3\pi \gamma}{4} - i\tilde{\theta} + i\gamma \ln \gamma} \cos g \quad (2.203)$$

$$I(18) \quad D_{-1+i\gamma} \left(2e^{\frac{3\pi i}{4}} T_0 \sqrt{\gamma} \right) \cong e^{\frac{\pi \gamma}{4} - i\tilde{\theta} + \frac{\pi i}{4}} \frac{\cos g}{\sqrt{\gamma}} - e^{-\frac{3\pi \gamma}{4} + i\tilde{\theta} - i\gamma \ln \gamma + \frac{\pi i}{4}} \frac{\sin g}{\sqrt{\gamma}} \quad (2.204)$$

$$I(13^*) \quad D_{-1+i\gamma} \left(2e^{-\frac{\pi i}{4}} T_0 \sqrt{\gamma} \right) \cong e^{\frac{\pi \gamma}{4} - i\gamma \ln \gamma + \frac{\pi i}{4} + i\tilde{\theta}} \frac{\sin g}{\sqrt{\gamma}} - e^{-\frac{3\pi \gamma}{4} + \frac{\pi i}{4} - i\tilde{\theta}} \frac{\cos g}{\sqrt{\gamma}} \quad (2.205)$$

Letting T_0 in (2.202) be a variable t , we can rewrite (2.188) as

$$\left[\frac{d^2}{dt^2} + 4\gamma^2(1 + t^2) + 2i\gamma \right] D_{-i\gamma} \left(2\sqrt{\gamma} e^{\frac{\pi i}{4}} t \right) = 0 \quad (2.206)$$

We may identify t as the Stueckelberg variable [574], [160]. For large γ , using perturbation theory, the transition points are given by $t = \pm i$, and the JWKB solutions, valid a suitable distance from $t = \pm i$, are given by

$$\frac{\exp \left(\pm 2i\gamma \int_{\pm i}^t (1 + T^2)^{\frac{1}{2}} dT \right)}{(1 + T^2)^{\frac{1}{4}}} \quad (2.207)$$

The upper Stokes lines are given by

$$0 = \operatorname{Re} \int_i^t (T - i)^{1/2} (T + i)^{1/2} dT \quad (2.208)$$

$$\approx \operatorname{Re} \int_i^t (T - i)^{1/2} (2i)^{1/2} dT \quad (2.209)$$

$$= \operatorname{Re} \frac{2}{3} (t - i)^{3/2} (2i)^{1/2} = \operatorname{Re} \frac{2\sqrt{2}}{3} e^{\frac{\pi i}{4} + \frac{3\delta i}{2}} \quad (2.210)$$

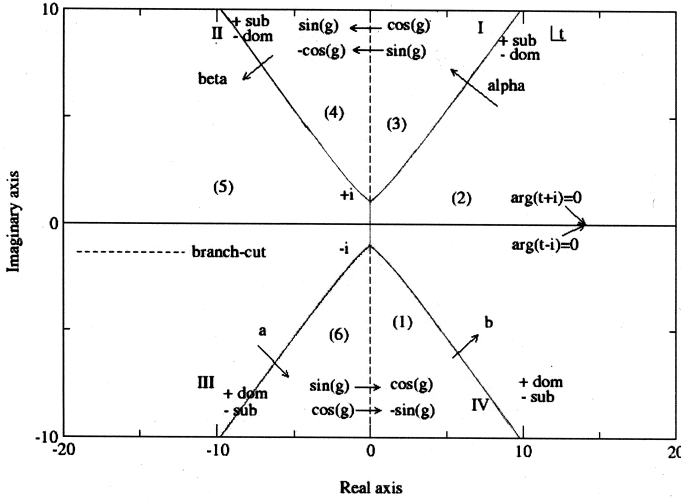


Fig. 2.6. Stokes lines for the two-transition-point problem (with transition points $+i$ and $-i$)

where

$$\arg(t - i) = \phi \quad (2.211)$$

so that

$$\cos\left(\frac{3\phi}{2} + \frac{\pi}{4}\right) = 0 \quad (2.212)$$

Then we have that

$$\phi = \frac{\pi}{6}, -\frac{\pi}{2}, -\frac{7\pi}{6} \quad (2.213)$$

give the initial directions of the Stokes lines [160]. The real part of the out/in-going wave is given by

$$\mp \sin\left(\frac{3\phi}{2} + \frac{\pi}{4}\right) \quad (2.214)$$

so that out/in-going waves are subdominant/dominant respectively on both $\phi = \pi/6$ and $\phi = -7\pi/6$ and vice versa on $\phi = -\pi/2$. The reverse is true concerning $\arg(t+i) = \phi$. These facts are summarised in Figure 2.6.

The Stokes constants crossing I, II, III, and IV, namely $\arg(t - i) = \pi/6, -7\pi/6$ and $\arg(t + i) = 7\pi/6, -\pi/6$, respectively, are α, β, a , and b . We note that $e^{\pm i\tilde{\theta}}$ are out/in-going respectively and behave as $e^{\pm \frac{\pi\gamma}{2}}$ (subdominant/dominant) near $t = i$ and as $e^{\pm \frac{\pi\gamma}{2}}$ (dominant/subdominant) near $t = -i$, that is, as viewed on the (positive) γ -axis. It follows that only $I(16)$ and $I(18)$ are truly dominant as functions of both t and γ in the upper half of the t -plane while only $I(17^*)$ and $I(13^*)$ are truly dominant as functions of both t and γ , in the lower half of the t -plane. This explains why we examine the Stokes phenomenon as applied to $I(13^*)$ in the lower-half t -plane and $I(16)$ in the upper-half t -plane. This is consistent with the approach and ideas of

Olver [477] and Dingle [226] who invoke error analysis. Numerically in the upper t -plane and for large γ , $I(17^*)$ and $I(13^*)$ are negligible; in the lower t -plane and for large γ , $I(16)$ and $I(18)$ are negligible.

Compared to Crothers [160] we map $g \rightarrow \pi/2 - g$. An important point concerns reversing the direction of application of the Stokes constant as the following argument shows. Suppose we cross the Stokes line and map

$$Au_{\text{dom}} + Bv_{\text{sub}} \rightarrow Au_{\text{dom}} + (B + \beta A)v_{\text{sub}} \quad (2.215)$$

Going back across the same Stokes line

$$Au_{\text{dom}} + (B + \beta A)v_{\text{sub}} \rightarrow Au_{\text{dom}} + (B + \beta A + \lambda A)v_{\text{sub}} \quad (2.216)$$

It follows that

$$\lambda = -\beta \quad (2.217)$$

not β^* as might be wrongly extrapolated from the one-transition-point problem ($\beta = i$).

For noncrossing we have, from (2.200),

$$\pm i\tilde{\theta} = \pm \frac{i\gamma}{2} \mp \frac{i\gamma}{2} \ln \gamma \pm \frac{\gamma\pi}{2} \mp 2i\gamma \int_{T_0}^{-i} (1 + T^2)^{1/2} dT \quad (2.218)$$

Then tracing clockwise, with B an arbitrary constant,

$$\begin{aligned} BI(13^*) &= BD_{-1+i\gamma} \left(2e^{-\frac{\pi i}{4}} T_0 \sqrt{\gamma} \right) \\ &\cong Be^{\frac{\pi\gamma}{4} - i\gamma + i\gamma \ln \gamma + \frac{\pi i}{4} + i\tilde{\theta}} \frac{\sin g}{\sqrt{\gamma}} - Be^{-\frac{3\pi\gamma}{4} + \frac{\pi i}{4} - i\tilde{\theta}} \frac{\cos g}{\sqrt{\gamma}} \end{aligned} \quad (2.219)$$

$$\begin{aligned} &= Be^{\frac{3\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4} - 2i\gamma \int_{T_0}^{-i} (1+T^2)^{1/2} dT} \frac{\sin g}{\sqrt{\gamma}} \\ &\quad - Be^{-\frac{5\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4} + 2i\gamma \int_{T_0}^{-i} (1+T^2)^{1/2} dT} \frac{\cos g}{\sqrt{\gamma}} \end{aligned} \quad (2.220)$$

in sector 2 of Figure 2.6. Crossing Stokes line IV and recalling (2.217), we connect with

$$\begin{aligned} &Be^{\frac{3\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4} - 2i\gamma \int_{T_0}^{-i} (1+T^2)^{1/2} dT} \frac{\sin g}{\sqrt{\gamma}} \\ &- B \left(e^{-\frac{5\pi\gamma}{4}} + be^{\frac{3\pi\gamma}{4}} \right) e^{-\frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4} + 2i\gamma \int_{T_0}^{-i} (1+T^2)^{1/2} dT} \frac{\cos g}{\sqrt{\gamma}} \end{aligned} \quad (2.221)$$

in sector 1 of Figure 2.6. Crossing the branch cut to sector 6, we obtain

$$\begin{aligned} &Be^{\frac{3\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4} + 2i\gamma \int_{T_0}^{-i} (1+T^2)^{1/2} dT} \frac{\cos g}{\sqrt{\gamma}} \\ &- B \left(e^{-\frac{5\pi\gamma}{4}} + be^{\frac{3\pi\gamma}{4}} \right) e^{-\frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4} - 2i\gamma \int_{T_0}^{-i} (1+T^2)^{1/2} dT} \frac{\sin g}{\sqrt{\gamma}} \end{aligned} \quad (2.222)$$

Finally, crossing Stokes line III we connect to

$$\begin{aligned}
& -B \frac{\cos g}{\sqrt{\gamma}} \left[e^{\frac{3\pi\gamma}{4}} - a \left(e^{-\frac{5\pi\gamma}{4}} + b e^{\frac{3\pi\gamma}{4}} \right) \right] e^{-\frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4} + 2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \\
& - B \left(e^{-\frac{5\pi\gamma}{4}} + b e^{\frac{3\pi\gamma}{4}} \right) e^{-\frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4} - 2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \frac{\sin g}{\sqrt{\gamma}}
\end{aligned} \quad (2.223)$$

in sector 5 of Figure 2.6. Matching (2.223) and (2.219) on the real t -axis (T_0 -axis) and given that $BI(13^*)$ dominates $AI(16)$, for B and A of the same order in γ , we have

$$-e^{-\frac{5\pi\gamma}{4}} - b e^{\frac{3\pi\gamma}{4}} = e^{\frac{3\pi\gamma}{4}} \quad (2.224)$$

and

$$+e^{-\frac{5\pi\gamma}{4}} = e^{\frac{3\pi\gamma}{4}} - a \left(e^{-\frac{5\pi\gamma}{4}} + b e^{\frac{3\pi\gamma}{4}} \right) \quad (2.225)$$

Solving equations (2.224) and (2.225) gives

$$a = -1 + \exp(-2\pi\gamma) \quad (2.226)$$

$$b = -1 - \exp(-2\pi\gamma) \quad (2.227)$$

which implies

$$\arg a = \pi = \arg b \quad (2.228)$$

Now, also for noncrossing we have

$$\pm i\tilde{\theta} = \pm \frac{i\gamma}{2} \mp \frac{i\gamma}{2} \ln \gamma \mp \frac{\pi\gamma}{2} \mp 2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT \quad (2.229)$$

so that tracing anticlockwise, with A and B arbitrary constants, in sector 2 of Figure 2.6 we have

$$AI(16) + BI(13^*) = AD_{-i\gamma} \left(2e^{\frac{\pi i}{4}} T_0 \sqrt{\gamma} \right) + BD_{-1+i\gamma} \left(2e^{-\frac{\pi i}{4}} T_0 \sqrt{\gamma} \right) \quad (2.230)$$

$$= A(\text{equation (2.202)}) + B(\text{equation (2.205)}) \quad (2.231)$$

$$\begin{aligned}
& = A e^{\frac{i\gamma}{2} - \frac{i\gamma}{2} \ln \gamma} \left[e^{\frac{3\pi\gamma}{4} + 2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \cos g \right. \\
& \quad \left. + e^{-\frac{5\pi\gamma}{4} - 2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \sin g \right] \\
& \quad + \frac{B}{\sqrt{\gamma}} e^{-\frac{\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4}} \left[e^{-2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \sin g \right. \\
& \quad \left. - e^{2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \cos g \right]
\end{aligned} \quad (2.232)$$

Crossing Stokes line I from sector 2 to sector 3, we have

$$\begin{aligned}
& A e^{\frac{i\gamma}{2} - \frac{i\gamma}{2} \ln \gamma} \left[e^{\frac{3\pi\gamma}{4} + 2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \cos g + \left(\alpha e^{\frac{3\pi\gamma}{4}} + e^{-\frac{5\pi\gamma}{4}} \right) e^{-2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \sin g \right] \\
& + \frac{B}{\sqrt{\gamma}} e^{-\frac{\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4}} \left[-e^{2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \cos g + (1 - \alpha) e^{-2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \sin g \right]
\end{aligned} \quad (2.233)$$

Crossing the upper branch cut from sector 3 to sector 4, we connect to

$$Ae^{\frac{i\gamma}{2} - \frac{i\gamma}{2} \ln \gamma} \left[e^{\frac{3\pi\gamma}{4} - 2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \sin g - \left(\alpha e^{\frac{3\pi\gamma}{4}} + e^{\frac{-5\pi\gamma}{4}} \right) e^{2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \cos g \right] \\ + \frac{B}{\sqrt{\gamma}} e^{\frac{-\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4}} \left[-e^{-2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \sin g - (1-\alpha) e^{2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \cos g \right] \quad (2.234)$$

Crossing Stokes line II from sector 4 to sector 5, we obtain

$$Ae^{\frac{i\gamma}{2} - \frac{i\gamma}{2} \ln \gamma} \left[\left(\alpha e^{\frac{3\pi\gamma}{4}} + e^{\frac{-5\pi\gamma}{4}} \right) e^{2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \cos g + \left\{ -\beta \left(\alpha e^{\frac{3\pi\gamma}{4}} + e^{\frac{-5\pi\gamma}{4}} \right) + e^{\frac{+3\pi\gamma}{4}} \right\} \right. \\ \times e^{-2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \sin g \left. \right] + \frac{B}{\sqrt{\gamma}} e^{\frac{-\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln \gamma + \frac{\pi i}{4}} \left[-(1-\alpha) e^{2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \cos g \right. \\ \left. - \{\beta(1-\alpha) + 1\} e^{-2i\gamma \int_{T_0}^i (1+T^2)^{1/2} dT} \sin g \right] \quad (2.235)$$

Equating (2.232) and (2.235) along the real $t(= T_0)$ axis, we have with $B = 0$,

$$-e^{\frac{3\pi\gamma}{4}} = \alpha e^{\frac{3\pi\gamma}{4}} + e^{\frac{-5\pi\gamma}{4}} \quad (2.236)$$

and

$$-e^{\frac{-5\pi\gamma}{4}} = \beta \left(\alpha e^{\frac{3\pi\gamma}{4}} + e^{\frac{-5\pi\gamma}{4}} \right) - e^{\frac{3\pi\gamma}{4}} \quad (2.237)$$

Solving equations (2.236) and (2.237) gives

$$\alpha = -1 - e^{-2\pi\gamma} \quad (2.238)$$

$$\beta = -1 + e^{-2\pi\gamma} \quad (2.239)$$

which implies

$$\arg \alpha = \pi = \arg \beta \quad (2.240)$$

Setting $A = 0$ gives

$$\alpha = 0, \quad \beta = -2 \quad (2.241)$$

which contradicts equations (2.238) and (2.239) and should be discarded, in view of our remarks between equations (2.214) and (2.215).

We have thus derived equations (2.226), (2.227), (2.238), and (2.239) which are expressions for the four Stokes constants, which underscore eqns (34)–(40) of Crothers [164], namely:

$$(34) \quad \alpha_l - \frac{i}{2} = (-1)^l Q \left(\frac{2}{\gamma k_0(\infty)} \right)^{\frac{1}{2}} e^{i(\eta_{0l} - \tilde{\theta} + \frac{\pi}{4}) + \frac{\pi\gamma}{4}} \quad (2.242)$$

$$(35) \quad \beta_l = -(-i)^l P \left(\frac{2}{k_1(\infty)} \right)^{\frac{1}{2}} e^{i(\eta_{1l} + \tilde{\theta}) + \frac{\pi\gamma}{4}} \quad (2.243)$$

$$(36) \quad -P\gamma D_{-1-i\gamma}(x_0) + QD_{i\gamma}(-ix_0) - i\Omega D_{-i\gamma}(x_0) = 0 \quad (2.244)$$

$$(37) \quad PD_{-i\gamma}(x_0) + QD_{-1+i\gamma}(-ix_0) + \Omega D_{-1-i\gamma}(x_0) = 0 \quad (2.245)$$

$$(38) \quad x_0 = 2e^{\frac{\pi i}{4}} \sqrt{\gamma} T_0 \quad (2.246)$$

$$(39) \quad P = \frac{-2\Omega e^{\frac{\pi i}{4}} \operatorname{Re} \left[e^{-\frac{\pi i}{4}} D_{-1-i\gamma}(x_0) \{D_{-i\gamma}(x_0)\}^* \right]}{\gamma |D_{-1-i\gamma}(x_0)|^2 + |D_{-i\gamma}(x_0)|^2} \quad (2.247)$$

$$(40) \quad Q = -\Omega \frac{\left[\gamma \{D_{-1-i\gamma}(x_0)\}^2 - i \{D_{-i\gamma}(x_0)\}^2 \right]}{\gamma |D_{-1-i\gamma}(x_0)|^2 + |D_{-i\gamma}(x_0)|^2} \quad (2.248)$$

These are parameterized by I (13):

$$\begin{aligned} D_{-1-i\gamma} \left(2e^{\frac{\pi i}{4}} T_0 \sqrt{\gamma} \right) &= \left(e^{-\frac{7\pi\gamma}{4}} + be^{\frac{\pi\gamma}{4}} \right) e^{i\gamma - i\gamma \ln \gamma - \frac{\pi i}{4} \tilde{\theta}} \frac{\sin g}{\sqrt{\gamma}} \\ &\quad - \left[e^{\frac{5\pi\gamma}{4}} - ae^{-\frac{3\pi\gamma}{4}} - abe^{\frac{5\pi\gamma}{4}} \right] e^{i\tilde{\theta} - \frac{\pi i}{4}} \frac{\cos g}{\sqrt{\gamma}} \end{aligned} \quad (2.249)$$

and I (16)

$$\begin{aligned} D_{-i\gamma} \left(2e^{\frac{\pi i}{4}} T_0 \sqrt{\gamma} \right) &= \left(\alpha e^{\frac{\pi\gamma}{4}} + e^{-\frac{7\pi\gamma}{4}} \right) e^{-i\tilde{\theta} + i\gamma - i\gamma \ln \gamma} \cos g \\ &\quad + \left(e^{\frac{5\pi\gamma}{4}} - \beta e^{-\frac{3\pi\gamma}{4}} - \alpha\beta e^{\frac{5\pi\gamma}{4}} \right) e^{i\tilde{\theta}} \sin g \end{aligned} \quad (2.250)$$

Notice that the dependence of (2.249) and (2.250) on the Stokes constants is nonlinear, via ab and $\alpha\beta$, respectively. The resulting S -matrix has the following properties:

$$|S_{01}|^2 = \sin^2 \mathcal{T} \operatorname{sech}^2 \pi\gamma \quad (2.251)$$

$$|S_{00}|^2 = 1 - |S_{01}|^2 = |S_{11}|^2 \quad (2.252)$$

and

$$S_{00}S_{01}^* + S_{01}S_{11}^* = 0 \quad (2.253)$$

Formula (2.251) is exact for perturbed symmetric resonance [162], [519]. The *single* transition probability p_{01} (see Chapter 4, (4.12)) corresponding to (2.251) is $[1 + \exp(2\pi\gamma)]^{-1}$, which is the basis of Miller [427] (2.50). The Massey parameter $\pi\gamma$ is often written as γ or δ . The effective frequency $(\nu\mathcal{T}/2\pi)$ is given by

$$\mathcal{F} = 2\tilde{\theta} - \gamma + \gamma \ln \gamma \quad (2.254)$$

$$= 2\gamma T_0 \sqrt{1 + T_0^2} + 2\gamma \ln \left(\sqrt{1 + T_0^2} + T_0 \right) \quad (2.255)$$

$$= 4\gamma \int_0^{T_0} \sqrt{1 + T^2} dT \quad (2.256)$$

$$= +2 \int_0^{2\gamma T_0} \sqrt{1 + T^2} d\tau \quad (2.257)$$

$$= \frac{1}{v} \int_0^{Z_0} \sqrt{4H_{12}^2 + (H_{22} - H_{11})^2} dZ \quad (2.258)$$

where $Z = v\tilde{t}$, v is the impact velocity, $Z_0 = v\tilde{t}_0$ and

$$T = \mp \frac{\tau}{2\gamma} + T_0 \quad (\tau \leq 0) \quad (2.259)$$

so that

$$T(\tau = 0) = T_0 > 0 \quad (2.260)$$

$$dT = -\frac{d\tau}{2\gamma} \quad (\tilde{t} < 0) \quad (2.261)$$

$$\tau = \int_0^{\tilde{t}} H_{12}(\tilde{t}) d\tilde{t} \quad (2.262)$$

The Stueckelberg variable T is related to the two-state Hamiltonian matrix elements by

$$T = \frac{H_{22} - H_{11}}{2H_{12}} \quad (2.263)$$

In summary we have used the JWKB /phase-integral analysis, supplemented by the comparison-equation method, to parameterize the two-state noncrossing parabolic model. However, on this occasion, we have explicitly derived simple algebraic expressions for the four Stokes constants: magnitudes and phases. The sign change in (2.259) at $\tau = t = 0$ ($\tau, t > 0 \Rightarrow T = \tau/2\gamma + T_0$) is an important consideration because it is associated with a classical turning point, that is, a simple transition point viewed from the fully quantal radial coordinate, from which the impact-parameter time-dependent problem is deduced.

2.3.3 The Crossing Parabolic Model

Let us now consider the curve-crossing parabolic model. The difference with the noncrossing model is that now T_0 is negative. However, for ease of calculation we map $T_0 \rightarrow -T_0$, with the new T_0 positive, and we absorb the minus sign into the arguments of the parabolic cylinder functions and map $g \rightarrow \pi/2 - g$. According to [163] the S -matrix is given by

$$S_{00} = \exp \left[2i\eta_0 - 2i\tilde{\theta} + \frac{\pi i}{2} \right] \left[\frac{\gamma \left(D_{-1-i\gamma}(x_0) \right)^2 - i \left(D_{-i\gamma}(x_0) \right)^2}{\gamma |D_{-1-i\gamma}(x_0)|^2 + |D_{-i\gamma}(x_0)|^2} \right] \quad (2.264)$$

$$S_{01} = S_{10} = -2i \sqrt{\gamma} \exp[i(\eta_0 + \eta_1)] \left[\frac{\operatorname{Re}[\exp(-\frac{\pi i}{4}) D_{-1-i\gamma}(x_0) (D_{-i\gamma}(x_0))^*]}{\gamma |D_{-1-i\gamma}(x_0)|^2 + |D_{-i\gamma}(x_0)|^2} \right] \quad (2.265)$$

$$S_{11} = \exp \left[2i\eta_1 + 2i\tilde{\theta} - \frac{\pi i}{2} \right] \left[\frac{\gamma (D_{-1-i\gamma}(x_0))^*{}^2 + i (D_{-i\gamma}(x_0))^*{}^2}{\gamma |D_{-1-i\gamma}(x_0)|^2 + |D_{-i\gamma}(x_0)|^2} \right] \quad (2.266)$$

where

$$x_0 = 2 \exp \left(-\frac{3\pi i}{4} \right) T_0 \sqrt{\gamma} \quad (T_0 > 0) \quad (2.267)$$

and

$$(4^*) \quad D_{-i\gamma}(x_0) \cong \exp \left(-\frac{3\pi\gamma}{4} + i\gamma - i\gamma \ln(\gamma) - i\tilde{\theta} \right) \cos g \\ + \frac{\sqrt{2\pi\gamma}}{\Gamma(1+i\gamma)} \exp \left(-\frac{\pi\gamma}{4} - i\gamma + i\gamma \ln(\gamma) + \frac{\pi i}{4} + i\tilde{\theta} \right) \sin g \quad (I17^*) \quad (2.268)$$

$$(5^*) \quad \sqrt{\gamma} D_{-1-i\gamma}(x_0) \cong -\exp \left(-\frac{3\pi\gamma}{4} + i\gamma - i\gamma \ln(\gamma) - \frac{\pi i}{4} - i\tilde{\theta} \right) \sin g \\ + \frac{\sqrt{2\pi\gamma}}{\Gamma(1+i\gamma)} \exp \left(-\frac{\pi\gamma}{4} - i\gamma + i\gamma \ln(\gamma) + i\tilde{\theta} \right) \cos g \quad (I18^*) \quad (2.269)$$

where the last two asymptotic expansions correspond to (4*) and (5*) of Crothers [163] and

$$\pm i\tilde{\theta} = \pm \frac{i\gamma}{2} \mp \frac{i\gamma}{2} \ln(\gamma) \pm \frac{\pi\gamma}{2} \mp 2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2} dT \quad (2.270)$$

Suffice it to say that (2.269) is derived by rearranging and conjugating (2.194) and expressing I(18)* in exact terms of I(13) and I(16)*. Notice that we make the coefficient of the dominant term more accurate by *not* expanding the $\Gamma(1+i\gamma)$ for large γ (this is also done by Fröman et al. [284] in their weak-coupling case; see 2.3.6). It follows that

$$\sqrt{\gamma} D_{-1-i\gamma}(x_0) \cong -\sin g \exp \left(-\frac{5\pi\gamma}{4} + \frac{i\gamma}{2} - \frac{i\gamma}{2} \ln(\gamma) - \frac{\pi i}{4} + 2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2} dT \right) \\ + \frac{\sqrt{2\pi\gamma}}{\Gamma(1+i\gamma)} \cos g \exp \left(\frac{\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln(\gamma) \right. \\ \left. - 2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2} dT \right) \quad (2.271)$$

Having mapped $g \rightarrow \pi/2 - g$, we see that setting $C_+ = 1$ and $D_+ = 0$ in equation (150) of Crothers [160] leads us to consider, in sector 5 of Figure 2.6:

$$\exp \left(-2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2} dT \right) \cos g \quad (2.272)$$

Tracing anticlockwise and crossing Stokes line III, this connects in sector 6 of Figure 2.6 to

$$\exp\left(-2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2}dT\right) \cos g + \tilde{a} \exp\left(+2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2}dT\right) \sin g \quad (2.273)$$

where the tilde distinguishes the “crossing” Stokes constant from the “noncrossing” Stokes constant of Section 2.3.2. Crossing the lower branch cut in Figure 2.6 we connect in sector 1 of Figure 2.6 to

$$-\exp\left(+2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2}dT\right) \sin g + \tilde{a} \exp\left(-2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2}dT\right) \cos g \quad (2.274)$$

Finally, crossing Stokes line IV we connect in sector 2 of Figure 2.6 with

$$-(1 + \tilde{a}\tilde{b}) \exp\left(2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2}dT\right) \sin g + \tilde{a} \exp\left(-2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2}dT\right) \cos g \quad (2.275)$$

Using

$$\begin{aligned} \Gamma(1+i\gamma) &= |\Gamma(1+i\gamma)| \exp(i \arg \Gamma(1+i\gamma)) \\ &= \sqrt{\frac{2\pi\gamma}{1-\exp(-2\pi\gamma)}} \exp\left(-\frac{\pi\gamma}{2} + i \arg \Gamma(1+i\gamma)\right) \end{aligned} \quad (2.276)$$

we may rewrite (2.271) as

$$\begin{aligned} &\exp\left(-\frac{3\pi\gamma}{4} - \frac{i\gamma}{2} + \frac{i\gamma}{2} \ln(\gamma) + \frac{\pi i}{4}\right) \sqrt{\gamma} D_{-1-i\gamma} \left(2 \exp(-\frac{3\pi i}{4}) T_0 \sqrt{\gamma}\right) \\ &\cong -\exp\left(-2\pi\gamma + 2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2}dT\right) \sin g + \sqrt{1-\exp(-2\pi\gamma)} \\ &\times \exp\left(\frac{\pi i}{4} - i\gamma + i\gamma \ln(\gamma) - i \arg \Gamma(1+i\gamma) - 2i\gamma \int_{T_0}^{-i} \sqrt{1+T^2}dT\right) \cos g \end{aligned} \quad (2.277)$$

Connecting along the real $t(T_0)$ axis, and from (2.275) and (2.277), we have

$$1 + \tilde{a}\tilde{b} = +e^{-2\pi\gamma} \quad (2.278)$$

$$\tilde{a} = \sqrt{1-e^{-2\pi\gamma}} \exp\left[i\left(\frac{\pi}{4} - \gamma + \gamma \ln \gamma - \arg \Gamma(1+i\gamma)\right)\right] \quad (2.279)$$

so that

$$\tilde{a}\tilde{b} = -(1 - e^{-2\pi\gamma}) \quad (2.280)$$

$$\tilde{b} = -\sqrt{1-e^{-2\pi\gamma}} \exp\left[-i\left(\frac{\pi}{4} - \gamma + \gamma \ln \gamma - \arg \Gamma(1+i\gamma)\right)\right] \quad (2.281)$$

Equations (2.279), (2.280), and (2.281) are in accord with equations (175), (83), and (176), respectively, of Crothers [160]. In retrospect we see that the choice of (2.272) is tantamount to taking $\tilde{a} = 1 = -\tilde{b}$ in the $\gamma \gg 1$ limit in the dominant term, near Stokes lines III and IV. Then tracing anticlockwise in the lower half-plane makes for greater accuracy. Also tracing from sector 5 to sector 2, (2.272)

is subdominant crossing the double Stokes line and is therefore continuous (in the absence of a dominant solution). Nor must we forget that the rules for $\sin g$ and $\cos g$ in Figure 2.6 in crossing the branch cuts are subject to the mapping $g \rightarrow \pi/2 - g$, so that (2.274) is correct.

In summary we have used the JWKB/phase-integral analysis, supplemented by the comparison-equation method, to parameterize the two-state diabatic curve crossing (avoided adiabatic/pseudo-crossing) parabolic model. However, on this occasion, we have explicitly derived algebraic expansions for the magnitudes and phases of the two Stokes constants associated with the lower half t -plane. Similar considerations apply to the upper half t -plane (see equations (175) and (176) of Crothers [160]).

2.3.4 Connection to Bárány-Crothers Phase-Integral Nikitin-Model Analysis

Let us refer to Bárány and Crothers [28] as II (see 2.4). In the limit as $\theta \rightarrow \pi/2$ we have Rosen-Zener-Demkov [519], [221] noncrossing, and equation II (61) gives, using BC as a subscript on the Stokes constants of II:

$$\arg a_{BC} + \frac{\pi}{2} = \arg c_{BC} - \frac{\pi}{2} = \arg a - \pi = 0 \quad (2.282)$$

where the latter is (2.228). We have the Nikitin [453] $T - \tau$ model:

$$T = \frac{\lambda}{2(\tau + \tau_\infty)} - \cot \theta = \frac{\lambda}{2\tau_\infty \left(1 + \frac{\tau}{\tau_\infty}\right)} \quad (2.283)$$

$$\cong \frac{-\lambda\tau}{2\tau_\infty^2} + \frac{\lambda}{2\tau_\infty} \quad (\tau_\infty \gg 1) \quad (2.284)$$

$$\equiv -\frac{\tau}{2\gamma} + T_0 \quad (2.285)$$

As usual, T is the Stueckelberg variable and τ is the reduced time.

Equation II (20) should be corrected to agree with (2.285) for $\tau < 0$. Further connection with the parabolic model requires

$$\gamma = \frac{\tau_\infty^2}{\lambda} \gg 1 \quad (2.286)$$

$$T_0 = \frac{\lambda}{2\tau_\infty} = \frac{\tau_\infty}{2\gamma} > 0 \quad (2.287)$$

where λ , γ , and τ_∞ are all large but T_0 is of order unity.

Similarly, we have a Landau-Zener-Stueckelberg crossing in the limit as $\lambda \rightarrow +\infty$, $\theta \rightarrow 0$ so that $\lambda(1 - \cos \theta)$ remains finite and again

$$\arg a_{BC} + \frac{\pi}{2} = \tilde{\gamma} \left(\frac{\lambda}{2} (1 - \cos \theta) \right) = \arg \tilde{a} \quad (2.288)$$

$$= \frac{\pi}{4} - \gamma + \gamma \ln(\gamma) - \arg \Gamma(1 + i\gamma) \quad (2.289)$$

where

$$\gamma = \frac{\lambda}{2}(1 - \cos \theta) \quad (2.290)$$

in agreement with II (61) and (2.279) and, of course, with (189) of Crothers [160].

By the same token we have

$$|a_{\text{BC}}| = \sqrt{1 - \exp(-2\pi\gamma)} = |\tilde{a}| \quad (2.291)$$

in agreement with (175) and (176) of Crothers [160]. The case of $\lambda \rightarrow +\infty$ and $\theta \rightarrow \pi$ so that $\lambda(1 + \cos \theta)$ remains finite and is noncrossing is given by equation (66) of Crothers [167]. As discussed there, this does not fall within the parabolic model, and unsurprisingly the transition probability is nugatory, because $H_{12} \rightarrow 0$ and $H_{22} - H_{11}$ is much greater than in (2.288)-(2.291). Analytic continuation of the Nikitin exponential model to nonzero impact parameters is discussed in detail by Nesbitt et al. [450].

2.3.5 Connections to Nakamura and Zhu Phase-Integral Analysis

Using expressions (2.249) and (2.250), we may, for *noncrossing*, write

$$S_{01} = \frac{-2i \left(b e^{\frac{\pi\gamma}{4}} + e^{-\frac{7\pi\gamma}{4}} \right) \left(e^{\frac{5\pi\gamma}{4}}(1 - ab) - a e^{-\frac{3\pi\gamma}{4}} \right) \sin \mathcal{T}}{\left(b e^{\frac{\pi\gamma}{4}} + e^{-\frac{7\pi\gamma}{4}} \right)^2 + \left(e^{\frac{5\pi\gamma}{4}}(1 - ab) - a e^{-\frac{3\pi\gamma}{4}} \right)^2} \quad (2.292)$$

which, in terms of the Stokes constants a and b , represents a cubic divided by a quartic. Notice that $\arg a = \pi$ (2.228) so that S_{01} is analytic in a and b .

Similarly, expression (2.269) and a similar expression, namely,

$$D_{-i\gamma} \left(e^{-\frac{3\pi i}{4}} 2T_0 \sqrt{\gamma} \right) \cong (1 + \tilde{a}\tilde{b}) \cos g e^{\frac{5\pi\gamma}{4} + i\gamma - i\gamma \ln \gamma - i\tilde{\theta}} + \tilde{a} \sin g e^{\frac{\pi\gamma}{4} + i\tilde{\theta}} \quad (2.293)$$

may be used, for *crossing*, to write

$$S_{01} = \frac{-2i \exp(\frac{3\pi\gamma}{2})(1 + \tilde{a}\tilde{b})|\tilde{a}| \sin(\mathcal{T} + \arg \tilde{a})}{(1 + \tilde{a}\tilde{b})^2 \exp(\frac{5\pi\gamma}{2}) + |\tilde{a}|^2 \exp(\frac{\pi\gamma}{2})} \quad (2.294)$$

which, in terms of the Stokes constants \tilde{a} and \tilde{b} , yet again represents a cubic divided by a quartic.

Notice that S_{01} here is a nonanalytic function of \tilde{a} and \tilde{b} because

$$(\pi - \arg \tilde{a}) = + \arg \tilde{b}^* \quad (2.295)$$

are nonzero (see (2.280) and (2.281)). It follows that the function $f(\lambda)$ given by

$$f(\lambda) = \int_0^\infty d\mathcal{T} e^{-\lambda\mathcal{T}} S_{01} = -e^{-\pi\gamma} \left[\frac{\tilde{a}}{\lambda - i} - \frac{\tilde{a}^*}{\lambda + i} \right] \quad (2.296)$$

is not a real function of λ and that

$$\arg \tilde{a} = \frac{-i}{2} \ln \left[\frac{\int^{(i-)} d\lambda \int_0^\infty d\mathcal{T} e^{-\lambda \mathcal{T}} S_{01}}{\int^{(-i+)} d\lambda \int_0^\infty d\mathcal{T} e^{-\lambda \mathcal{T}} S_{01}} \right] \quad (2.297)$$

essentially because, to repeat, S_{01} is not an analytic function.

We may compare equations (5.15)–(5.18) of Nakamura [447] in the crossing case. Adapting his notation to ours, Nakamura obtains for his four-point cluster of transition points,

$$S_{01} = -U_2 \quad (2.298)$$

where

$$U_2 = \frac{2i \operatorname{Im} U_1}{1 + |U_1|^2} \quad (2.299)$$

The single transition probability is given by

$$p_{01} = \frac{1}{1 + |U_1|^2} \quad (2.300)$$

For crossing, our corresponding p_{01} is given by

$$p_{01} = e^{-2\pi\gamma} \quad (2.301)$$

which tends to zero as $\gamma \rightarrow +\infty$. This in turn implies that $|U_1|$ tends to $+\infty$ as $\gamma \rightarrow +\infty$, that U_2 tends to zero, and that the S -matrix becomes the unit matrix. It may be noted that our crossing Stokes constants $\tilde{a} \rightarrow 1$ and $\tilde{b} \rightarrow -1$ are finite as $\gamma \rightarrow +\infty$. On the other hand, an infinite change in the coefficient of the subdominant solution when crossing a Stokes line with Stokes constant U_1 would appear to be nonphysical, perhaps because it is associated with the momentum plane [447].

Another difference is that equation (4.38) of Nakamura [447] and the last equation of Section A.4 of [324] for the Stokes constant U for the Weber equation are based on weak-coupling asymptotics, that is, in terms of our notation in Section 2.3.2 and (2.188), $|z^2| \gg (1, |p|)$ rather than our $|z|^2 \sim |p| \gg 1$. To tie up the three notations (our γ , Heading's a , and Nakamura's β), we have

$$p = -i\gamma = -\frac{1}{2} - \frac{1}{2}ia^2 = -\frac{1}{2} - i\beta \quad (2.302)$$

A symptom of the difference between their weak-coupling and our strong-coupling derivations is the occurrence of $\ln 2$ in their expressions. As observed by Crothers ([161], [175], and Crothers and O'Rourke [193], strong- and weak-coupling asymptotic expansions have different algebraic forms [324]; the advantage of our (2.271) treatment of crossing is that by making the coefficient of the dominant term more accurate, we are able to obtain an expression for the argument/phase of the Stokes constants \tilde{a}, \tilde{b} , which interpolates uniformly between $\gamma \rightarrow +0$ and $\gamma \rightarrow +\infty$. Re non-crossing, Nakamura [447] does not appear to have applied (2.295)–(2.297). However, if we do, then

$$p_{01} = \frac{1}{1 + e^{2\pi\gamma}} \quad (2.303)$$

so that

$$U_1 = e^{\pi\gamma + i(\mathcal{T} + \arg a)} \quad (2.304)$$

$$S_{01} = -i \sin \mathcal{T} \operatorname{sech} \pi\gamma \quad (2.305)$$

in accord with (2.252). However, once again this implies that $|U_1| \rightarrow +\infty$ as $\gamma \rightarrow +\infty$ whereas $a \rightarrow 1$ and $b \rightarrow 1$ as $\gamma \rightarrow +\infty$, with similar implications, as in the crossing case.

2.3.6 Connections to the Frömans-Lundborg Phase-Integral Analysis

For the crossing problem, let us consider, for the two-transition point problem, Fröman et al. [284] and their equation (5.6.4d) for the Stokes constant corresponding to our Stokes line III (of Figure 2.6), namely,

$$b_2 = \frac{i\sqrt{2\pi}}{\Gamma(\frac{1}{2} - \frac{i\bar{K}}{\lambda})} \exp \left\{ -\frac{i\bar{K}}{\lambda} \ln \left(\frac{\bar{K}_0}{\lambda} \right) - \frac{\pi\bar{K}}{2\lambda} + \frac{i\phi^{(1)}}{\lambda} \right\} \quad (2.306)$$

Identifying their equation (5.3.8) with our (2.188), with

$$i\gamma \rightarrow -\frac{i\bar{K}}{\lambda} - \frac{1}{2} \quad (2.307)$$

and

$$2T_0 \sqrt{\gamma} \rightarrow \frac{\phi}{\sqrt{\gamma}} \quad (2.308)$$

we may set, identifying $O(\gamma)$ with $O(\frac{1}{\lambda})$,

$$\frac{\bar{K}}{\lambda} = -\gamma + \frac{i}{2} \quad (2.309)$$

$$\frac{\bar{K}_0}{\lambda} = -\gamma = \frac{\phi^{(1)}}{\lambda} \quad (2.310)$$

whereupon we get agreement with our \tilde{a} of (2.279), apart, that is, from the factor of i in (2.306). This is due to the Stueckelberg [574] choice of branch cut [284]. As shown by Crothers [160] the i disappears upon making the choice of branch cut of our Figure 2.6 or Figure 7 of [160]. After all, the $D_p(z)$ are continuous in the finite plane. In any case the definition of the *effective* Stokes constants depends on one's point of view. We rewrite (2.275) as

$$\begin{aligned} & \frac{(i \sin g)}{i} (1 + \tilde{A}\tilde{B}) \exp \left(2i\gamma \int_{T_0}^{-i} \sqrt{1 + T^2} dT \right) \\ & + \tilde{A} \exp \left(-2i\gamma \int_{T_0}^{-i} \sqrt{1 + T^2} dT \right) \frac{\cos g}{i} \end{aligned} \quad (2.311)$$

Here the i in the denominator comes from the change in the particular part of $\sin g$ and $\cos g$, namely $(1 + T^2)^{-1/4}$, when crossing the branch cut. The $(-i \sin g)/\cos g$ may be regarded as part of the in-/out-going fundamental solution, respectively, just as $(-\sin g)$ and $(\cos g)$ were in (2.275). It follows that

$$\tilde{A} = i \sqrt{1 - e^{-2\pi\gamma}} \exp\left(\frac{\pi i}{4} - i\gamma + i\gamma \ln \gamma - i \arg \Gamma(1 + i\gamma)\right) \quad (2.312)$$

$$\tilde{B} = i \sqrt{1 - e^{-2\pi\gamma}} \exp\left(-\frac{\pi i}{4} + i\gamma - i\gamma \ln \gamma + i \arg \Gamma(1 + i\gamma)\right) \quad (2.313)$$

now in complete agreement with b_2 and a_1 , of Fröman et al. [284]. There is also latitude in the choice of branch cuts in $(1 + T^2)^{-1/4}$: $T = \pm i, \infty$ are three branch points. Each branch point must be connected to another branch point with connecting branch cut. We choose to connect $+i$ to $+i\infty$ and $-i$ to $-i\infty$. Fröman et al. choose to connect $-i$ to $+i$ and to $-i\infty$. These considerations apply equally well to the noncrossing case of Section 2.3.2. However, close examination of their equations (5.5.1a,b) shows that like Nakamura they (see Section 2.3.5) have used weak-coupling asymptotic expansions [1]. In their equation (5.5.1b), nevertheless they have made the coefficient of their dominant term more accurate using the exact recurrence relation, just as we did in the strong-coupling case in (2.271) and in Crothers [160], [161], [163], [167]; they have, however, continued the expansion of the argument of the exponential in b_2 in inverse powers of γ , which is particularly appropriate to our strong-coupling treatment ($\gamma \gg 1$).

2.3.7 Conclusions

We effect a JWKB phase-integral analysis for the crossing and noncrossing parabolic-model nonadiabatic transitions using strong-coupling asymptotics based on the Weber comparison (second-order ordinary-differential) equation for parabolic-cylinder functions. We have shown how to calculate the Stokes constants for noncrossing and have given the simple algebraic expressions ((2.226)–(2.228) and (2.239)–(2.241)) and similarly for crossing ((2.279)–(2.281)). In Sections 2.3.3–2.3.6, we have compared, where possible, with our previous phase-integral analysis [28] of the Nikitin model [459] and with the phase-integral analysis of Nakamura and Zhu [447] and Fröman et al. [284].

There are many intricacies of calculation in applying these models, not least concerning the bending of the double Stokes line as the impact parameter (or azimuthal quantum number) increases [27], [29]; for, of course, it is not difficult to generalize one-dimensional problems to nonzero impact parameters, by analytic continuation. There are many other physical problems, for example, predissociation and resonant scattering [152]. We have not discussed the Kummer model [468], [472] nor generalizations to the complex Nikitin model [467].

Moreover, we recall that it was said at the time [160], following Stueckelberg [574], that the pure phase-integral method for the two-transition-point problem could

only predict three of the four Stokes constants, having invoked unitarity and analyticity. However [198], the comparison-equation method and the parabolic model in particular, resolve the otherwise indeterminate fourth Stokes constant.

We also recall writing [160] “A non-adiabatic transition is thus the physical manifestation of the Stokes phenomenon,” which was echoed by Eu [256], and we note the conclusions of Nakamura [447]. We *have* developed a unified uniform theory of crossing and noncrossing.

2.3.8 Curve Crossing Reflection Probabilities in One Dimension

Let us summarize the improved Stueckelberg treatment of [160], hereafter referred to as I, as applied to curve crossings in I (Section 3.2). Electron translation factors and centrifugal potentials are suppressed and we set

$$r = \exp(x) \quad (2.314)$$

so that $(0, \infty)$ maps to $(-\infty, +\infty)$, where r is the internuclear radial coordinate. Neglecting radial coupling between the stationary-state molecular wave functions, the total wave function Φ is given by

$$r\Phi = u_0^{SS}(r)\chi_0(r) + u_1^{SS}(r)\chi_1(r) \quad (2.315)$$

where

$$\left(\frac{d^2}{dr^2} + v_j^2(r)\right)u_j^{SS}(r) = 0 \quad (\hbar = 1) \quad (2.316)$$

$$\frac{v_j^2(r)}{2m} = E - \epsilon_j(r), \quad (j = 0, 1) \quad (2.317)$$

Here m is the reduced mass, E is the total energy, and the $\epsilon_j(r)$ are the molecular eigenenergies. Making the JWKB approximation we have

$$u_j^{SS}(r) = \alpha_j^+ S_j^+(r) + \alpha_j^- S_j^-(r) \quad (j = 0, 1) \quad (2.318)$$

where α_j^\pm are arbitrary constants. The JWKB functions are given by

$$S_j^\pm(r) = v_j^{-\frac{1}{2}}(r) \exp\left[\pm i \left(\int_{r_j}^r v_j(s) ds + \frac{\pi}{4}\right)\right] \quad (2.319)$$

where the superscript $+$ ($-$) indicates out-going (in-going), r_j is the classical turning/transition point at which $v_j^2(r)$ has a zero and the ubiquitous $\pi/4$ is half the phase of the Stokes constant for the one-transition-point problem. We make the linear-combinations-of-atomic-orbitals approximation:

$$\begin{aligned} \chi_0 &= \phi_0 \sin g - \phi_1 \cos g \\ \chi_1 &= \phi_0 \cos g - \phi_1 \sin g \end{aligned} \quad (2.320)$$

where the ϕ_j are r -invariant and

$$\sqrt{2} \left\{ \frac{\sin}{\cos} \right\} g = \exp \left[\pm \frac{1}{2} \int_0^t \frac{d\tilde{t}}{(1 + \tilde{t}^2)^{1/2}} - \frac{1}{2} \int_0^t \frac{\tilde{t} d\tilde{t}}{1 + \tilde{t}^2} \right] \quad (2.321)$$

where t is the Stueckelberg variable given in the LCAO approximation by

$$1 + t^2 = \frac{m^2(v_0^2 - v_1^2)^2}{H_{12}^2} \quad (2.322)$$

and on the real t - and r - axes

$$\sqrt{2} \left\{ \frac{\sin}{\cos} \right\} g = \sqrt{1 \pm \frac{t}{\sqrt{1 + t^2}}} \quad (2.323)$$

Assuming that $t = \pm i$ and $r = r_c, r_c^*$ are complex conjugate transition points, we note that as usual α_j^\pm suffer discontinuities on crossing the appropriate Stokes lines in accordance with the Stokes phenomenon, the physical manifestation of which is a nonadiabatic transition.

Defining

$$\delta + i\mathcal{T} = i \int_{r_0}^{r_c^*} v_0 dr - i \int_{r_1}^{r_c^*} v_1 dr \quad (2.324)$$

where r_c^* is in the lower half-plane, I gives the following connection formulae, where

$$u_0 = u_0^{PSS} \sin g + u_1^{PSS} \cos g \quad (2.325)$$

$$u_1 = -u_0^{PSS} \cos g + u_1^{PSS} \sin g \quad (2.326)$$

namely:

$$u_0 \sqrt{2} = (\alpha_0^+ S_0^+ + \alpha_0^- S_0^-) \sin g + (\alpha_1^+ S_1^+ + \alpha_1^- S_1^-) \cos g \quad (2.327)$$

$$u_1 \sqrt{2} = -(\alpha_0^+ S_0^+ + \alpha_0^- S_0^-) \cos g + (\alpha_1^+ S_1^+ + \alpha_1^- S_1^-) \sin g \quad (2.328)$$

where $r_{0,1} < r < r_X = \text{Re } r_c$, and

$$u_0 \sqrt{2} = (\beta_0^+ S_0^+ + \beta_0^- S_0^-) \sin g + (\beta_1^+ S_1^+ + \beta_1^- S_1^-) \cos g \quad (2.329)$$

$$u_1 \sqrt{2} = -(\beta_0^+ S_0^+ + \beta_0^- S_0^-) \cos g + (\beta_1^+ S_1^+ + \beta_1^- S_1^-) \sin g \quad (2.330)$$

where $r > r_X$ and

$$\beta_0^+ = a\alpha_0^+ + \exp(-\delta - i\mathcal{T})\alpha_1^+ \quad (2.331)$$

$$\beta_0^- = a^*\alpha_0^- + \exp(-\delta + i\mathcal{T})\alpha_1^- \quad (2.332)$$

$$\beta_1^+ = a^*\alpha_1^+ - \exp(-\delta + i\mathcal{T})\alpha_0^+ \quad (2.333)$$

$$\beta_1^- = a\alpha_1^- - \exp(-\delta - i\mathcal{T})\alpha_0^- \quad (2.334)$$

while the Stokes constant a is given by

$$|a| = \sqrt{1 - e^{-2\delta}} \quad (2.335)$$

$$\arg a = \frac{\pi}{4} + \gamma \ln \gamma - \gamma - \arg \Gamma(1 + i\gamma) \quad (2.336)$$

$$\gamma = \frac{\delta}{\pi} \quad (2.337)$$

The statement by Jakushina and Linnaeus [340] that I considered only “the model problem with linear potentials and constant coupling.” is erroneous, although we will consider such a model problem. In fact, their notation, t of (2.322) is given by

$$t = \frac{[\Phi_1(r) - \Phi_2(r)]}{2\alpha(r)} \quad (2.338)$$

Case A: Similar Slopes

Let us now apply the preceding formulation to the model problem of Child [116], Zhu [612], and Nakamura [447]:

$$\left[\frac{1}{2m} \frac{d^2}{dx^2} + E - H_{00}(x) \right] u_0 = H_{01} u_1 \quad (2.339)$$

$$\left[\frac{1}{2m} \frac{d^2}{dx^2} + E - H_{11}(x) \right] u_1 = H_{01} u_0 \quad (2.340)$$

and in our notation, where the diabatic potentials are (Figure 2.7)

$$H_{jj}(x) = -F_j x \quad (j = 0, 1) \quad (2.341)$$

$$H_{01} = A \quad (2.342)$$

and for similar slopes, we have

$$F_0 > F_1 > 0 \quad (2.343)$$

The Stueckelberg variable t is given by:

$$t = \frac{(F_0 - F_1)x}{2A} \quad (2.344)$$

By translation of axes, the curve-crossing and the energy-reference level are located at the origin, without loss of generality. The adiabatic turning points are given by

$$2F_0 F_1 x_0^2 = -E(F_0 + F_1) \mp \sqrt{4A^2 F_0 F_1 + E^2 (F_0 - F_1)^2} \quad (2.345)$$

and the adiabatic energies by

$$\frac{v_j^2(x)}{2m} = E - \epsilon_j(x) \quad (2.346)$$

where

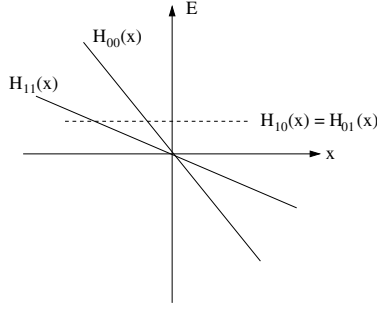


Fig. 2.7. Linear curve crossing: same sign of slopes

$$\epsilon_0(x) = -(F_0 + F_1) \frac{x}{2} \mp A \sqrt{1 + t^2} \quad (2.347)$$

We assume that $E > 0$

From (2.331)–(2.334) and setting (Jeffreys' connection)

$$\alpha_0^+ = -\alpha_0^- = -c \quad (2.348)$$

$$\alpha_1^+ = -\alpha_1^- = -d \quad (2.349)$$

then [324], we have reflection amplitudes ($g = \pi/2$) given by

$$R_0 = -\frac{\beta_0^+}{\beta_0^-} = -\frac{(-ac + e^{-\delta-i\mathcal{T}}d)}{(a^*c - e^{-\delta+i\mathcal{T}}d)} \quad (2.350)$$

$$R_1 = -\frac{\beta_1^+}{\beta_0^-} = -\frac{(-a^*d + e^{-\delta+i\mathcal{T}}c)}{(a^*c - e^{-\delta+i\mathcal{T}}d)} \quad (2.351)$$

where c/d is given (no in-going incident wave in channel 1)

$$\beta_1^- = 0 \quad (2.352)$$

so that

$$R_0 = \left[e^{-2\delta-2i\mathcal{T}} + e^{2i\arg a}(1 - e^{-2\delta}) \right] \quad (2.353)$$

$$R_1 = -2i \sin(\mathcal{T} + \arg a) e^{-\delta} \sqrt{1 - e^{-2\delta}} \quad (2.354)$$

It follows that unitarity is fulfilled

$$|R_0|^2 + |R_1|^2 = 1 \quad (2.355)$$

where

$$|R_1|^2 = 4e^{-2\delta}(1 - e^{-2\delta}) \sin^2(\mathcal{T} + \arg a) \quad (2.356)$$

Averaging the Stueckelberg oscillations gives

$$P_{01} = 2P(1 - P) \quad (2.357)$$

the familiar Landau-Zener formula where

$$P = e^{-2\delta} \quad (2.358)$$

and δ is the familiar Massey parameter. Even in this one-dimensional reflection problem, the pseudo-curve-crossing arises on the way in and on the way out:

$$P(1 - P) + (1 - P)P = 2P(1 - P) \quad (2.359)$$

that is, either transition going in and none going out or vice versa. It may be noted that in this derivation, it was not necessary to use the momentum representation that in effect is the impact parameter formulation, unfortunately sometimes also confusingly called the semiclassical treatment.

Case B: Dissimilar Slopes

In Case B we have

$$F_0 > 0 > F_1 \quad (2.360)$$

in contrast with (2.343) in Case A. Further we refer to Figure 2.8 and make the concrete assumption that

$$E > E_b \quad (2.361)$$

Because u_1^{PS} of (2.318) is now associated with the upper potential-energy curve, the Bohr–Sommerfeld connection requires

$$\alpha_1^+ + \alpha_1^- = 0 \quad (2.362)$$

but

$$\beta_1^+ e^{i(\frac{\pi}{2} - \overline{\mathcal{T}})} + \beta_1^- e^{i(\overline{\mathcal{T}} - \frac{\pi}{2})} = 0 \quad (2.363)$$

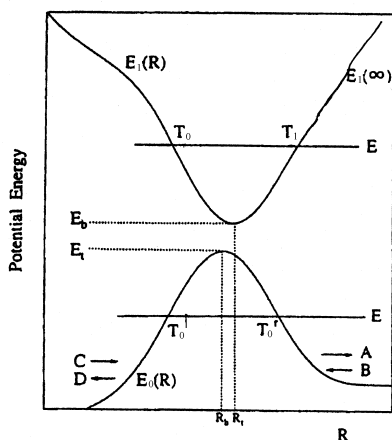


Fig. 2.8. Nonadiabatic tunneling-type curve crossing

where

$$\overline{\mathcal{T}} = - \int_{x_0}^{x_1} v_1(x) dx \quad (2.364)$$

There are no incident waves in channel 0 from negative x so that

$$\alpha_0^+ = 0 \quad (2.365)$$

noting that in the x -representation, for negative x , in-going and out-going reverse their meanings and therefore their superscripts. Solving (2.331)–(2.334) gives the reflection amplitude in channel 0 and the transition amplitude in channel 1, respectively, by

$$R_0 = \frac{-ie^{-2\delta-2i\mathcal{T}+i\overline{\mathcal{T}}}}{2e^{-i\arg a}(1-e^{-2\delta})\cos(\overline{\mathcal{T}}+\arg a)+e^{-2\delta+i\overline{\mathcal{T}}}} \quad (2.366)$$

$$T_1 = \frac{2i\cos(\overline{\mathcal{T}}+\arg a)\sqrt{1-e^{-2\delta}}}{2e^{-i\arg a}(1-e^{-2\delta})\cos(\overline{\mathcal{T}}+\arg a)+e^{-2\delta+i\overline{\mathcal{T}}}} \quad (2.367)$$

As for Case A we have unitarity, but now given by

$$|R_0|^2 + |T_1|^2 = 1 \quad (2.368)$$

where

$$|T_1|^2 = \frac{4(1-e^{-2\delta})\cos^2(\overline{\mathcal{T}}+\arg a)}{4(1-e^{-2\delta})\cos^2(\overline{\mathcal{T}}+\arg a)+e^{-4\delta}} \quad (2.369)$$

The transition amplitude is zero, when

$$\overline{\mathcal{T}} + \arg a = n\pi + \frac{\pi}{2} \quad (2.370)$$

However because $\overline{\mathcal{T}}$ is negative and $\arg a \in (\pi/4, \pi/2)$, including weak and strong coupling, we envisage negative integers n , in which case we have perfect reflection, as remarked by Nakamura [447] and when (2.370) is not satisfied, nonadiabatic tunnelling obtains.

The cases that arise when (2.361) is not fulfilled are considered by Nakamura and by Coveney et al. [152].

2.4 Addition of a Simple Pole

2.4.1 Introduction

A simple but versatile atomic collision model for treating nonadiabatic phenomena associated with curve crossings and noncrossings is the exponential model of Nikitin. This two-state model leads, within a semiclassical framework, to a collision S -matrix made up of classical trajectory transition probabilities and semiclassical phases. It

can be used to discuss physical processes such as excitation and charge transfer. In applying the model expressions to real situations, phase-integral expressions for the S -matrix elements are needed. Such expressions have been obtained earlier by Crothers through a process of interpretation and abstraction. To shed new light on this interpretation we give a phase-integral derivation of the two-state semiclassical collision S -matrix within a general exponential model [28].

Representing the S -matrix as a product of two halfway house matrices and assuming only one principal transition zone in each half, we may parameterize the elements of S in a semiclassically consistent way. The parameters are computed in terms of certain Stokes constants and complex Coulomb phases arising from the classical trajectory equations describing the evolution of the diabatic linear combination of atomic orbitals electronic states. The Stokes constants and complex Coulomb phases associated with the canonical (pure exponential model) one-pole, two-transition-point problem are parameterized via the comparison equation method, supplemented by strong-coupling asymptotics. The corresponding quantities for a perturbed canonical form (general exponential model) are suitably abstracted in terms of simple known functions and physically significant phase integrals. In this way the complete semiclassical collision S -matrix is derived. A short discussion of its applicability is given.

Many physical processes can be discussed successfully within the framework of simple mathematical models. These models usually select and put forward some special mechanism as being primarily responsible for the observed behaviour of the physical system. Through the simplification of the problem offered by the model, one can get a better understanding of the workings of the mechanism. This can be done by analytical or numerical studies of the model equations, but although numerical investigations may be more straightforward to perform, analytical results are often more useful when it comes to understanding the models and their application to real situations. In this work we present an analytical investigation of a simple but versatile atomic collision model: the exponential model.

In treating low-energy inelastic atomic collision processes (such as excitation, charge transfer, or transfer ionization), one is faced with a complicated quantum mechanical many-body system. Through a series of approximations one may, in many cases, reduce the problem to a manageable semiclassical form, namely, a set of equations describing the quantum mechanical evolution of the electronic states as the nuclei follow classical trajectories (see for example [220]). Using these classical trajectory equations, together with semiclassical phase shifts for the nuclear motion, many collision processes may be explained. Prime examples are the nonadiabatic phenomena, such as curve-crossing transitions and interferences observed as distinct structures in the total and differential collision cross sections [457].

Essential for the understanding of the nonadiabatic collision processes have been two simple two-state models formulated in the semiclassical framework described earlier. One is the Landau–Zener curve-crossing model [376], [611] and the other is the Rosen–Zener noncrossing model [519]. These models represent two extreme situations in which the coupling between adiabatic states is due solely to variation of the diabatic energy difference (Landau–Zener) or to variation of the nonadiabatic cou-

pling element (Rosen–Zener). As a generalization of these two extreme situations, the two-state exponential semiclassical model for atomic collisions was introduced by Nikitin [453], [454] and independently by Ellison and Borowitz [242]. In this model both the diabatic energy difference and the nondiabatic coupling element may vary, and through the choice of a certain mixing parameter θ both crossing and non-crossing situations are covered.

To understand the properties of these types of model and to be able to apply them to real situations, general phase-integral expressions for the transition probabilities and phases entering the semiclassical scattering matrix are needed (cf. [175]). The original inventors of the exponential model used confluent hypergeometric functions and weak-coupling asymptotic expansions [161], [167] to derive expressions for the nonadiabatic transition probability and its behaviour under various limiting conditions. A first step towards a more general derivation was taken by Dubrovskiy [232] in tackling the general two-state problem of nonadiabatic transitions. He used both phase-integral [574] and comparison-equation [428] techniques and derived closed-form expressions for the transition probability in the case of an avoided crossing between adiabatic energy levels. His final expressions have been criticized by one of us [160] on the grounds that they vanish for certain types of interaction potentials. Also an attempt by Child [115] to generalize Dubrovskiy's results has been criticized [163]. We will discuss the application of their results to the exponential model in Section 2.4.6. A general discussion on the calculation of transition probabilities was given by Nikitin [455], who stressed the importance of the complex analytic structure of the adiabatic energy difference. An excellent review of the status of the exponential model at the end of the 1960s was written by Nikitin [456]. During the 1970s some major steps towards the understanding of the applicability of the exponential model were taken. First, the validity of the semiclassical treatment (classical trajectories, phase-integral expressions) were investigated in depth. (For classical trajectories, see, for example, [40], [217], [220]. For phase integrals, see the introduction to Bárány and Crothers [27], the review by Crothers [175], and, in a more general context, the review by Berry and Mount [72].) Secondly, the phases of the exponential model were derived [52], [167], [458], [169]. Thirdly, and perhaps most importantly, there were serious applications of the model to real physical collision processes [169], [174], [319].

The applications made by Crothers and Todd [169], [174] rely on a Zwaan–Stueckelberg phase-integral interpretation (abstraction) of the exponential model. Although the results in general were encouraging, there were some difficulties in applying the model to the charge transfer reaction $\text{Mg}^{2+} + \text{H} \rightarrow \text{Mg}^+ + \text{H}^+$, because of the existence of two distinct transition regions (of which only one was found to be effective). To pinpoint possible defects of the phase-integral interpretation, it was felt that a phase-integral derivation was needed. That such a derivation might lead to new insights had been shown for the linear model [24], [25], [26].

2.4.2 The Semiclassical Scattering Matrix

The information that is needed for the calculation of differential and total cross sections is conveniently summarized in the partial-wave-scattering matrix. This quantum mechanical scattering matrix can be defined in terms of the solutions to a set of coupled Schrödinger differential equations. Here we shall only consider the semiclassical scattering matrix that can be derived by using semiclassical elastic phase shifts and classical trajectory equations (see, for example, [160]). Even though some of our expressions formally hold true for an arbitrary number of states, we shall immediately specialize to two states only.

The two-state impact-parameter-dependent scattering matrix $\mathbf{S} = \mathbf{S}(E, \rho)$ is unitary and symmetric. This implies that it can be represented as

$$\mathbf{S} = \tilde{\mathbf{S}}_h \mathbf{S}_h, \quad (2.371)$$

where \mathbf{S}_h is unitary and $\tilde{\mathbf{S}}_h$ signifies the transposed matrix. In general this representation is purely formal, but for heavy-particle scattering (where semiclassical concepts apply) it is possible to interpret \mathbf{S}_h as a halfway house scattering matrix. The semiclassical structure of \mathbf{S}_h depends on the number of localized transition zones, but for the simplest case of just one zone it is given [52] by

$$\mathbf{S}_h = \mathbf{O} \exp(i\Delta) \mathbf{T}_h \exp[i(\boldsymbol{\eta} - \Delta)] \quad (2.372)$$

Here Δ is a diagonal matrix containing the phases that develop between the turning points and the transition zone, $\boldsymbol{\eta}$ is the diagonal semiclassical phase-shift matrix and \mathbf{T}_h is a unitary transition matrix characteristic of the transition zone. This transition matrix is determined by a set of classical trajectory equations and has determinant equal to unity. It is possible to parameterize it as

$$\mathbf{T}_h = \begin{bmatrix} (1 - z^2)^{1/2} \exp(i\phi) & -z \exp(-i\chi) \\ z \exp(i\chi) & (1 - z^2)^{1/2} \exp(-i\phi) \end{bmatrix} \quad (2.373)$$

where $0 \leq z \leq 1$ and ϕ and χ are real phases.

The matrix \mathbf{O} is a (real orthogonal) rotation matrix that takes into account the fact that the two states forming a basis at infinity may be mixed close to the turning point. It has been found, both analytically and numerically, that for low-energy heavy-particle collisions the matrix \mathbf{O} may be put equal to the unit matrix if the representation is taken to be the adiabatic one, i.e., if Δ and $\boldsymbol{\eta}$ are adiabatic phases [160], [344], [215]. Then the parameters z , ϕ , and χ are well-behaved functions of E and ρ . This follows from the fact that a correct semiclassical treatment necessarily introduces adiabatic phases, a point already stressed by one of us [160], [164], [167].

Consider then the classical trajectory equations in adiabatic (l.c.a.o.) formulation [216]

$$i \frac{d}{d\tau} a_{1,2} = a_{2,1} \exp \left[\mp 2i \int_0^\tau T(\tau' d\tau') \right] \quad (2.374)$$

The independent variable τ is defined as

$$\tau = \int_0^t H_{12} dt' \quad (2.375)$$

with the supposition that

$$\tau_\infty = \int_0^{+\infty} H_{12} dt' < +\infty \quad (2.376)$$

and the Stueckelberg variable T by

$$T = (H_{22} - H_{11})/2H_{12} \quad (2.377)$$

where $H_{22} - H_{11} \geq 0$ at infinity. The classical trajectory $R = R(t)$ is assumed to be symmetric, $R(-t) = R(t)$, so that T is an even function of τ and the vector $\mathbf{a}(\tau_\infty)$ is related to $\mathbf{a}(-\tau_\infty)$ by

$$\mathbf{a}(\tau_\infty) = \tilde{\mathbf{G}}^d \mathbf{G}^d \mathbf{a}(-\tau_\infty) \quad (2.378)$$

Here the matrix \mathbf{G}^d propagates \mathbf{a} from $\tau = -\tau_\infty$ to the origin $\tau = 0$. Reverting to the adiabatic representation then gives [218]

$$\mathbf{G}^a = \tilde{\mathbf{R}} \mathbf{G}^d \exp(-i\frac{1}{2}\zeta) \quad (2.379)$$

where the matrix ζ is diagonal with elements $\pm\zeta$, given by

$$\zeta = 2 \int_{-\tau_\infty}^0 [(1 + T^2)^{1/2} - T] d\tau' \quad (2.380)$$

The matrix \mathbf{R} is a (real orthogonal) rotation matrix transforming from the adiabatic to the diabatic representation. From the correspondence

$$\mathbf{G}^a \exp(i\eta) = \mathbf{S}_h \quad (2.381)$$

we find, using the explicit expression for \mathbf{S}_h with $\mathbf{O} = 1$

$$\mathbf{G}^a = \exp(i\Delta) \mathbf{T}_h \exp(-i\Delta) \quad (2.382)$$

2.4.3 Phase-Integral Treatment

We now set out to determine (within the l.c.a.o. approximation) the matrix \mathbf{G}^a , using phase-integral methods. Because of symmetry we need only consider the elements of the first column, G_{11}^a and G_{21}^a . Then we have

$$G_{22}^a = (G_{11}^a)^*, \quad G_{12}^a = -(G_{21}^a)^* \quad (2.383)$$

Introducing first a new set of dependent variables, c_1, c_2 through

$$c_{1,2} = a_{1,2} \exp \left[\pm i \int_0^\tau T(\tau') d\tau' \right] \quad (2.384)$$

we find that

$$i \, dc_{1,2}/d\tau = \mp T c_{1,2} + c_{2,1} \quad (2.385)$$

Differentiation and elimination show that c_1 and c_2 satisfy the second-order equations

$$d^2 c_{1,2}/d\tau^2 + Q_{1,2}^2(\tau) c_{1,2} = 0 \quad (2.386)$$

where

$$Q_{1,2}^2 = 1 \mp i \, dT/d\tau + T^2 \quad (2.387)$$

We now introduce the following model assumptions: with positive parameters λ and θ subject to $0 < \theta < \pi$ and fulfilling the general inequalities

$$1 \lesssim \lambda \lesssim 2\tau_\infty / \sin \theta \quad (2.388)$$

the function T is given for $\text{Re } \tau \leq 0$ by

$$T(\tau) = \lambda/2(\tau + \tau_\infty) - \cot \theta + F(\tau) \quad (2.389)$$

This contrasts [164] with

$$T(\tau) = -\frac{\tau}{2\gamma} + T_0 \quad (2.390)$$

which when substituted into (2.386) yields the so-called parabolic models [163], [164]. In the model relation (2.389) $F(\tau)$ acts as a perturbation in a wide region surrounding the origin ($\tau = 0$) and the pole ($\tau = -\tau_\infty$). For $F = 0$ we retrieve the pure exponential model (with impact parameter zero, rectilinear trajectory, and constant velocity). The canonical form is then a pole plus a constant. The more general case treated here includes generalizations to nonzero impact parameters, curved trajectories, and varying velocity. It also includes certain other potential models, e.g., the Demkov-Kunike [222] model.

To find out the relation between λ , θ , and the physical potentials, we suppose that

$$\left. \begin{aligned} \lim_{R \rightarrow +\infty} (H_{22} - H_{11}) &= \Delta\epsilon > 0 \\ \lim_{R \rightarrow +\infty} H_{12} &\propto \exp(-\alpha R) \end{aligned} \right\} \quad (2.391)$$

Calculating the residue of $T(\tau)$ then gives

$$\lambda = \Delta\epsilon/\alpha v \quad (2.392)$$

where $v = \dot{R}(+\infty)$. Again, provided

$$\lambda \ll 2\tau_\infty \cot \theta \quad (2.393)$$

we have

$$-\cot \theta \approx T(0) = [(H_{22} - H_{11})/2H_{12}]|_{R(0)} \quad (2.394)$$

This relation shows, among other things, that, broadly speaking, the potentials H_{11} and H_{22} cross for acute θ , while they are noncrossing for obtuse θ . The angle $\theta =$

$1/2\pi$ corresponds to perturbed symmetric resonance [160], i.e., to potentials that run approximately parallel [221].

We now introduce the Langer-corrected functions

$$q_{1,2}^2(\tau) = Q_{1,2}^2(\tau) - \frac{1}{4(\tau + \tau_\infty)^2} \\ = 1 + \cot^2 \theta - \lambda \cot \theta / (\tau + \tau_\infty) + (\lambda \pm i)/4(\tau + \tau_\infty)^2 + \dots \quad (2.395)$$

Writing

$$q_{1,2}(\tau) = [(\tau - \tau_{1,2})(\tau - \tau_{2,1}^*)]^{1/2} / (\tau + \tau_\infty) \sin \theta \quad (2.396)$$

we define the argument of the square root to be zero on the real axis as $\tau \rightarrow +\infty$. The branch cuts are inserted from the zeros $\tau_{1,2}$ (upper half-plane) and $\tau_{1,2}^*$ (lower half-plane) according to Figure 2.9. Note that τ_1 and τ_2^* belong to $q_1^2(\tau)$, while τ_2 and τ_1^* belong to $q_2^2(\tau)$.

Concentrating now on the function $c_2(\tau)$, we consider the pattern of Stokes lines emanating from the zeros τ_1^* and τ_2 of q_2^2 . These are lines on which

$$\operatorname{Re} \left(\int_{\tau_1^*, \tau_2}^{\tau} q_2 d\tau' \right)$$

is constant, so that

$$\exp \left(i \int_{\tau_1^*, \tau_2}^{\tau} q_2 d\tau' \right)$$

has nonoscillating behaviour. In Figures 2.10a, b, and c these patterns are shown for different values of θ .

We note that two Stokes lines spiral into the pole. An investigation shows that these are logarithmic spirals revolving an infinite number of times around the pole. The choice of branch cuts in Figure 2.9 is, of course, to some extent arbitrary, so that we could, for instance, without loss of generality draw the upper branch cut in Figure 2.10a and the lower branch cut in Figure 2.10c so that they do not cross a Stokes line in the finite plane.

To satisfy the boundary conditions at the pole ($a_1(t = -\infty) = 1$, $a_2(t = -\infty) = 0$) we write

$$c_{1,2}(\tau) = B_{1,2} q_{1,2}^{-1/2} \exp \left(i \int_0^{\tau} q_{1,2} d\tau' \right) \quad (2.397)$$

and let τ tend to $-\tau_\infty$. In order that the integrals be well defined we insert a branch cut from $-\tau_\infty$ along the negative real axis in the direction of $-\infty$. Actual computations (with use of the first-order equations to connect c_1 and c_2) then give (to within semiclassical accuracy)

$$B_1 = -\frac{1}{2B_2^*} \quad (2.398)$$

$$B_2 = -\frac{1}{\sqrt{2}} [(1 + T_0^2)^{1/2} - T_0]^{1/2} \exp(-\nu + i\Theta + \frac{1}{2}i\zeta) \quad (2.399)$$

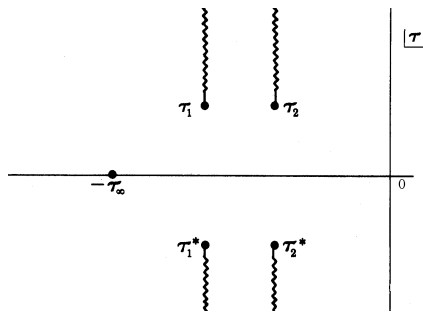


Fig. 2.9. Complex τ -plane showing zeros of $q_{1,2}^2$ and branch cuts (wiggly lines). τ_1 and τ_2^* concern c_1 and τ_1^* and τ_2 concern c_2

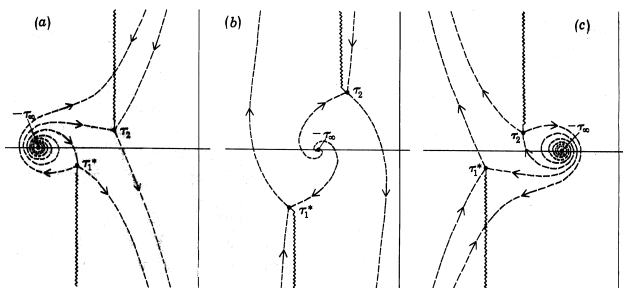


Fig. 2.10. Complex τ -plane showing qualitative behaviour of Stokes lines for c_2 for (a) $0 < \theta < 1/2\pi$, (b) $\theta = 1/2\pi$, (c) $1/2\pi < \theta < \pi$. Arrows show direction of increasing $\exp[i \int q_2 d\tau]$

where $T_0 = T(\tau = 0)$ and

$$-v + i\Theta = i \int_{-\tau_\infty}^0 \left[q_2 - (1 + T^2)^{1/2} - \frac{i dT/d\tau}{2(1 + T^2)^{1/2}} \right] d\tau' \quad (2.400)$$

An alternative expression for B_2 is (again to within semiclassical accuracy)

$$B_2 = -\frac{1}{\sqrt{2}} [(1 + T_0^2)^{1/2} + T_0]^{1/2} \exp(-u + i\Theta + \frac{1}{2}i\zeta) \exp(y_2) \quad (2.401)$$

where y_2 is defined through

$$-\frac{1}{2}x_{1,2} + \frac{1}{2}iy_{1,2} = \int_0^{\tau_{1,2}} q_{1,2} d\tau' \quad (2.402)$$

and

$$u = \frac{1}{2}(y_1 + y_2) + \text{Im} \int_{-\tau_\infty}^{\tau_1^*} \left[q_2 - \frac{idT/d\tau}{2(1 + T^2)^{1/2}} \right] d\tau' - \text{Im} \int_{\tau_2}^0 \left[q_2 - \frac{idT/d\tau}{2(1 + T^2)^{1/2}} \right] d\tau' \quad (2.403)$$

Using B_1 and B_2 as determined earlier we have approximate solutions $c_1(\tau)$ and $c_2(\tau)$ that satisfy the boundary conditions at the pole. The solution c_2 may (for acute θ) be traced out into the complex plane on a path leading above the transition region around τ_2 . When crossing the Stokes line (see Figure 2.10a) emanating from τ_2 at an angle of $1/3\pi$, the approximate solution experiences the Stokes phenomenon and picks up a multiple of the subdominant solution. On the real axis, close to the origin, the approximate solution becomes

$$c_2(\tau) = iB_2q_2^{-1/2}(\tau) \left[\exp\left(-y_2 - ix_2 - i \int_0^\tau q_2 d\tau'\right) + a_{BC} \exp\left(i \int_0^\tau q_2 d\tau'\right) \right] \quad (2.404)$$

Here a_{BC} is the Stokes constant belonging to the Stokes line considered. Applying the first-order equations to find c_1 close to the origin and then the fact that the Wronskian of c_1^* and c_2 has the same value at the pole as at the origin, we obtain (for $0 < \theta < 1/2\pi$)

$$|a_{BC}|^2 = [1 - \exp(-2u)] / \exp(-2v) \quad (2.405)$$

For obtuse θ we may trace c_2 from the pole to the origin along the real axis. This means that a Stokes line emanating from τ_2 has to be crossed (see Figure 2.10c). Introducing a Stokes constant c_{BC} gives for c_2 close to the origin

$$c_2(\tau) = B_2q_2^{-1/2} \left[\exp\left(i \int_0^\tau q_2 d\tau'\right) + c_{BC} \exp\left(-y_2 - ix_2 - i \int_0^\tau q_2 d\tau'\right) \right] \quad (2.406)$$

Use of the first-order equations to find c_1 and the Wronskian of c_1^* and c_2 to connect between the pole and the origin gives (for $1/2\pi < \theta < \pi$)

$$|c_{BC}|^2 = [1 - \exp(-2v)] / \exp(-2u) \quad (2.407)$$

Considering now the approximate solutions c_1 and c_2 at the origin and introducing the notations

$$\cos g_0 = \left[\frac{(1 + T_0^2)^{1/2} - T_0}{2(1 + T_0^2)^{1/2}} \right]^{1/2}, \quad \sin g_0 = \left[\frac{(1 + T_0^2)^{1/2} + T_0}{2(1 + T_0^2)^{1/2}} \right]^{1/2} \quad (2.408)$$

we find (using $a_{1,2}(0) = c_{1,2}(0)$) that

$$\mathbf{a}(0) = \mathbf{R} \begin{bmatrix} G_{11}^a \\ G_{21}^a \end{bmatrix} \exp\left(\frac{1}{2}i\zeta\right) \quad (2.409)$$

with

$$\mathbf{R} = \begin{bmatrix} \sin g_0 & \cos g_0 \\ -\cos g_0 & \sin g_0 \end{bmatrix} \quad (2.410)$$

The adiabatic propagated elements are given by

$$G_{11}^a = \begin{cases} i[1 - \exp(-2u)]^{1/2} \exp[i(\theta + \arg a_{BC})] & (0 < \theta < \frac{1}{2}\pi) \\ \exp(-v) \exp(i\theta) & (\frac{1}{2}\pi < \theta < \pi) \end{cases} \quad (2.411)$$

$$G_{21}^a = \begin{cases} -i \exp(-u) \exp[i(\theta - x_2)] & (0 < \theta < \frac{1}{2}\pi) \\ -[1 - \exp(-2v)]^{1/2} \exp[i(\theta - x_2 + \arg c_{BC})] & (\frac{1}{2}\pi < \theta < \pi) \end{cases} \quad (2.412)$$

Because the phase-integral derivation is bound to break down when the complex transition points are close to the pole (see Figure 2.10b), we cannot expect the two different expressions given to join up for $\theta = 1/2\pi$ unless there is strong coupling between the states ($y_1, y_2 \gtrsim 1$), in which case we find that provided

$$\arg a_{BC} \rightarrow -\frac{1}{2}\pi, \quad \arg c_{BC} \rightarrow +\frac{1}{2}\pi \quad (2.413)$$

we do indeed get consistent results. This is because

$$u \approx \frac{1}{2}(y_1 + y_2) = y, \quad v \approx \frac{1}{2}(y_1 - y_2) \approx 0 \quad (2.414)$$

and

$$\begin{aligned} [1 - \exp(-2u)]^{1/2} &\approx [1 - \exp(-2y)]^{1/2} \approx 1 \\ \exp(-v) &\approx 1 \end{aligned} \quad (2.415)$$

Invoking now the parameterization of \mathbf{T}_h we find

$$\begin{aligned} (1 - z^2)^{1/2} \exp(i\phi) &= G_{11}^a \\ z \exp(i\chi) \exp[i(\mathcal{A}_2 - \mathcal{A}_1)] &= G_{21}^a \end{aligned} \quad (2.416)$$

Then we have

$$z^2 = \begin{cases} \exp(-2u) & (0 < \theta < \frac{1}{2}\pi) \\ 1 - \exp(-2v) & (\frac{1}{2}\pi < \theta < \pi), \end{cases} \quad (2.417)$$

while

$$\phi = \begin{cases} \Theta + \arg a_{BC} + \frac{1}{2}\pi & (0 < \theta < \frac{1}{2}\pi) \\ \Theta & (\frac{1}{2}\pi < \theta < \pi) \end{cases} \quad (2.418)$$

and

$$\chi = \begin{cases} \Theta & (0 < \theta < \frac{1}{2}\pi) \\ \Theta + \arg c_{BC} - \frac{1}{2}\pi & (\frac{1}{2}\pi < \theta < \pi) \end{cases} \quad (2.419)$$

We have used the abstraction

$$\mathcal{A}_1 - \mathcal{A}_2 = x_2 + \frac{1}{2}\pi \quad (2.420)$$

to connect between the true adiabatic phases and the model quantity x_2 . The factor $1/2\pi$ enters because $x_2 + 1/2\pi \approx x_1 - 1/2\pi$. Note that the phases of the Stokes constants a_{BC} and c_{BC} are undetermined, as is usual in these matters. In the next section we use the comparison-equation technique to derive expressions for $\arg a_{BC}$ and $\arg c_{BC}$.

2.4.4 Comparison Equation

We start by considering the case when the Stueckelberg variable T reduces to the canonical exponential model form (we use a hat to designate canonical quantities)

$$\hat{T}(\tau) = \lambda/2(\tau + \tau_\infty) - \cot \theta \quad (2.421)$$

so that

$$\begin{aligned} T_0 &\equiv \hat{T}(0) = \frac{\lambda}{2\tau_\infty} - \cot \theta \\ &\equiv \frac{\lambda}{\gamma \sin \theta} - \cot \theta \equiv \frac{[\frac{d\epsilon}{A} - \cos \theta]}{\sin \theta} \end{aligned} \quad (2.422)$$

where $\gamma = A/(v\alpha)$ and A is defined by (2.442) or (2.443). This is the case of the exponential model of Nikitin [453], [454], but other models may also reduce to this form when suitable variables are used. It can be shown, by using appropriate recurrence relations, namely equations (2.4.9) and (2.5.1) of [562] that the exact solution is given by

$$\begin{aligned} \hat{c}_1(\tau) &= \exp[-\frac{1}{4}\pi\lambda + \frac{1}{2}i(\gamma \cos \theta - \lambda \ln \gamma)][M_{\kappa, -\mu}(\beta)]^* \\ \hat{c}_2(\tau) &= -\frac{1}{2} \frac{\sin \theta}{1+i\lambda} \exp[\frac{1}{4}\pi\lambda + \frac{1}{2}i(\gamma \cos \theta - \lambda \ln \gamma)]M_{\kappa, \mu}(\beta) \end{aligned} \quad (2.423)$$

where

$$\kappa = \frac{1}{2}i\lambda \cos \theta, \quad \mu = \frac{1}{2}(1 + i\lambda), \quad \beta = (2i/\sin \theta)(\tau + \tau_\infty) \quad (2.424)$$

and the functions $M_{\kappa, \pm\mu}$ are Whittaker functions (cf. [562]).

Using strong-coupling asymptotic expansions [161], [167] one finds (after some heavy algebra) that

$$\hat{\mathbf{a}}(0) = \hat{\mathbf{R}} \begin{bmatrix} \hat{G}_{11}^a \\ \hat{G}_{21}^a \end{bmatrix} \exp(\frac{1}{2}i\hat{\zeta}) \quad (2.425)$$

where $\hat{\mathbf{R}}$ and $\hat{\zeta}$ are defined as in the general case, but with the model variable \hat{T} and

$$\begin{aligned} \hat{G}_{11}^a &= \left(\frac{1 - \cos \theta}{2} \right)^{\frac{1}{2}} \left| \frac{\Gamma(1 + i\lambda)}{\Gamma(1 + \frac{1}{2}i\lambda(1 - \cos \theta))} \right| \\ &\quad \exp[\frac{1}{4}\pi\lambda(1 + \cos \theta)] \exp[i\{\tilde{\gamma}[\frac{1}{2}\lambda(1 - \cos \theta)] - \tilde{\gamma}(\lambda)\}] \end{aligned} \quad (2.426)$$

$$\begin{aligned} \hat{G}_{21}^a &= \left(\frac{1 + \cos \theta}{2} \right)^{\frac{1}{2}} \left| \frac{\Gamma(1 + i\lambda)}{\Gamma(1 + \frac{1}{2}i\lambda(1 + \cos \theta))} \right| \\ &\quad \exp[-\frac{1}{4}\pi\lambda(1 - \cos \theta)] \exp[-i\hat{x} + i\{\tilde{\gamma}[\frac{1}{2}\lambda(1 + \cos \theta)] - \tilde{\gamma}(\lambda)\}] \end{aligned} \quad (2.427)$$

Here

$$\hat{x} = \hat{x}_1 - \frac{1}{2}\pi = \hat{x}_2 + \frac{1}{2}\pi = -2\text{Re} \int_0^{\tau_c} (1 + \hat{T}^2)^{1/2} d\tau' \quad (2.428)$$

where τ_c is the zero of $1 + \hat{T}^2$ in the second quadrant and

$$\tilde{\gamma}(\alpha) = \frac{1}{4}\pi + \alpha \ln \alpha - \alpha - \arg \Gamma(1 + i\alpha) \quad (2.429)$$

Introducing the parameterization of the semiclassical scattering matrix and abstracting $\mathcal{A}_1 - \mathcal{A}_2$ as in Section 2.4.3, we find

$$\left. \begin{aligned} \hat{z}^2 &= \{\sinh[\tfrac{1}{2}\pi\lambda(1 + \cos\theta)] / \sinh(\pi\lambda)\} \exp[-\tfrac{1}{2}\pi\lambda(1 - \cos\theta)] \\ \hat{\phi} &= \hat{\gamma}(\tfrac{1}{2}\lambda(1 - \cos\theta)) - \hat{\gamma}(\lambda) \\ \hat{\chi} &= \hat{\gamma}(\tfrac{1}{2}\lambda(1 + \cos\theta)) - \hat{\gamma}(\lambda) \end{aligned} \right\} \quad (2.430)$$

The parameters $\lambda(1 \pm \cos\theta)$ may be abstracted as integrals through

$$\begin{aligned} \hat{y} &= \tfrac{1}{2}\lambda(1 - \cos\theta) = \tfrac{1}{2}(\hat{y}_1 + \hat{y}_2) = \tfrac{1}{\pi} \text{Im} \int_{\hat{\tau}_1}^{\hat{\tau}_2} \hat{q}_2 \, d\tau' \\ \hat{\mu} &= \tfrac{1}{2}\lambda(1 + \cos\theta) = \lambda - \tfrac{1}{2}(\hat{y}_1 + \hat{y}_2) = -\tfrac{1}{\pi} \text{Im} \int_{\hat{\tau}_1}^{\hat{\tau}_2} \hat{q}_2 \, d\tau' \end{aligned} \quad (2.431)$$

where the bar on the integral for $\hat{\mu}$, signifies that it should be evaluated on a contour to the left of the pole at $-\tau_\infty$.

We now compare the expressions just derived with those of equations (2.416)–(2.419) of the last section. First, we find expressions for the phases of the Stokes constants, namely

$$\begin{aligned} \arg a_{BC} &= \tilde{\gamma}(y) - \tilde{\gamma}(\mu) - \tfrac{1}{2}\pi & (0 < \theta < \tfrac{1}{2}\pi) \\ \arg c_{BC} &= \tilde{\gamma}(\mu) - \tilde{\gamma}(y) + \tfrac{1}{2}\pi & (\tfrac{1}{2}\pi < \theta < \pi) \end{aligned} \quad (2.432)$$

Then the phase-integral expressions become, for $0 < \theta < 1/2\pi$,

$$\begin{aligned} z^2 &= \exp(-2u) \\ \phi &= \Theta + \tilde{\gamma}(y) - \tilde{\gamma}(\mu) \\ \chi &= \Theta \end{aligned} \quad (2.433)$$

For $1/2\pi < \theta < \pi$,

$$\begin{aligned} z^2 &= 1 - \exp(-2v) \\ \phi &= \Theta \\ \chi &= \Theta + \tilde{\gamma}(\mu) - \tilde{\gamma}(y) \end{aligned} \quad (2.434)$$

We note that

$$y = \tfrac{1}{2}(y_1 + y_2) \quad (2.435)$$

while μ is more complicated and in fact contains contributions from secondary complex transition points in the R -plane [174].

It is of course also possible to take over more of the comparison equation. Thus for $0 < \theta < \pi$, we realize that in the canonical exponential case ($F \equiv 0$ in expression

(2.389)) the imaginary part $\hat{\theta}$ of the complex Coulomb phase (cf. [283]) of (2.400) is a semiclassical approximation to

$$\tilde{\gamma}\left(\frac{1}{2}\lambda(1 + |\cos \theta|)\right) - \tilde{\gamma}(\lambda) \quad (2.436)$$

which is interesting in that it has a discontinuous first derivative (with respect to θ) at $\theta = 1/2\pi$.

2.4.5 General Phase-Integral Abstraction

We now propose to parameterize the transition matrix \mathbf{T}_h of (2.373) for $F(\tau) \neq 0$ by calibration with the exact Coulomb case of Section 2.4.4. Thus we propose the following phase-integral abstraction for $0 < \theta < \pi$:

$$\phi \approx \text{Re} \int_{-\tau_\infty}^0 [q_2 - \hat{q}_2 + (1 + \hat{T}^2)^{1/2} - (1 + T^2)^{1/2}] d\tau + \tilde{\gamma}(y) - \tilde{\gamma}(\lambda) \quad (2.437)$$

$$\chi \approx \text{Re} \int_{-\tau_\infty}^0 [q_2 - \hat{q}_2 + (1 + \hat{T}^2)^{1/2} - (1 + T^2)^{1/2}] d\tau + \tilde{\gamma}(\mu) - \tilde{\gamma}(\lambda) \quad (2.438)$$

while for $0 < \theta < 1/2\pi$ we propose

$$\begin{aligned} z^2 \approx & \frac{\exp(-2y)[1 - \exp(-2\mu)]}{1 - \exp[-2(y+\mu)]} \exp \left[-2\text{Im} \int_{-\tau_\infty}^{\tau_1^*} (p_2 - \hat{p}_2) d\tau \right] \\ & \times \exp \left[-2\text{Im} \int_{\tau_1^*}^{\tau_2} (q_2 - \hat{q}_2) d\tau + 2\text{Im} \int_{\tau_2}^0 (p_2 - \hat{p}_2) d\tau \right] \end{aligned} \quad (2.439)$$

where

$$p_2 \equiv q_2 - \frac{i}{2} \frac{d}{d\tau} \ln[T + (1 + T^2)^{1/2}] \quad (2.440)$$

and for $1/2\pi < \theta < \pi$ we propose

$$z^2 \approx 1 - \frac{[1 - \exp(-2y)]}{1 - \exp[-2(y + \mu)]} \exp \left[-2\text{Im} \int_{-\tau_\infty}^0 (p_2 - \hat{p}_2) d\tau \right] \quad (2.441)$$

the different topologies of Figures 2.10a and c being clearly reflected in (2.439) and (2.441).

2.4.6 Discussion

Some interesting mathematical points arising from the preceding treatment appear to be worthy of discussion.

First, the choice of $M_{\kappa, -\mu}(\beta)$ to express $\hat{c}_1^*(\tau)$ in (2.423) is not quite as straightforward [453], [454] as it might appear at first sight, since both $W_{\kappa, \mu}(\beta)$ and $W_{-\kappa, \mu}(\beta)$ are worthy alternative candidates to satisfy the boundary conditions on \hat{c}_1^* at $\tau = -\tau_\infty$. Although physical intuition is suggestive, the correct choice is only dictated by application of the exact first-order coupled equations.

Secondly, there arises the natural question: is $-\tau_\infty$ a transition point, in so far as Stokes lines emanating from the complex transition points pass through $-\tau_\infty$? The

answer is no, except in some technical semantic sense, because, *reductio ad absurdum*, no Stokes phenomenon occurs as we trace the solutions around $-\tau_\infty$ while excluding the other (transition) points. To put it another way, the Stokes constants take zero value. Another indicator is that both arrows in Figures 2.10a–c are outward on the Stokes lines emanating from $-\tau_\infty$. Finally, we note that in the limit as $\lambda \rightarrow i$, for acute θ the lower transition point τ_1^* coalesces with the double pole to yield a simple pole that is a transition point [282]. No contradiction arises. (For obtuse θ , the upper transition point τ_2 coalesces with $-\tau_\infty$.) It will also be observed in Figures 2.10a–c that we have adopted “physical” branch cuts [160]. This choice is essential for the comparison-equation method of Section 2.4.4, if we are to avoid discontinuities in both amplitude and wave function [163].

Next, in deriving expressions (2.404) and (2.406) for θ acute and obtuse respectively, we have of course assumed that there exists a “good path” in the sense of Fröman and Fröman [282]. This is not unreasonable bearing in mind that \hat{c}_2 is necessarily subdominant near $-\tau_\infty$. Perhaps on less firm ground, one may for instance trace \hat{c}_1^* , from $-\tau_\infty$ to 0, circumventing τ_1^* , in the lower half-plane of Figure 2.10a (acute θ). To the right of the branch cut there are two Stokes lines to be crossed, each with its own Stokes constant. There is thus in effect a double Stokes phenomenon [167], and it may be shown that the effective compound Stokes constant is related to c_{BC} , the Stokes constant occurring in equation (2.406).

Perhaps we should say a few words about other related work. One of the principal advantages of the JWKB or Liouville–Green approximation, which we have adopted here, is that it is a *uniform* approximation as emphasized by Olver [478]. However, it should be noted that the latter is primarily concerned with isolated transition points, thus excluding the case of a uniform pair of transition points considered here. As mentioned in the Introduction, an earlier JWKB attempt to describe uniformly two transition points and a pole [232], later applied by Child [115], was not satisfactory in that a transformation of the dependent variable (the amplitude a_2 in our notation), involving the square root of the interaction potential, resulted in a second-order differential equation rather more complicated than our equation (2.386). Indeed, one of the advantages of our choice of dependent and independent variables is that the model represents a holomorphic mapping in that just as [167]

$$\begin{aligned} H_{22} - H_{11} &\equiv \Delta\epsilon - A \cos \theta \exp(-\alpha R) \\ H_{12} &\equiv \frac{1}{2} A \sin \theta \exp(-\alpha R) \end{aligned} \quad (2.442)$$

yield the pure exponential model, so do

$$\begin{aligned} H_{22} - H_{11} &\equiv \Delta\epsilon(1 + \tanh(\alpha R)) - A \cos \theta \operatorname{sech}^2(\alpha R) \\ H_{12} &\equiv \frac{1}{2} A \sin \theta \operatorname{sech}^2(\alpha R) \end{aligned} \quad (2.443)$$

Notice that neither $H_{22} - H_{11}$ nor H_{12} is constant (cf. [340]). Another defect in the treatment of Dubrovskiy [232] is his use of weak-coupling asymptotics [163] in the resolution of his comparison equations. This results in an erroneous factor in his transition probability and arises from an incorrect handling of $\hat{\mathbf{R}}$ in equation (2.425).

2.5 Other Generalizations

2.5.1 Four Close Curve-Crossing Transition Points

A discussion of the semiclassical two-channel close curve-crossing S -matrix is given, with special reference to Stueckelberg phases as calculated within the non-adiabatic parabolic model [166]. It is shown that the phase T_1 , normally associated with elastic adiabatic evolution through the curve crossing, is considerably in error when calculated within the Landau–Zener approximation - but shows favourable agreement with earlier numerical evaluations from coupled equations, provided the full Zwaan–Stueckelberg phase-integral interpretation is effected.

Previously we reviewed the status of Stueckelberg curve-crossing phases within the parabolic model [163], and in Crothers [165], we refined the nonadiabatic theory of the semiclassical two-channel S -matrix by fully developing the two-state exponential model to describe both crossing and noncrossing. Happily the Zwaan–Stueckelberg phase-integral method [160] provides a consistent interpretation of both models, and it is our purpose to report that such an interpretation effectively applies to the close-curve-crossing problem, in which the impact parameter increases until the classical turning point approaches and eventually reaches the diabatic crossing point.

The close curve-crossing problem was originally formulated by Bykovskii et al. [105] and later analysed by Delos and Thorson [216], [217], and by Child [116]. In summary, with reference to [216], the diabatic two-state impact-parameter equations for the state amplitudes c_1 and c_2 may be reduced to

$$i \frac{dc_1}{ds} = c_2 \exp \left(-2i \int_0^s T(s') ds' \right) \quad (2.444)$$

$$i \frac{dc_2}{ds} = c_1 \exp \left(+2i \int_0^s T(s') ds' \right) \quad (2.445)$$

where the Stueckelberg variable T is given in terms of the diabatic interaction matrix V by

$$T = (V_{22} - V_{11})/(2V_{12}) \quad (2.446)$$

where

$$s(\tilde{t}) = \int_0^{\tilde{t}} V_{12} dt' \quad (2.447)$$

in which the time is given by \tilde{t} . The essence of the close curve-crossing model is to assume that T may be expanded thus

$$T(s) = -\epsilon + 4s^2/\beta^2 \quad (2.448)$$

in which β and ϵ are two independent constant parameters. Equations (2.444) and (2.445) are solved subject to

$$c_1(s(-\infty)) = 1 \quad (2.449)$$

$$c_2(s(-\infty)) = 0 \quad (2.450)$$

in which case the S matrix is given by

$$S_{21} = S_{12} = c_2(s(+\infty)) = -2iz(1 - z^2)^{1/2} \sin(\Gamma_1 + \Gamma_2) \quad (2.451)$$

$$S_{22}^* = S_{11} = e^{-i\zeta} c_1(s(+\infty)) = (1 - z^2)e^{2i\Gamma_1} + z^2 e^{-2i\Gamma_2} \quad (2.452)$$

The extra adiabatic phase ζ is fully explained in [167] and need not be elaborated here. Delos and Thorson [217] calculated z , Γ_1 , and $\Gamma_1 + \Gamma_2 - \pi$ in particular for large β , as recorded in their figures 8, 10, and 9, respectively. Although Stueckelberg estimates of z and $\Gamma_2 - \pi$ were given, none was given for Γ_1 . Numerical values of z have also been compared with Stueckelberg estimates by Child [116] for $\beta = 5$. It is therefore of interest to obtain a Stueckelberg estimate of Γ_1 . Within the Zwaan–Stueckelberg interpretation of the parabolic model [160], [167], the parameters of the S -matrix are given by

$$\Gamma_1 = \frac{\pi}{4} + \frac{y}{\pi} \ln\left(\frac{y}{\pi}\right) - \frac{y}{\pi} - \arg \Gamma\left(1 + i\frac{y}{\pi}\right) \quad (2.453)$$

$$\Gamma_2 = x \quad (2.454)$$

$$z = \exp(-y) \quad (2.455)$$

where

$$x + iy = 2 \int_0^{\frac{1}{2}\beta(i+\epsilon)^{1/2}} (1 + T^2)^{1/2} ds = \frac{\beta}{2} \int_{-\epsilon}^i \left(\frac{1 + T^2}{\epsilon + T} \right)^{1/2} dT \quad (2.456)$$

We note that these formulae differ in two respects from those of Delos and Thorson [219] and therefore of Delos [215]. Firstly, there is a formal difference of π in the definition of Γ_2 . This is due to our adoption of an external minus in expression (2.451), in accordance with a positive potential V_{12} [167]. Secondly, and of some fundamental importance, the y in (2.453) is given by (2.456) and not by $\pi T_0/2$, the Landau–Zener value adopted by Delos (cf. also expression (72) of [160]) in which T_0 is the value of the Stueckelberg variable T at the diabatic curve crossing.

Expression (2.456) may be evaluated as follows. Setting

$$2s/\beta = (T + \epsilon)^{1/2} = \sin \theta(i + \epsilon)^{1/2} \quad (2.457)$$

we obtain

$$\begin{aligned} x + iy &= \beta \exp\left(\frac{1}{4}\pi i\right) (1 - i\epsilon)(1 + i\epsilon)^{1/2} \\ &\times \int_0^{\pi/2} d\theta \cos^2 \theta \left(1 + \frac{(1 - i\epsilon)}{(1 + i\epsilon)} \sin^2 \theta\right)^{1/2} \end{aligned} \quad (2.458)$$

$$= \beta \exp\left(\frac{1}{4}\pi i\right) (1 - i\epsilon)(1 + i\epsilon)^{1/2} \frac{1}{4} \pi {}_2F_1\left(-\frac{1}{2}, \frac{1}{2}; 2; -\frac{(1 - i\epsilon)}{(1 + i\epsilon)}\right) \quad (2.459)$$

$$\begin{aligned} &= \frac{\beta \exp\left(\frac{1}{4}\pi i\right) (1 + \epsilon^2) \pi^{3/2}}{4\sqrt{2}} \left[\left(\frac{{}_2F_1\left(\frac{1}{4}, \frac{5}{4}; \frac{1}{2}; -\epsilon^2\right)}{\Gamma\left(\frac{3}{4}\right)\Gamma\left(\frac{7}{4}\right)} \right) \right. \\ &\quad \left. - 2i\epsilon \left(\frac{{}_2F_1\left(\frac{3}{4}, \frac{7}{4}; \frac{3}{2}; -\epsilon^2\right)}{\Gamma\left(\frac{5}{4}\right)\Gamma\left(\frac{1}{4}\right)} \right) \right] \end{aligned} \quad (2.460)$$

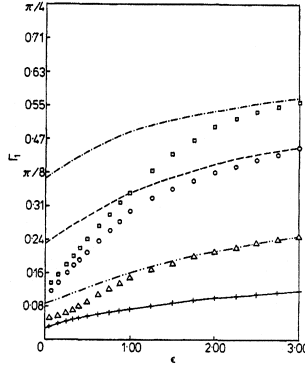


Fig. 2.11. The phase $\Gamma_1(\beta, \epsilon)$ as given by (2.453). This work: --- $\beta = 1$; ---- $\beta = 2$; - · - $\beta = 5$; — $\beta = 10$. [217] square $\beta = 1$; circle $\beta = 2$; triangle $\beta = 5$; cross $\beta = 10$

where we have applied the binomial series in (2.458) and used identities (5.4.14) and (8.1.4) of [1] to obtain (2.460) from (2.459). Expression (2.460) may of course be continued analytically for larger values of ϵ^2 . For $\epsilon = 0$, the curve-crossing point coincides with the point of closest approach, that is, the classical turning point, so that T_0 is zero and the Γ_1 of [219] is $1/4\pi$, whereas (2.460) gives

$$x + iy = \frac{\beta \exp\left(\frac{1}{4}\pi i\right) \pi^{3/2}}{4\sqrt{2} \Gamma\left(\frac{3}{4}\right) \Gamma\left(\frac{7}{4}\right)} \approx 0.618(1 + i)\beta \quad (2.461)$$

For larger positive values of ϵ , it was found more expedient to put $T = i\tau$ to evaluate y as

$$y = \frac{1}{2}\beta \int_0^1 (1 - \tau^2)^{1/2} (\epsilon^2 + \tau^2)^{-1/4} \cos\left[\frac{1}{2} \tan^{-1}(\tau/\epsilon)\right] d\tau \quad (2.462)$$

To evaluate expression (2.453) for Γ_1 we used

$$\arg \Gamma(1 + iy) = -\gamma c + \sum_{n=0}^{\infty} \left[\frac{\gamma}{n+1} - \tan^{-1} \left(\frac{\gamma}{n+1} \right) \right] \quad (2.463)$$

$$= \gamma \ln \gamma - \gamma + \frac{1}{4}\pi - \sum_{n=1}^{\infty} \frac{(-1)^{n-1} B_{2n}}{(2n-1)(2n)\gamma^{2n-1}} \quad (\gamma \gg 1) \quad (2.464)$$

where c is Euler's constant and B_{2n} is a Bernoulli number. The results for Γ_1 are presented in Figure 2.11. As β increases, the accuracy of our Γ_1 improves rapidly over an ever-increasing range of ϵ . Even for the worst case shown, namely $\beta = 1$ and $\epsilon = 0$, which corresponds to a very close crossing at high speed, the antithesis of nonadiabatic conditions, the error is only of the order of 15° . We therefore conclude that for the Stokes constant Γ_1 the Stueckelberg strong-coupling limit, namely zero, is a better approximation than the Landau-Zener weak-coupling limit, namely $1/4\pi$ at ($\epsilon = 0$), the more so the higher is β .

We have not attempted comparison between the Φ_A of figure 9 of [217] and our $\Gamma_1 + \Gamma_2$ since we note considerable difference between their adiabatic-perturbation estimate and our $x - \pi$ at $\epsilon = 0$, particularly for $\beta = 10$. However, we do note that addition of our Γ_1 to their adiabatic-perturbation estimates improves agreement with their coupled-equation values, at the higher ϵ -values and lower β -values of their figure 9.

In conclusion, we observe that the acceleration effects at the close crossing, represented by the occurrence of T in the denominator of (2.456), may largely be simulated by the correct Zwaan–Stueckelberg interpretation of the parabolic model. Semiclassical deflection functions [25] and semiclassical probabilities [26] are presented for close curve-crossing.

2.5.2 Circuit-Dependent Adiabatic Phase Factors from Phase Integral Theory

We show that circuit-dependent adiabatic phase factors occur naturally in the phase-integral theory of atomic collisions, being a physical manifestation of the Stokes phenomenon familiar in asymptotic analysis. This implies a generalisation of Berry’s work on geometric phase factors for situations involving adiabatic parallel transport around closed circuits in *the complex plane* [153].

There has been considerable interest in “geometric” phase factors arising from adiabatic transitions [69] in many areas of physics, including optics [114], [582], [70], and quantum theory [561], [374], [375], [397], [4], [80], [540]. When a system is adiabatically transported around a closed circuit, the system returns to its original state apart from a phase factor. This factor contains, in addition to the usual dynamical phase e^{-iEt} , a circuit-dependent component [69].

These latter adiabatic phases arise naturally in the phase-integral theory [324], [477] of heavy-atom collision processes, due originally to Zwaan [614] and Stueckelberg [574]. The nature of the adiabatic phase then depends on particular properties of the adiabatic potentials governing the motion, which must be analytically continued into the complex plane.

Indeed, such phases occur generally in the theory of differential equations, whether associated with classical or quantal phenomena [324]; their origin is rooted within the Liouville–Green (more commonly known as the JWKB) phase-integral method of solution. The Zwaan–Stueckelberg technique is based on continuing analytically the asymptotic JWKB phase integrals into the complex R -plane (R being, for example, the internuclear distance in typical atomic problems) at sufficient distance from any points where such solutions break down (turning points, etc.) [160]. An alternative yet related method based on convergent series expansions, but still involving analytical continuation, is that due to Fröman and Fröman [282]. The point we wish to draw attention to here is the key role played by the *Stokes phenomenon* in obtaining the correct phase-integral solutions [160], [28], [152].

For the description of nonadiabatic transitions accompanying atomic collisions, a consistent phase-integral analysis can only be made within the adiabatic representation [160], [152]. The adiabatic phase that arises may then be due to a branch point of the quantal wave function at a regular singular point, where a JWKB solution is

uniformly valid. Equally, it may result from the presence of a (complex) adiabatic degeneracy, which is an isolated transition point at which JWKB solutions break down [175], [28], [152].

For integral transition points in the context of coupled channels, the adiabatic phase is typically an elastic Stueckelberg phase, which in turn is related to the phase of a Stokes constant associated with a particular Stokes line [160], [28], [152].

More generally, when both types of point occur [28], the adiabatic phase derives from a Stokes constant and/or a complex Coulomb phase. For the purposes of illustration, consider a time-dependent treatment in which the wave function is written

$$\Psi = c_1(\tilde{t})\psi_1(\mathbf{R}, \mathbf{r}) + c_2(\tilde{t})\psi_2(\mathbf{R}, \mathbf{r}) \quad (2.465)$$

with \tilde{t} being the time, R the internuclear separation of two heavy nuclei, and r denoting the internal electronic degrees of freedom; ψ_1 and ψ_2 are assumed to be orthogonal and to have adiabatic eigenenergies E_1 and E_2 . Then in the one-pole, two-transition-point theory [28], the time-dependent coefficients c_1 and c_2 are given by

$$-\infty \leq \tilde{t} \ll -t_x :$$

$$c_1(\tilde{t}) = \exp\left(-i \int_{-\infty}^{\tilde{t}} E_1 dt'\right) \quad c_2(\tilde{t}) = 0$$

$$-t_x \ll \tilde{t} \ll t_x :$$

$$c_1(\tilde{t}) = (1 - P)^{1/2} \exp\left(i\phi - i \int_{-\infty}^{\tilde{t}} E_1 dt'\right)$$

$$c_2(\tilde{t}) = P^{1/2} \exp\left(i\chi - i \int_{-\infty}^{-t_x} E_1 dt' - i \int_{-t_x}^{\tilde{t}} E_2 dt'\right)$$

$$t_x \ll \tilde{t} \leq +\infty :$$

$$c_1(\tilde{t}) = (1 - P) \exp\left(2i\phi - i \int_{-\infty}^{\tilde{t}} E_1 dt'\right)$$

$$+ P \exp\left(2i\chi - i \int_{-\infty}^{-t_x} E_1 dt' - i \int_{-t_x}^{t_x} E_2 dt' - i \int_{t_x}^{\tilde{t}} E_1 dt'\right)$$

$$c_2(\tilde{t}) = -P^{1/2}(1 - P)^{1/2} \exp\left(i\phi - i\chi - i \int_{-\infty}^{t_x} E_1 dt' - i \int_{t_x}^{\tilde{t}} E_2 dt'\right)$$

$$+ P^{1/2}(1 - P)^{1/2} \exp\left(i\chi - i\phi - i \int_{-\infty}^{-t_x} E_1 dt' - i \int_{-t_x}^{\tilde{t}} E_2 dt'\right)$$

from which the independent elements of the scattering matrix are obtained as

$$S_{11} = [P \exp(-2i\sigma + 2i\chi) + (1 - P) \exp(2i\phi)] \exp(2i\eta_1) \quad (2.466a)$$

$$S_{12} = -2iP^{1/2}(1 - P)^{1/2} \sin(\sigma + \phi - \chi) \exp[i(\eta_1 + \eta_2)] \quad (2.466b)$$

In these equations, P is the single transition probability

$$P = \exp(-\delta) \sinh \mu / \sinh(\mu + \delta)$$

the elastic scattering phase shifts are

$$\eta_j = -\frac{1}{2} \int_{-\infty}^{+\infty} E_j dt' \quad j = 1, 2$$

and the real nonadiabatic parameters σ and δ are defined in terms of the phase integral

$$\sigma + i\delta = \int_0^{t_c} (E_2 - E_1) dt'$$

In the last equation, t_c is a zero of the integrand (point of complex adiabatic degeneracy); t_x is the point at which the double Stokes line connecting t_c , with t_c^* intersects the real axis. The important additional phases ϕ and χ can be expressed as

$$\begin{aligned}\phi &= \mathcal{A}(\delta) - \mathcal{A}(\lambda) \\ \chi &= \mathcal{A}(\mu) - \mathcal{A}(\lambda)\end{aligned}$$

where μ and λ are defined phase integrals [28], and

$$\mathcal{A}(x) = \frac{1}{2}\pi + x \ln x - x - \arg \Gamma(1 + ix)$$

where Γ is the gamma function.

Now the adiabatic limit corresponds to that in which both λ and μ tend to $+\infty$: P , ϕ , and χ then all tend to zero. However, P tends to zero much faster than \mathcal{A} and therefore χ and ϕ (see, e.g., [459]); indeed ϕ must remain finite for any collision process. It follows that the additional adiabatic phase γ , which is the difference between twice the dynamical adiabatic phase η_1 and the phase of the exact S_{11} matrix element in (2.466a), is given by

$$\gamma(\tilde{t}) = \phi[H(\tilde{t} + t_x) + H(\tilde{t} - t_x)]$$

where $H(x)$ is the Heaviside step function. Hence

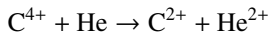
$$\dot{\gamma}(\tilde{t}) = \phi[\delta(\tilde{t} + t_x) + \delta(\tilde{t} - t_x)]$$

with $\delta(x)$ the one-dimensional Dirac delta function. γ is thus a discontinuous constant that arises from the fact that JWKB phase integrals must be traced away from the points t_x , t_c , and t_c^* .

Defining the vector of coefficients $\begin{bmatrix} c_1(t) & c_2(t) \end{bmatrix}^T$ from (2.465), then what we have done amounts to adiabatic parallel transport of $\begin{bmatrix} c_1 & c_2 \end{bmatrix}^T$ around the perimeter of an infinite semicircle in the complex plane whose base is the real t -axis, as a result of which an adiabatic phase factor $\exp(i\gamma)$ is acquired.

Other two-transition-point (parabolic) problems are all special limits of this case [28]. Moreover, the phase integral analysis can easily be adapted to handle fractional transition points [426], [183].

An example of the application of phase-integral methods to experimental atomic collision phenomena concerns the two-electron capture process:



at energies from 300 eV to 1.5 keV. Oscillations in the experimental energy gain, and differential cross sections for this reaction are interpreted as being due to Stueckelberg interferences arising from a phase-integral analysis; agreement between theory and experiment is very good [29].

We conclude that, from the standpoint of phase-integral theory, both nonadiabatic transitions [160] and the adiabatic phase γ are physical manifestations of the Stokes phenomenon. There is a certain similarity between γ and Berry's geometric phase: both are associated with cyclic evolution in the adiabatic limit of a gauge-invariant theory [4]. However, whereas the latter arises as a real-surface anholonomic phase, in our situation the closed circuit lies in the complex plane and the resulting phase is associated with a different geometric structure. Simon [561] points out that Berry's phase can only arise in connection with phenomena involving magnetic fields or some other condition producing a nonreal Hamiltonian. By contrast, the phase-integral approach deals with real Hamiltonians, which are continued analytically into the complex plane in order to derive consistent solutions on the real axis.



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