PHYSICAL REVIEW A VOLUME 36, NUMBER 4 AUGUST 15, 1987

# Theory of inelastic scattering of a particle in the near-adiabatic limit

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(Received 27 January 1987)

A semiclassical theory for inelastic scattering of a particle by a two-state system in the near-adiabatic limit is developed. The exponentially small transition amplitude is calculated. The theory is an extension of Pokrovskii and Khalatnikov's theory for above-barrier reflection (Zh. Eksp. Teor. Fiz. **40**, 1713 (1961) [Sov. Phys.—JETP **13**, 1207 (1961)]). The analysis involves studies of the WKB solutions in the complex coordinate plane along certain contours. The region of validity of the theory is established. Our result has the same form as the Landau-Zener-Stueckelberg formula; however, our theory is applicable to more general systems. Numerical comparisons with exact solutions are presented; the differences between our results and exact solutions become negligible as the adiabatic limit is approached.

## I. INTRODUCTION

The inelastic scattering problem of a particle by dynamical systems with internal degrees of freedom is an important problem in many fields of physics and chemistry. In various contexts the internal degrees of freedom could represent phonons in solid, vibrational states of a molecule, atomic energy levels, ionization states, etc. Consider the scattering of a particle by a harmonic oscillator, for example. In the adiabatic limit in which a heavy particle is incident with low velocity, the oscillator wave function follows the interaction potential due to the particle adiabatically and returns to its initial state as the particle leaves the interaction region; even if inelastic scattering is energetically possible, the inelastic transition amplitude approaches zero in the adiabatic limit. For a small but finite incident velocity the transition amplitude is exponentially small as a function of a parameter which characterizes the deviation from the adiabatic limit. Near the adiabatic limit a WKB expansion in the appropriate small parameter is natural; such an expansion yields a vanishing transition amplitude in any finite order. Many approaches[1] have been developed in the past to deal with the problem with various degrees of success. However, questions of the validity and generality of those approaches have remained unresolved. In this work we have developed a rigorous treatment of this problem to obtain exponentially small transition amplitudes for general interaction potentials between a particle and a system with two internal states.

Stueckelberg[2] was the first to apply a Zwaan type of analysis of the WKB solutions to the problem of the inelastic transition. His theory was based on the so-called Stokes constant method. There have been a number of studies[1,3] of the justification of Stueckelberg's method. In the classical trajectory theory, for example, the Stokes constant has been derived and the ambiguity in its phase has been eliminated. However, this has been justified only for two special situations: where the trajectories nearly cross,[1] and where the trajectories have nearly the same turning points.[4] We are not aware of any other methods which convincingly justify the Stokes constant method in more general cases.

The present theory is an extension of Pokrovskii and Khalatnikov's theory[5] for above-barrier reflection. Our result agrees with the Landau-Zener-Stueckelberg formula. However, our theory is not limited to the above-mentioned special situations and its region of validity is clearly established. This region includes cases which previously were believed to be outside the range of applicability of Stueckelberg's method.[6]

In Sec. II we review the work of Pokrovskii and Khalatnikov and in Sec. III we review the two-state model and the adiabatic basis. Our procedure for obtaining the transition amplitude is presented in Sec. IV and numerical results are described in Sec. V. Mathematical proofs of the propositions used in Sec. IV are given in the Appendix.

## II. ABOVE-BARRIER REFLECTION

Consider a one-dimensional potential scattering problem with a localized repulsion potential $V(x)$. If $E > V(x)$ everywhere on the real axis, the Schrödinger equation

$$\frac{d^2\Psi(x)}{d^2x}+\alpha^2[E-V(x)]\Psi(x)=0 , \tag{1}$$

$$\alpha \equiv \frac{\sqrt{2M}}{\hbar} , \tag{2}$$

has a physical solution corresponding to incidence from the left, which satisfies the following asymptotic conditions:

$$\Psi(x) \rightarrow \begin{cases} \dfrac{1}{\sqrt{\bar{q}}}(e^{i\alpha\bar{q}x}+Re^{i\alpha\bar{q}x}), & x\rightarrow -\infty \quad (3)\\[2ex] \dfrac{T}{\sqrt{\bar{q}}}e^{i\alpha\bar{q}x}, & x\rightarrow +\infty \quad (4)\end{cases}$$

where

 

$$\bar{q}=\lim_{x\to\pm\infty}\sqrt{E-V(x)}\ , \tag{5}$$

$R$ is the reflection coefficient, and $T$ is the transmission coefficient. In the semiclassical limit $\alpha\to\infty$, $T$ tends to one and $R$ is exponentially small in $\alpha$. On the real axis the WKB solutions of Eq. (1) are

$$\Psi^{\pm}(x,\tilde{z})=\frac{1}{\sqrt{q(x)}}\exp\left[\pm i\alpha\int_{\tilde{z}}^{x}q(x)dx\right]\ , \tag{6}$$

where

$$q(x)=\sqrt{E-V(x)}\ , \tag{7}$$

and $\tilde{z}$ is an arbitrary but fixed lower bound which may be real or complex. These solutions have an error of order $\alpha^{-1}$. In the following we shall use the symbol $\approx$ to denote an approximate equality which becomes exact in the limit $\alpha\to\infty$. According to the boundary condition (3), the physical solution can be expressed in terms of the WKB solution,

$$\Psi(x)\approx A^{+}\Psi^{+}(x,\tilde{z}),\quad x\to\infty \tag{8}$$

where $A^{+}$ is a constant. As we trace the solution along the real axis beginning at $+\infty$, Eq. (8) remains valid uniformly all the way to $-\infty$. But $\Psi^{+}$ does not include the exponentially small reflected wave. In fact, $R$ cannot be obtained even if we expand the solution to higher orders in powers of $\alpha^{-1}$. Pokrovskii and Khalatnikov[5] developed a method for obtaining the exponentially small $R$ to leading order. We now review their work briefly.

Throughout this work we shall use $z$ to denote a complex coordinate and use $x$ to denote a real coordinate. We assume that all potentials can be analytically continued into those regions of the $z$ plane which are relevant to our discussions. In order to obtain $R$ we must construct a solution of the Schrödinger equation along a path in the $z$ plane where, even as $\alpha\to\infty$, the ratio of reflected to incident wave functions [see Eq. (3)] remains finite and does not tend exponentially to zero. This path passes through a point $z_c$, defined by $q(z_c)=0$,[7] where the WKB solution breaks down. However, similar to the familar case of a classical turning point on the real axis, near $z_c$ an exact solution of the Schrödinger equation can be obtained and joined to WKB solutions. If there are more than one $z_c$, the one closest to the real axis must be chosen.

Consider now the transition point $z_c$. The appropriate lines passing through $z_c$ are given by the condition

$$\mathrm{Im}\int_{z_c}^{z}q(z')dz'=0\ . \tag{9}$$

They are the so-called anti-Stokes lines, on which the functions $\Psi^{+}(z,z_c)$ and $\Psi^{-}(z,z_c)$ have the same magnitude, regardless of the value of $\alpha$ [see Eq. (6)]. There are altogether three anti-Stokes lines, two of which are shown schematically in Fig. 1. $L_1$ and $L_2$ are useful to us because they form a contour connecting $+\infty$ and $-\infty$. Asymptotically they run parallel to the $x$ axis at a distance which we denote by $y_1$. The procedure of Ref. 5 for obtaining $R$ is as follows.

Starting with the right-going wave (4) at $+\infty$ on $L_1$, we find the wave function in the asymptotic region,

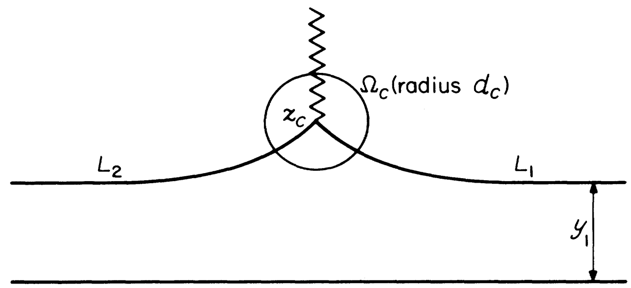


FIG. 1. Typical topology of the complex transition point $z_c$ and anti-Stokes lines $L_1$ and $L_2$ are shown for above barrier reflection problem. $L_1$ extends to $+\infty$ and becomes parallel to the real axis at a distance $y_1$ asymptotically. $L_2$ behaves similarly as it extends to $-\infty$.

$$\Psi(z)=\frac{T}{\sqrt{\bar{q}}}e^{i\alpha\bar{q}z}\ , \tag{10}$$

where $z=x+iy_1$. Except in a small neighborhood of radius $O(\alpha^{-2/3})$ near $z_c$, $\Psi(z)$ can be represented on $L_1$ by

$$\Psi(z)\approx A^{+}\Psi^{+}(z,z_c)\ , \tag{11}$$

where

$$A^{+}=Te^{-i\alpha\eta^{+}}\ , \tag{12}$$

and

$$\eta^{\pm}=\pm\left[\int_{z_c}^{\pm\infty}[q(z')-\bar{q}]dz'-\bar{q}z_c\right]\ . \tag{13}$$

The solution is then matched to the exact solutions of the Schrödinger equation in the vicinity of $z_c$, which are the familar Airy functions. The Airy solutions are valid in a neighborhood $\Omega_c$ of radius $d_c$ around $z_c$ (see Fig. 1), where $d_c$ is the range in which the term $[E-V(z)]$ can be approximated by the linear term of its Taylor expansion at $z_c$; $d_c$ is evidently independent of $\alpha$. The matching region lies between $|z-z_c|=d_c$ and $|z-z_c|\sim\alpha^{-2/3}$. $\alpha$ must be large enough so that the matching region exists. Similarly, except for a small neighborhood of $z_c$, the physical solution on $L_2$ can be represented by a linear combination of the two WKB solutions, Eq. (6),

$$\Psi(z)\approx[B^{+}\Psi^{+}(z,z_c)+B^{-}\Psi^{-}(z,z_c)]\ , \tag{14}$$

where $B^{+}$ and $B^{-}$ are determined by a similar matching procedure to the Airy solution in the vicinity of $z_c$. $B^{+}$ and $B^{-}$ have the same magnitude. On $L_2$, as $x\to-\infty$, $\Psi(z)$, Eq. (14) takes the form

$$\Psi(z)\approx\frac{1}{\sqrt{\bar{q}}}(B^{+}e^{-i\alpha\eta^{-}}e^{i\alpha\bar{q}z}+B^{-}e^{i\alpha\eta^{-}}e^{-i\alpha\bar{q}z})\ . \tag{15}$$

When the appropriate values of $A^{+}$, $B^{+}$, and $B^{-}$ are used and comparison with Eqs. (3) and (4) is made one finds

$$T\approx e^{i\alpha(\eta^{+}+\eta^{-})}\ , \tag{16}$$

$$R\approx -ie^{2i\alpha\eta^{-}}\ . \tag{17}$$

Notice that $|T|\approx 1$, while $R$ is exponentially small.

Let us note in passing that $R$ *cannot* be obtained by using a contour consisting of $L_1^*$ and $L_2^*$, corresponding to $L_1$ and $L_2$, but passing through $z_c^*$, the complex conjugate of $z_c$. The reason is that whereas on $L_1$ and $L_2$, the asymptotic magnitudes of the incident, transmitted, and reflected waves are all equal, on $L_1^*$ and $L_2^*$ the magnitude of the reflected wave is exponentially smaller than those of the incident and transmitted waves by a factor of $e^{-4\alpha\bar{q}y_1}$. Such an exponentially small term is "missed" by our procedure.

## III. ADIABATIC BASIS

We consider the one-dimensional scattering of a particle of mass $M$ by a two-state system with energy splitting $\hbar\omega$. We denote the internal states by $|0\rangle$, the lower-energy state, and $|1\rangle$, the higher-energy one. They form the so-called diabatic basis for a two-dimensional vector space. The Hamiltonian of the total system can be written as

$$H = H_p + H_s + H_{\text{int}} , \tag{18}$$

$$H_p = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + V_0(x) , \tag{19}$$

$$H_s = -\frac{\hbar\omega}{2}\sigma_z , \tag{20}$$

$$H_{\text{int}} = \tilde{V}_1(x)\sigma_z + V_2(x)\sigma_x , \tag{21}$$

where $H_p$ is the Hamiltonian of the particle, $H_s$ is the Hamiltonian of the two-state system, $H_{\text{int}}$ is the interaction Hamiltonian, and $\sigma_x, \sigma_z$ are Pauli matrices. The two-component Schrödinger equation in this basis is

$$H \begin{bmatrix} \Psi_0(z) \\ \Psi_1(z) \end{bmatrix} = E \begin{bmatrix} \Psi_0(z) \\ \Psi_1(z) \end{bmatrix} . \tag{22}$$

We assume that $V_0(x)$, $\tilde{V}_1(x)$, and $V_2(x)$ all tend to zero as $x \to \infty$ and that the particle comes in from the right. For a fixed energy, the velocity of the incoming particle decreases as the mass is increased. In the limit of large $\alpha$ the particle acts on the two-state system as a slowly varying external field and the two-state system follows nearly adiabatically; in the infinite $\alpha$ limit there is no inelastic transition. In the extreme adiabatic limit ($\alpha = \infty$) the Hamiltonian is trivially diagonalized at each $z$ by the transformation[1,2]

$$U = \begin{bmatrix} \cos\theta(z) & \sin\theta(z) \\ -\sin\theta(z) & \cos\theta(z) \end{bmatrix} , \tag{23}$$

where

$$\tan 2\theta(z) = \frac{V_2(z)}{V_1(z)} , \tag{24}$$

with

$$V_1(z) \equiv \tilde{V}_1(z) - \frac{\hbar\omega}{2} . \tag{25}$$

Equation (25) does not determine $\theta(z)$ uniquely; we make the choice of $\theta(z)$ to tend to 0 as $x \to \infty$ so that

$$\cos\theta(z) = \frac{1}{\sqrt{2}} \left[ 1 - \frac{V_1(z)}{[V_1^2(z) + V_2^2(z)]^{1/2}} \right]^{1/2} , \tag{26}$$

and

$$\sin\theta(z) = -\frac{1}{\sqrt{2}} \left[ 1 + \frac{V_1(z)}{[V_1^2(z) + V_2^2(z)]^{1/2}} \right]^{1/2} . \tag{27}$$

We shall assume that there is a pair of points $z_c$ and $z_c^*$ where $V_1^2 + V_2^2$ vanishes. If there are more than one pair of $z_c$ we choose the one which is closest to the real axis. $(V_1^2 + V_2^2)^{1/2}$ is defined to be positive along the real axis with one cut going from $z_c$ to $i\infty$ and the other from $z_c^*$ to $-i\infty$. This choice of branch cuts insures that the mixing angle $\theta(z)$ is a continuous function of $x$ on the real axis. For $z$ real, $U$ is unitary. The new basis vectors

$$\begin{bmatrix} |0,z\rangle \\ |1,z\rangle \end{bmatrix} = U \begin{bmatrix} |0\rangle \\ |1\rangle \end{bmatrix} \tag{28}$$

constitute the so-called adiabatic basis. In this basis the Hamiltonian takes the form

$$H_a = UHU^{-1} \tag{29}$$

$$= \begin{bmatrix} -\frac{\hbar^2}{2M}\frac{d^2}{dz^2} + \frac{\hbar^2}{2M}(\theta')^2 + U_0(z) & \frac{\hbar^2}{2M}\theta'' + \frac{\hbar^2}{M}\theta'\frac{d}{dz} \\ -\frac{\hbar^2}{2M}\theta'' - \frac{\hbar^2}{M}\theta'\frac{d}{dz} & -\frac{\hbar^2}{2M}\frac{d^2}{dz^2} + \frac{\hbar^2}{2M}(\theta')^2 + U_1(z) \end{bmatrix} , \tag{30}$$

where $U_0, U_1$ are the adiabatic potentials,

$$U_0(z) \equiv V_0(z) - [V_1(z)^2 + V_2(z)^2]^{1/2} , \tag{31}$$

and

$$U_1(z) \equiv V_0(z) + [V_1(z)^2 + V_2(z)^2]^{1/2} . \tag{32}$$

The Schrödinger equation becomes

$$H_a \begin{bmatrix} \Phi_0(z) \\ \Phi_1(z) \end{bmatrix} = E \begin{bmatrix} \Phi_0(z) \\ \Phi_1(z) \end{bmatrix} , \tag{33}$$

where

$$\begin{bmatrix} \Phi_0(z) \\ \Phi_1(z) \end{bmatrix} \equiv U \begin{bmatrix} \Psi_0(z) \\ \Psi_1(z) \end{bmatrix} . \tag{34}$$

It is easy to see that

$$\Psi_0(z)|0\rangle + \Psi_1(z)|1\rangle \equiv \Phi_0(z)|0,z\rangle + \Phi_1(z)|1,z\rangle . \tag{35}$$

If the off-diagonal terms of $H_a$ are neglected, $\Phi_0$ and $\Phi_1$ are uncoupled. The WKB solutions ($\alpha \to \infty$) for these uncoupled equations have the usual form,

$$\Phi_0^{\pm}(z,z^{(0)})=\frac{1}{\sqrt{q_0(z)}}\exp\left[\pm i\alpha\int_{z}^{z}q_0(z)dz\right], \tag{36}$$

and

$$\Phi_1^{\pm}(z,z^{(1)})=\frac{1}{\sqrt{q_1(z)}}\exp\left[\pm i\alpha\int_{z}^{z}q_1(z)dz\right], \tag{37}$$

where

$$q_i(z)=\sqrt{E-U_i(z)}\ , \tag{38}$$

and $z^{(i)}$ is an arbitrary but fixed lower bound. The branch of $q_i(z)$ is defined so that $q_i(x)=\sqrt{|E-V_i(x)|}$ for $x>x_i$ and $q_i(x)=i\sqrt{|E-V_i(x)|}$ for $x<x_i$, where $x_i$ is the classical turning point defined by

$$E-U_i(x_i)=0,\quad i=0,1\ . \tag{39}$$

If we treat these solutions at the classical turning points $x_i$, we will obtain a reflection coefficient of magnitude 1 and a vanishing inelastic transition amplitude. This remains true in all higher-order WKB approximations. We need to go into the complex $z$ plane and follow the solutions along appropriate contours. We need to consider the singular points: $x_0$, $x_1$, and $z_c$ (see Fig. 2). Note that at $z_c$ the function $\theta(z)$ diverges and hence the off-diagonal terms of $H_a$ also diverge, which signals the failure of the adiabatic solutions. In Fig. 2 we show the anti-Stokes lines defined as follows:

$$L_1,L_2:\mathrm{Im}\int_{z_c}^{z}[q_0(z)-q_1(z)]dz=0\ , \tag{40}$$

$$L_3:\mathrm{Im}\int_{x_1}^{z}q_1(z)dz=0\ , \tag{41}$$

and

$$L_4:\mathrm{Im}\int_{x_0}^{z}q_0(z)dz=0\ . \tag{42}$$

$L_3$ and $L_4$ are just the anti-Stokes lines for ordinary potential scattering problems with classical turning points at $x_1$ and $x_0$. $L_1$ and $L_2$ are the lines on which $\Phi_0^+(z,z_c)[\Phi_0^-(z,z_c)]$ have the same magnitude as $\Phi_1^+(z,z_c)[\Phi_1^-(z,z_c)]$. The topology of Fig. 2 depends on the potentials and the energy. Since $U_1>U_0$, $x_1>x_0$. Both $x_0$ and $x_1$ shift to the right as the energy is decreased, whereas $z_c$ does not depend on the energy. In most previous discussions of Stueckelberg's theory, only the cases where $\mathrm{Re}(z_c)\gg x_0,x_1$ are discussed. We will see that this restriction is not necessary. The general features of $L_1$ and $L_2$ are (1) $L_1$ extends to infinity and becomes parallel to the real axis at a distance $y_1$ for $x\to\infty$, and (2) $L_2$ intercepts the real axis at a point $\bar{x}$ which can easily be shown to be always less than $x_1$. Both $y_1$ and $\bar{x}$ depend on the energy for given potentials.

## IV. INELASTIC TRANSITION AMPLITUDE

Consider the physical solution of the Schrödinger equation (22) along the real axis with the following asymptotic conditions:

$$\Psi_0(x)\to\frac{1}{\sqrt{\bar{q}_0}}(e^{-i\alpha\bar{q}_0x}+A_0^+e^{i\alpha\bar{q}_0x}),\quad x\to\infty$$
$$\to 0,\quad x\to-\infty \tag{43}$$

$$\Psi_1(x)\to\frac{A_1^+}{\sqrt{\bar{q}_1}}e^{i\alpha\bar{q}_1x},\quad x\to\infty$$
$$\to 0,\quad x\to-\infty \tag{44}$$

where $\bar{q}_i=q_i(x\to\infty)$. In the adiabatic limit $A_1^+=0$ and $|A_0^+|$ is 1. In the near-adiabatic limit, $A_1^+$ cannot be determined from the usual treatment of the WKB solutions to all orders whereas $A_0^+$ can be determined to leading order, since its magnitude is $\sim 1$. We have seen in Sec. III that at the complex transition point $z_c$ the adiabatic solutions break down. We shall obtain the transition from one state to the other by a careful treatment of the Schrödinger equation near $z_c$; we need to obtain the exact solutions near $z_c$ in order to connect the WKB solutions on $L_1$ and $L_2$. One might hope to obtain the exponentially small amplitude following a procedure similar to that described in Sec. II; however, the geometry of $L_1$ and $L_2$ are very different for the two

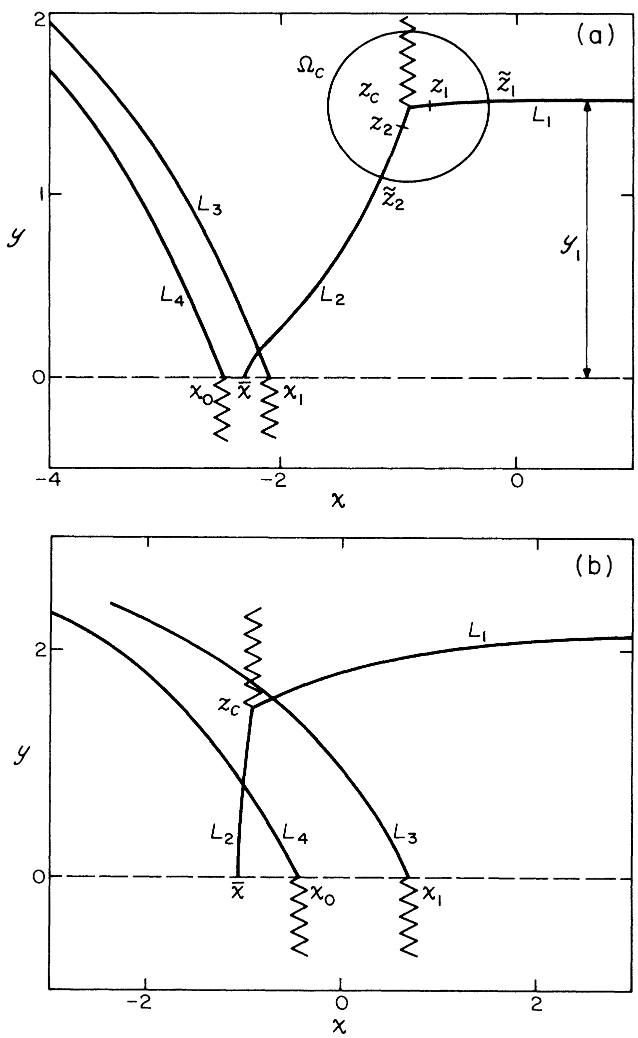


FIG. 2. Transition points $x_0$, $x_1$, $\bar{x}$, $z_c$ and anti-Stokes lines $L_1$, $L_2$, $L_3$, $L_4$ are shown for the curve-noncrossing case in Sec. V: (a) for $E=10$ and (b) for $E=1$.

cases. In the case of above-barrier reflection $L_2$ extends to $-\infty$ where WKB solutions become the exact solutions and yield the exponentially small reflection amplitude. In the present case $L_2$ goes down to the real axis where the potentials do not vanish and hence the exact solutions are not known. A different strategy is needed in making use of the solutions on $L_1$ and $L_2$.

It is helpful to think of the physical solution as a linear combination of two-component Jost functions (JF).[8] A JF is a (nonphysical) solution of the Schrödinger equation which asymptotically has only one incoming or one outgoing wave in one channel. The exact *physical* solution corresponding to the asymptotic conditions (42) and (43) can be written as

$$\Psi_0(x)=\Psi_0^{(0-)}(x)+A_0^\dagger\Psi_0^{(0+)}(x)+A_1^\dagger\Psi_0^{(1+)}(x)\ , \quad (45)$$

$$\Psi_1(x)=\Psi_1^{(0-)}(x)+A_0^\dagger\Psi_1^{(0+)}(x)+A_1^\dagger\Psi_1^{(1+)}(x)\ , \quad (46)$$

where $\Psi_i^{(j\pm)}(x)$ is the component in channel $i$ of the JF with unit incoming $(-)$ or outgoing $(+)$ amplitude in channel $j$. Our objective is to determine the coefficient $A_1^\dagger$ which, by Eq. (44), is the transition amplitude. The procedure is as follows.

(1) We first obtain $A_0^\dagger$, whose magnitude is $\sim 1$, by ordinary WKB techniques, applied entirely within channel 0. (Ordinary reflection by a barrier.)

(2) Next we note that as $x\to-\infty$ each of the JF components in Eqs. (45) and (46) grows exponentially like $\Phi_1^\dagger$, Eq. (37), which is the most rapidly growing exponential. We shall choose $A_1^\dagger$ so that the total coefficient of $\Phi_1^\dagger$ vanishes.

(3) To accomplish step (2), for Eq. (46), we need to know the coefficient of $\Phi_1^\dagger$, for $x\to-\infty$, of each of the JF components $\Psi_1^{(0-)}(x)$, $\Psi_1^{(0+)}(x)$, and $\Psi_1^{(1+)}(x)$. The first two coefficients are exponentially small and need to be carefully calculated on appropriate contours (see below). The last coefficient is of order 1 and can be easily obtained by ordinary WKB techniques, applied entirely to channel 1.

(4) Since this procedure determines $A_1^\dagger$ uniquely, it is not surprising that, in fact, it also makes the leading exponentially growing term of Eq. (45) equal to zero.

We shall need a number of propositions which are proved in the Appendix and which have been verified in our numerical calculations.

*Proposition 1.* Consider the Schrödinger equation (33) on the real axis. Under conditions detailed in the Appendix, the physical solution, which vanishes at $-\infty$ and has an incoming wave in channel 0, has the following components:

$$\Phi_0(x)\approx\left[\frac{d\xi_0}{dx}\right]^{-1/2}\mathrm{Ai}[-\alpha^{2/3}\xi_0(x)],\ \text{everywhere} \quad (47)$$

$$\frac{\Phi_1(x)}{\Phi_0(x)}\approx 0,\ \ x\le x_0\ ,$$
$$\alpha^{1/6}\Phi_1(x)\approx 0,\ \ x>x_0\ , \quad (48)$$

where

$$\tfrac{2}{3}[\xi_i(x)]^{3/2}=\int_{x_i}^{x}q_i\,dx\ , \quad (49)$$

and $q_i$ is given by Eq. (38). The branch of $\xi_i$ in Eq. (49) is defined so that $\xi_i(z)=[-U'(x_i)]^{1/3}(z-x_i)$ in the vicinity of $x_i$. Proposition 1 established the validity of the ordinary WKB solution.

Proposition 2 gives the exact solutions in the vicinity of $z_c$.

*Proposition 2.* Consider a circle $\Omega_c$ of radius $d_c$ around $z_c$. We denote the intersection of $\Omega_c$ with $L_1$ and $L_2$ by $\tilde{z}_1$ and $\tilde{z}_2$, respectively (see Fig. 2). Assume that $V_1'V_1+V_2'V_2$ does not vanish at $z_c$. Then for sufficiently small $d_c$ the general solutions of the Schrödinger equation (22) in $\Omega_c$ are given by

$$\Psi_0(z)\approx e^{i\alpha q_c\zeta}[a_+\mathrm{Ai}(-\alpha^{2/3}C^{2/3}\zeta)+b_+\mathrm{Bi}(-\alpha^{2/3}C^{2/3}\zeta)]$$
$$+e^{-i\alpha q_c\zeta}[a_-\mathrm{Ai}(-\alpha^{2/3}C^{2/3}\zeta)$$
$$+b_-\mathrm{Bi}(-\alpha^{2/3}C^{2/3}\zeta)]\ , \quad (50)$$

to the leading order in $\zeta$, where

$$\zeta=z-z_c\ , \quad (51)$$

$$q_c=\sqrt{E-V_0(z_c)}\ , \quad (52)$$

$$C=\left.\frac{[(V_1^2+V_2^2)']^{1/2}}{2q_c}\right|_{z_c}\ , \quad (53)$$

and $a_\pm$ and $b_\pm$ are arbitrary constants.

Propositions 3 and 4 give the WKB solutions on $L_1$ and $L_2$ which are needed for finding $\Psi_0^{(0+)}(z)$.

*Proposition 3.* Consider the anti-Stokes line $L_1$. Let $z_1$ denote a point on $L_1$ at a fixed distance from $z_c$ and let $L_1^-$ denote $L_1$, excluding the segment from $z_c$ to $z_1$. Under conditions detailed in the Appendix there is a solution of the following form:

$$\Phi_0(z)\approx\Phi_0^+(z,z_c)\ , \quad (54)$$

$$\frac{\Phi_1(z)}{\Phi_0(z)}\approx 0\ , \quad (55)$$

for $z$ on $L_1^-$.

*Proposition 4.* Consider the anti-Stokes line $L_2$. Let $z_2$ denote a point on $L_2$ at a fixed distance from $z_c$ and let $L_2^-$ denote $L_2$, excluding the segment from $z_c$ to $z_2$. Under conditions detailed in the Appendix, there is a solution of the following form:

$$\Phi_0(z)\approx\Phi_0^+(z,z_c)\ , \quad (56)$$

$$\Phi_1(z)\approx\Phi_1^+(z,z_c)\ , \quad (57)$$

for $z$ on $L_2^-$.

On $L_2$, $\Phi_0^+(z,z_c)$ and $\Phi_1^+(z,z_c)$ have the same magnitude. Therefore their coefficients can be determined accurately. To the left of the point $\bar{x}$, $\Phi_1^+(x,z_c)$ becomes exponentially larger than $\Phi_0^+(x,z_c)$, since the real part of the exponent of the former is larger than that of the latter for $x<\bar{x}$.

We now proceed to find the leading exponentially growing parts (for $x\rightarrow-\infty$) of the JF components. Consider first the JF component $\Psi_0^{(0+)}(z)$ in Eq. (45). As $x\rightarrow+\infty$, $\Psi_0^{(0+)}(z)$ on $L_1$ is an outgoing wave in channel 0,

$$\Psi_0^{(0+)}(z)\rightarrow\frac{1}{\sqrt{\bar{q}_0}}e^{i\alpha\bar{q}_0 z},\quad x\rightarrow+\infty \tag{58}$$

where $z=x+iy_1$. According to proposition 3, the continuation of this function on $L_1$ is given by

$$\Psi_0^{(0+)}(z)\approx A_{0,z_c}^{(0+)}\Phi_0^{+}(z,z_c)\cos\theta(z)\ , \tag{59}$$

where $\Phi_0^{+}(z,z_c)$ is the WKB approximation, Eq. (36), of the component of the exact solution along the adiabatic basis vector $|0,z\rangle$;

$$A_{0,z_c}^{(0+)}\equiv e^{-i\alpha\eta_c}\ , \tag{60}$$

$$\eta_c=\int_{z_c}^{\infty}(q_0-\bar{q}_0)dz-\bar{q}_0 z_c\ ; \tag{61}$$

and $\cos\theta(z)$ is given by Eq. (26). The approximation is valid on $L_1$, from $+\infty$ up to a point $a_1$, where $|a_1-z_c|=O(\alpha^{-2/3})$.

We now match this WKB solution (59) to the appropriate linear combination of Airy functions, Eq. (50), at a point $m_1$ at which both the WKB solutions and the Airy solutions become exact in the limit $\alpha\rightarrow\infty$. By taking, for example, $|m_1-z_c|\sim\alpha^{-1/3}$, we see that $|m_1-z_c|/|z_1-z_c|\sim\alpha^{1/3}$, validating the WKB solutions, and $|m_1-z_c|/|\tilde{z}_1-z_c|\sim\alpha^{-1/3}$, validating the Airy solutions. At $m_1$ we can use the asymptotic form of the Airy functions, since the argument, $|\alpha^{2/3}C^{2/3}(m_1-z_c)|$, is $O(\alpha^{1/3})$,

$$\mathrm{Ai}(-w)\sim\frac{1}{\sqrt{\pi}}\frac{1}{w^{1/4}}\sin\left[\tfrac{2}{3}w^{3/2}+\frac{\pi}{4}\right]\ , \tag{62}$$

$$\mathrm{Bi}(-w)\sim\frac{1}{\sqrt{\pi}}\frac{1}{w^{1/4}}\cos\left[\tfrac{2}{3}w^{3/2}+\frac{\pi}{4}\right]\ , \tag{63}$$

where $-2\pi/3<\arg(w)<2\pi/3$. Accordingly, inside $\Omega_c$, the JF component is given by

$$\Psi_0^{(0+)}(z)\approx e^{i\pi/4}\frac{(\alpha^{1/3}C^{1/3}\pi)^{1/2}}{\sqrt{q_c}}\sqrt{-D}\,A_{0,z_c}^{(0+)}e^{iaq_c\zeta}\times[\mathrm{Ai}(-\alpha^{2/3}C^{2/3}\zeta)-i\,\mathrm{Bi}(-\alpha^{2/3}C^{2/3}\zeta)]\ , \tag{64}$$

where $C$ is given by Eq. (53) and

$$D\equiv\left.\frac{V_1}{[(V_1^2+V_2^2)']^{1/2}}\right|_{z_c}\ . \tag{65}$$

In the same way we match the Airy-type solution (64) inside $\Omega_c$, to the appropriate WKB solution on $L_2$, where the asymptotic forms of Airy functions can be found using the following identities:

$$\mathrm{Ai}(e^{-i2\pi/3}w)=e^{-i\pi/3}\left[\tfrac{1}{2}\,\mathrm{Ai}(w)+\frac{i}{2}\mathrm{Bi}(w)\right]\ , \tag{66}$$

$$\mathrm{Bi}(e^{-i2\pi/3}w)=e^{-i\pi/3}[\tfrac{3}{2}i\,\mathrm{Ai}(w)+\tfrac{1}{2}\mathrm{Bi}(w)]\ . \tag{67}$$

This yields, on $L_2$,

$$\Psi_0^{(0+)}(z)\approx A_{0,z_c}^{(0+)}\Phi_0^{+}(z,z_c)\cos\theta(z)-A_{1,z_c}^{(0+)}\Phi_1^{+}(z,z_c)\sin\theta(z)\ , \tag{68}$$

$$A_{1,z_c}^{(0+)}=\epsilon A_{0,z_c}^{(0+)}\ , \tag{69}$$

where $\epsilon=\pm1$ and for any specific potentials is given by

$$\epsilon=\lim_{z\rightarrow z_c}i\cot\theta(z)\ . \tag{70}$$

To be definite we choose $\epsilon=+1$ for the following calculations. From Proposition 4, Eq. (68) is valid on the whole $L_2^-$ down to the real axis. (See Fig. 2.) On the real axis, to the left of the point $\bar{x}$, the JF component is dominated by $\Phi_1^{+}(x,z_c)$.

Therefore, on the real axis, we have

$$\Psi_0^{(0+)}(x)\rightarrow\frac{1}{\sqrt{\bar{q}_0}}e^{i\alpha\bar{q}_0 x},\quad x\rightarrow+\infty \tag{71}$$

$$\approx-\Phi_1^{(0+)}(x)\sin\theta(x),\quad x<\bar{x} \tag{72}$$

where

$$\Phi_1^{(0+)}(x)=A_{1,x_1}^{(0+)}\Phi_1^{+}(x,x_1)\ , \tag{73}$$

$$A_{1,x_1}^{(0+)}=e^{-\alpha\gamma}e^{i\alpha\eta-i\alpha\eta_0}\ , \tag{74}$$

$$\eta_i=\int_{x_i}^{\infty}[q_i(x)-\bar{q}_i]dx-\bar{q}_i x_i\ , \tag{75}$$

and

$$\eta+i\gamma=\int_{x_0}^{z_c}q_0(z)dz-\int_{x_1}^{z_c}q_1(z)dz\ . \tag{76}$$

It is easy to see that $\gamma$ is positive, hence $A_{1,x_1}^{(0+)}$ is exponentially small. The 0 component of the JF, $\Psi_0^{(0-)}(x)$, needed in Eq. (45) can be obtained simply by taking the complex conjugate of $\Psi_0^{(0+)}(x)$,

$$\Psi_0^{(0-)}(x)\rightarrow\frac{1}{\sqrt{\bar{q}_0}}e^{-i\alpha\bar{q}_0 x},\quad x\rightarrow+\infty \tag{77}$$

$$\approx-\Phi_1^{(0-)}(x)\sin\theta(x),\quad x<\bar{x} \tag{78}$$

where

$$\Phi_1^{(0-)}(x)=A_{1,x_1}^{(0-)}\Phi_1^{+}(x,x_1)\ , \tag{79}$$

$$A_{1,x_1}^{(0-)}=ie^{-\alpha\gamma}e^{-i\alpha\eta+i\alpha\eta_0}\ . \tag{80}$$

Finally we require, for Eq. (45), $\Psi_0^{(1+)}$, the 0 component of the JF corresponding to channel 1 outgoing. In the adiabatic basis this JF is, for our purpose, obtainable everywhere on the real axis by ordinary WKB turning point methods,

$$\Phi_1^{(1+)}(x)\rightarrow\frac{1}{\sqrt{\bar{q}_1}}e^{i\alpha\bar{q}_1 x},\quad x\rightarrow+\infty \tag{81}$$

$$\approx A_{1,x_1}^{(1+)}\Phi_1^{+}(x,x_1),\quad x<x_1 \tag{82}$$

where

$$A_{1,x_1}^{(1+)}=e^{-i\alpha\eta_1} \tag{83}$$

and

$$\frac{\Phi_0^{(1+)}(x)}{\Phi_1^{(1+)}(x)}\approx 0, \quad \text{everywhere} . \tag{84}$$

The reason is that for this JF a single component, $\Phi_1^{(1+)}(x)$, is dominant everywhere on the $x$ axis; this is *not* the case for the JF's $(0+)$ and $(0-)$, for which $\Phi_0^{(0\pm)}(x)$ is dominant for $x>\bar{x}$, while $\Phi_1^{(0\pm)}(x)$ is dominant for $x<\bar{x}$. The required component $\Psi_0^{(1+)}(x)$ in the diabatic basis is given by

$$\Psi_0^{(1+)}(x)\approx -\Phi_1^{(1+)}(x)\sin\theta(x), \quad \text{everywhere} . \tag{85}$$

We are now ready to determine the required coefficient $A_1^+$ from the condition that the coefficient of the dominant exponential, for $x\to-\infty$, in Eq. (45) vanishes. Substituting Eqs. (72), (78), and (85) into Eq. (45) gives

$$A_{1,x_1}^{(0-)}+A_0^+A_{1,x_1}^{(0-)}+A_1^+A_{1,x_1}^{(1+)}=0 . \tag{86}$$

For a wave incident in channel 0 with unit amplitude,

$$A_0^+\approx -ie^{2i\eta_0} . \tag{87}$$

Substituting in Eq. (86) for $A_0^+$, $A_{1,x_1}^{(0-)}$, $A_{1,x_1}^{(0+)}$, and $A_{1,x_1}^{(1+)}$, we obtain, on solving for $A_1^+$,

$$A_1^+\approx -2\sin(\alpha\eta)e^{-\alpha\gamma}e^{i\alpha(\eta_0+\eta_1)} . \tag{88}$$

Incidently, we can verify that the coefficient of $\Phi_1^+(x,x_1)$ in Eq. (46), for $x<\bar{x}$, also vanishes as it should if $A_1^+$ is given by Eq. (88).

Following the standard definition of the $S$ matrix,

$$\Psi_0(x)\to\frac{1}{\sqrt{\bar{q}_0}}(e^{-i\alpha\bar{q}_0x}-S_{00}e^{i\alpha\bar{q}_0x}), \quad x\to+\infty \tag{89}$$

$$\Psi_1(x)\to-\frac{S_{01}}{\sqrt{\bar{q}_1}}e^{i\alpha\bar{q}_1x}, \quad x\to+\infty \tag{90}$$

we find that

$$S_{00}\approx ie^{2i\alpha\eta_0} \tag{91}$$

and

$$S_{01}\approx 2\sin(\alpha\eta)e^{-\alpha\gamma}e^{i\alpha(\eta_0+\eta_1)} . \tag{92}$$

[If $\epsilon$ is chosen to be $-1$, the right-hand side of Eq. (92) would change sign.]

Equation (92) has the same form as the Landau-Zener-Stueckelberg formula in the near-adiabatic limit. However, whereas the earlier derivation was limited to the case where $z_c$ is near the real axis (almost crossing adiabats on the real axis) and well to the right of the classical turning points $x_0$ and $x_1$, our derivation is not limited by these restrictions.

We shall now indicate the conditions under which our near-adiabatic approximation is valid. It requires the existence of admissible matching points $m_1$ on $L_1$ and $m_2$ on $L_2$ (see Fig. 2). It is easy to see that if $m_1$ exists so does $m_2$. The existence of $m_1$ requires that

$$|z_1-z_c|\ll d_c . \tag{93}$$

Here $z_1$ is given by the condition

$$\left|\frac{1}{\alpha}\frac{d}{dz}\frac{1}{q_i(z)-q_c}\right|_{z_1}=1 , \tag{94}$$

which is the analog of the condition signaling the breakdown of the standard WKB approximation,[9]

$$\left|\frac{1}{\alpha}\frac{d}{dz}\frac{1}{q(z)}\right|=1 ; \tag{95}$$

and $d_c$ is the distance from $z_c$ over which the following expansion is valid:

$$q_0(z)\equiv\{E-V_0(z)+[V_1(z)^2+V_2(z)^2]^{1/2}\}^{1/2}$$
$$=q_c+C(z-z_c)^{1/2} , \tag{96}$$

where $q_c$ and $C$ are defined in Eqs. (52) and (53). Combining (93) and (94) gives

$$\alpha d_c^{3/2}|C|\gg 1 . \tag{97}$$

Since $\alpha=\sqrt{2M}/\hbar$ it is evident that for any given potentials and given incident energy, the condition (97) will always be satisfied for sufficiently large $M$.

The left-hand side of Eq. (97) is the dimensionless large parameter which characterizes the deviation from the adiabatic limit. [Let us remark that condition (97) is not necessarily equivalent to the intuitively suggestive criterion that the exponent $\alpha\gamma$, in Eq. (92), be $\gg 1$.]

## V. COMPARISON WITH NUMERICAL RESULTS

We present comparisons between our results and exact numerical solutions. We choose exponential potentials,

$$V_0(z)=u_0e^{-z} , \tag{98}$$

$$V_1(z)=u_1e^{-z}-\frac{\hbar\omega}{2} , \tag{99}$$

$$V_2(z)=u_2e^{-z} , \tag{100}$$

where the $u_i$ are the strengths of $V_i(z)$. Varying $u_i$'s we can study both curve-crossing and curve-noncrossing cases. We shall set $\hbar\omega=1$.

(1) Curve noncrossing. In this case we choose $u_0=1.02$, $u_1=0.02$, $u_2=0.2$. Two energies $E=1,10$ are studied for different values of $\alpha$. The two cases have very different topology of $z_c$, $x_0$, $x_1$ and anti-Stokes lines as shown in Figs. 2(a) and 2(b). Although the diabatic potentials $V_0(x)\pm\tilde{V}_1(x)$ cross at $x=-3.2$, this point is far to the left of the classical turning points. In the region where the transition takes place the adiabatic potentials are almost parallel to each other. In Fig. 3 the absolute values of $\Phi_0^{(0+)}(x)$ and $\Phi_1^{(0+)}(x)$ for $E=10$ are plotted for different values of $\alpha$. For large $\alpha$, channel 1 is seen to dominate for $x<\bar{x}$. Numerical results for the $S$ matrix are listed in Table I. The differences between semiclassical and exact solutions diminish in the limit of large $\alpha$ for both energies.

(2) Curve crossing. In this case we choose $u_0=1.2$, $u_1=0.5$, $u_2=0.2$. The diabatic potentials cross at $x=0$.

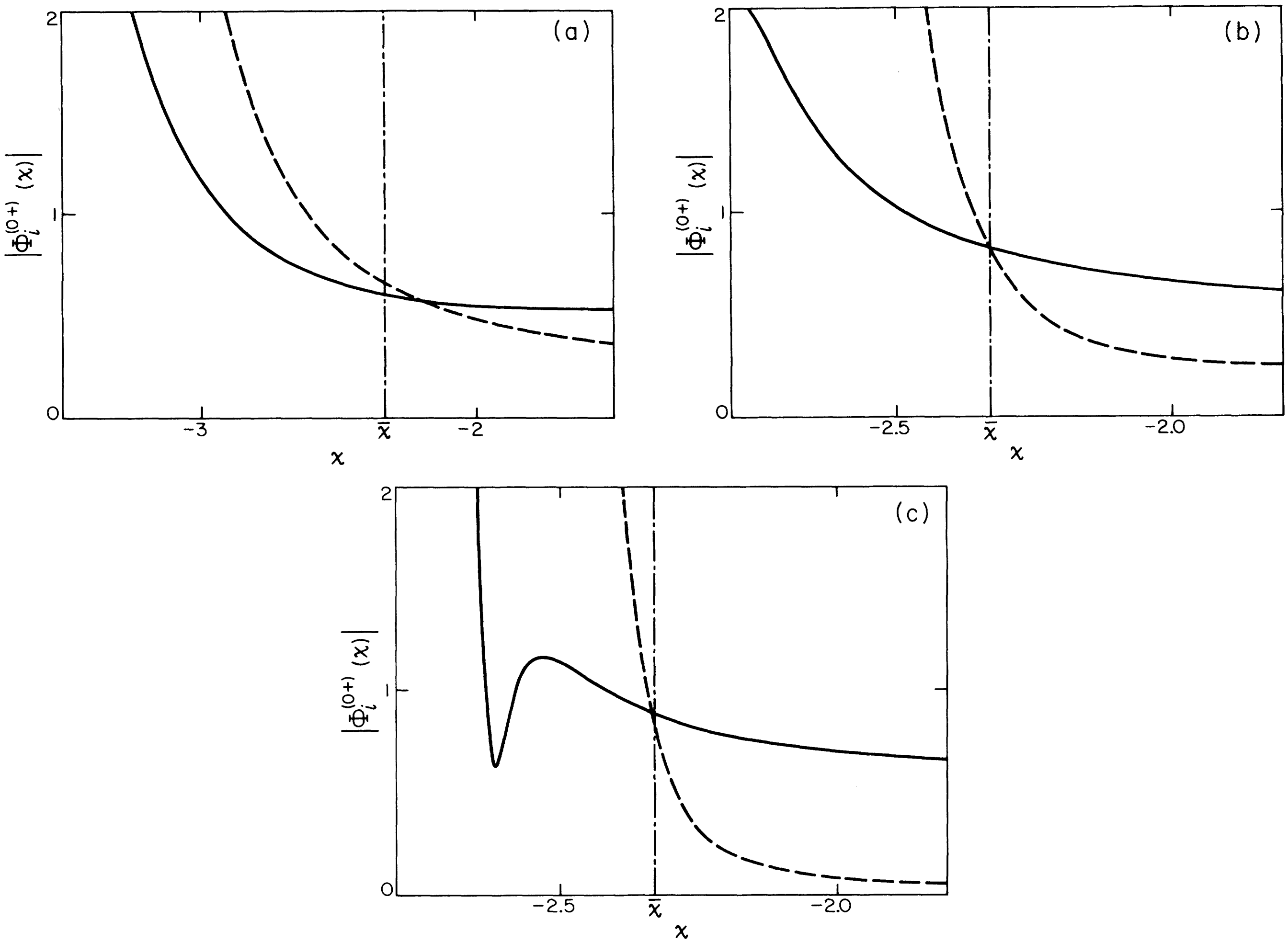


FIG. 3. Absolute values of $\Phi_0^{(0+)}(x)$ and $\Phi_1^{(0+)}(x)$ for the case of Fig. 2(a) are shown for several values of $\alpha$: (a) for $\alpha=1$, (b) for $\alpha=5$, and (c) for $\alpha=10$. $|\Phi_0^{(0+)}(x)|$ is represented by the solid line and $|\Phi_1^{(0+)}(x)|$ by the dashed line. The vertical dot-dashed line marks the position of $\bar{x}$. Note that for large $\alpha$, $|\Phi_1^{(0+)}(x)|$ becomes greater than $|\Phi_0^{(0+)}(x)|$ as $x$ moves to the left of $\bar{x}$.

TABLE I. The numerical results of exact and semiclassical solutions for the $S$ matrix are shown. The first number in parentheses is the real part of the matrix element, the second number is the imaginary part. The semiclassical results are calculated from Eqs. (91) and (92). Note that the differences between them decrease as $\alpha$ is increased.

| Case I | | $S_{00}$ | | $S_{01}$ | |
|---|---|---|---|---|---|
| $E$ | $\alpha$ | Exact | Semiclassical | Exact | Semiclassical |
| 1 | 1 | (0.532, 0.808) | (0.488, 0.873) | (0.072, −0.243) | (0.130, −0.323) |
| | 5 | (0.552, −0.834) | (0.557, −0.831) | (0.308. 0.103)$\times10^{-2}$ | (0.260, 0.092)$\times10^{-2}$ |
| | 10 | (−0.924, 0.383) | (−0.925, 0.380) | (−0.166, −0.132)$\times10^{-4}$ | (−0.157, −0.127)$\times10^{-4}$ |
| 10 | 5 | (0.564, −0.825) | (0.343, −0.939) | (0.454, −0.017)$\times10^{-1}$ | (0.574, −0.019)$\times10^{-1}$ |
| | 10 | (−0.734, 0.678) | (−0.644, 0.765) | (−0.328, 0.022)$\times10^{-1}$ | (−0.345, 0.022)$\times10^{-1}$ |
| | 20 | (−0.993, 0.115) | (−0.985, 0.171) | (−0.608, 0.080)$\times10^{-2}$ | (−0.613, 0.080)$\times10^{-2}$ |

| Case II | | $S_{00}$ | | $S_{01}$ | |
|---|---|---|---|---|---|
| $E$ | $\alpha$ | Exact | Semiclassical | Exact | Semiclassical |
| 0.7 | 10 | (0.999, −0.038) | (0.999, −0.038) | (0.207, 0.042)$\times10^{-1}$ | (0.165, 0.035)$\times10^{-1}$ |
| | 20 | (−0.079, −0.997) | (−0.079, −0.997) | (0.258, 0.114)$\times10^{-3}$ | (0.227, 0.102)$\times10^{-3}$ |
| | 30 | (−0.993, 0.119) | (−0.993, 0.118) | (0.143, 0.104)$\times10^{-5}$ | (0.126, 0.093)$\times10^{-5}$ |
| 1.5 | 10 | (0.979, −0.126) | (0.739, −0.674) | (−0.103, −0.120) | (−0.258, −0.305) |
| | 20 | (−0.874, −0.402) | (−0.996, −0.091) | (0.045, −0.269) | (0.053, −0.311) |
| | 30 | (0.430, 0.887) | (0.604, 0.797) | (0.144, −0.085) | (0.147, −0.087) |

Two energies, $E=0.7, 1.5$, are studied. For $E=1.5$, the topology of $z_c$, $x_0$, $x_1$ and anti-Stokes lines is similar to Fig. 2(a) and for $E=0.7$, it is similar to Fig. 2(b). Results of the $S$ matrix are also included in Table I. The differences between semiclassical and exact solutions also diminish in the limit of large $\alpha$ for both energies.

## VI. CONCLUSION

We have presented a rigorous treatment of the semiclassical theory for obtaining exponentially small inelastic transition amplitudes. The region of validity of our theory is established. Our result, Eq. (92), has the same form as the Landau-Zener-Stueckelberg formula in the near-adiabatic limit. However, our theory is more general and is applicable to a wide range of systems.

## ACKNOWLEDGMENTS

One of us (W.K.) acknowledges with thanks that I. M. Khaltatnikov referred him to the important Ref. 4, by Pokrovskii and Khalatnikov. We also acknowledge correspondence with V. L. Pokrovskii about the behavior of a closely related system (a particle incident on a harmonic oscillator) in regimes other than the near-adiabatic limit considered in the present paper. This work is supported by the Office of Naval Research Grant No. N00014-84-K-0548 and the National Science Foundation Grant No. DMR-8310117.

## APPENDIX

In the following propositions we make the same assumptions about the potentials as in the text. The proofs of propositions 1, 3, and 4 are analogous to Jeffreys's proof[10] for the ordinary potential scattering problem. For convenience we shall use $N$ to denote a bounded constant independent of $\alpha$. The value and the dimensionality of $N$ may be different at different places and are irrelevant to our discussions.

*Proposition 1.* Consider the Schrödinger equation (33) on the real axis. We assume that for a given energy $E$ each adiabatic potential $U_i$, $i=0,1$, has only one classical turning point, $x_i$, and that $U_i'(x_i)<0$, which will normally be the case. If the following functions are bounded,

$$F_0(x)=\int_{-\infty}^{x}\left[|f_{00}(x')|+\left|f_{01}(x')\left[\frac{\xi_0(x')}{\xi_1(x')}\right]^{1/4}\right|\right]\left|\frac{q_0(x')}{\xi_0(x')}\right|dx' , \tag{101}$$

$$F_1(x)=\int_{-\infty}^{x}\left[|f_{11}(x')|+\left|f_{10}(x')\left[\frac{\xi_1(x')}{\xi_0(x')}\right]^{1/4}\right|\right]\left|\frac{q_1(x')}{\xi_1(x')}\right|dx' , \tag{102}$$

and if the following quantities can be bounded by $\alpha^{1/6}N$,

$$F_2^{i\pm}=\int_{-\infty}^{x_i^-}+\int_{x_i^-}^{\infty}\left|\frac{d}{dx'}\left[\frac{q_j(x')h(x')}{[\xi_0(x')\xi_1(x')]^{1/4}[q_0(x')\pm q_1(x')]}\right]\right|dx',\quad (i,j)=(0,1),(1,0) , \tag{103}$$

where $x_i^{\pm}=x_i\pm N\alpha^{-2/3}$, $\xi_i$ is given by Eq. (49), $f_{ij}$, and $h$ are given by Eqs. (109)–(112), then the physical solution, which vanishes at $-\infty$ and has an incoming wave in channel 0, has the following form:

$$\Phi_0(x)\approx\left[\frac{d\xi_0}{dx}\right]^{-1/2}\text{Ai}[-\alpha^{2/3}\xi_0(x)],\quad\text{everywhere} \tag{104}$$

$$\frac{\Phi_1(x)}{\Phi_0(x)}\approx 0,\quad x\le x_0$$
$$\alpha^{1/6}\Phi_1(x)\approx 0,\quad x>x_0 . \tag{105}$$

*Proof.* Defining a new set of variables

$$\chi_i(\xi_i(x))=\left[\frac{d\xi_i}{dx}\right]^{1/2}\Phi_i(x),\quad i=0,1 \tag{106}$$

the Schrödinger equation (33) can be written as

$$\frac{d^2}{d\xi_0^2}\chi_0+\alpha^2\xi_0\chi_0=f_{00}(\xi_0)\chi_0+f_{01}(\xi_0)\xi_1+h(\xi_0)\frac{d}{d\xi_0}\chi_1 , \tag{107}$$

$$\frac{d^2}{d\xi_1^2}\chi_1+\alpha^2\xi_1\chi_1=f_{11}(\xi_1)\chi_1+f_{10}(\xi_1)\chi_0-h(\xi_1)\frac{d}{d\xi_1}\chi_0 , \tag{108}$$

where

$$h(\xi_i)=\frac{2\theta'}{(\xi_0'\xi_1')^{1/2}} , \tag{109}$$

$$f_{ii}(\xi_i)=\frac{1}{2}\frac{\xi_i'''}{(\xi_1')^3}-\frac{3}{4}\frac{(\xi_i'')^2}{(\xi_i')^4}+\frac{(\theta')^2}{(\xi_i')^2},\quad i=0,1 \tag{110}$$

$$f_{01}(\xi_0)=\frac{1}{(\xi_0'\xi_1')^{3/2}}(\theta''\xi_1'-\theta'\xi_1'') , \tag{111}$$

$$f_{10}(\xi_1)=\frac{1}{(\xi_0'\xi_1')^{3/2}}(-\theta''\xi_0'+\theta'\xi_0'') . \tag{112}$$

In Eqs. (107) and (108) $\chi_i$ are functions of $\xi_i$. The correspondence between $\xi_0$ and $\xi_1$ is one to one. If $\chi_1$ is negligible, Eq. (107) involves only channel 0. The solution of $\chi_0$ is given by Eq. (104). To show that $\chi_1$ is indeed negligible we transform Eq. (108) into an integral equation.[10] We need to construct the Green's function. The general solutions of the homogeneous equation,

$$\frac{d^2}{d\xi_1^2}\chi_1^{(0)}+\alpha^2\xi_1\chi_1^{(0)}=0 , \tag{113}$$

are Airy functions,

$$\chi_1^{(0)}(\xi_1)=a_1\,\mathrm{Ai}(-\alpha^{2/3}\xi_1)+b_1\,\mathrm{Bi}(-\alpha^{2/3}\xi_1)\ , \tag{114}$$

where $a_1$ and $b_1$ are arbitrary constants. The required Green's function which satisfies the differential equation,

$$\frac{d^2}{d\xi_1^2}G_1(\xi_1,\tilde{\xi}_1)+\alpha^2\xi_1 G_i(\xi_1,\tilde{\xi}_1)=\delta(\xi_1-\tilde{\xi}_1)\ , \tag{115}$$

has the following form:

$$\begin{aligned}G_1(\xi_1,\tilde{\xi}_1)&=\mathrm{Ai}(-\alpha^{2/3}\xi_1)P_1(\tilde{\xi}_1),\quad \xi_1<\tilde{\xi}_1\\ &=[i\,\mathrm{Ai}(-\alpha^{2/3}\xi_1)\\ &\quad+\mathrm{Bi}(-\alpha^{2/3}\xi_1)]\tilde{P}_1(\tilde{\xi}_1),\quad \xi_1>\tilde{\xi}_1\end{aligned} \tag{116}$$

where $G_1\to 0$ as $\xi_1\to-\infty$ and, as $\xi_1\to+\infty$, $G_1$ is an outgoing wave in channel 1 for fixed $\tilde{\xi}_1$. Solving for $G_1$, we obtain

$$\begin{aligned}G_1(\xi_1,\tilde{\xi}_1)&=-\frac{\pi}{\alpha^{2/3}}\mathrm{Ai}(-\alpha^{2/3}\xi_1)[i\,\mathrm{Ai}(-\alpha^{2/3}\tilde{\xi}_1)+\mathrm{Bi}(-\alpha^{2/3}\tilde{\xi}_1)],\quad \xi_1<\tilde{\xi}_1\\ &=-\frac{\pi}{\alpha^{2/3}}\mathrm{Ai}(-\alpha^{2/3}\tilde{\xi}_1)[i\,\mathrm{Ai}(-\alpha^{2/3}\xi_1)+\mathrm{Bi}(-\alpha^{2/3}\xi_1)],\quad \xi_1>\tilde{\xi}_1\ .\end{aligned} \tag{117}$$

The integral equation for the required solutions is

$$\chi_1(\xi_1)=\int_{-\infty}^{+\infty}d\tilde{\xi}_1G_1(\xi_1,\tilde{\xi}_1)\left[f_{11}\chi_1+f_{10}\chi_0-h\frac{d}{d\tilde{\xi}_1}\chi_0\right]\ , \tag{118}$$

where the homogeneous term is chosen to be 0. (We have omitted some arguments of the functions to shorten the notation.) The first interation of Eq. (118) is obtained by substituting $\chi_1$ with 0 and $\chi_0$ with $\mathrm{Ai}(-\alpha^{2/3}\xi_0)$,

$$\chi_1(\xi_1)=\int_{-\infty}^{+\infty}d\tilde{\xi}_1G_1(\xi_1,\tilde{\xi}_1)\left[f_{10}-h\frac{d}{d\tilde{\xi}_1}\right]\mathrm{Ai}(-\alpha^{2/3}\xi_0)\ . \tag{119}$$

The right-hand side of Eq. (119) can be written as a sum of three terms,

$$\begin{aligned}\chi_1^{(1)}(\xi_1)=i\frac{\pi}{\alpha^{2/3}}&\mathrm{Ai}(-\alpha^{2/3}\xi_1)\\ &\times\int_{-\infty}^{+\infty}d\tilde{\xi}_1\,\mathrm{Ai}(-\alpha^{2/3}\tilde{\xi}_1)\left[f_{10}-h\frac{d}{d\tilde{\xi}_1}\right]\\ &\times\mathrm{Ai}(-\alpha^{2/3}\xi_0)\ ,\end{aligned} \tag{120}$$

$$\begin{aligned}\chi_1^{(2)}(\xi_1)=-\frac{\pi}{\alpha^{2/3}}\int_{-\infty}^{\xi_1}d\tilde{\xi}_1K_\alpha^+(\xi_1,\tilde{\xi}_1)&\left[f_{10}-h\frac{d}{d\tilde{\xi}_1}\right]\\ &\times\mathrm{Ai}(-\alpha^{2/3}\xi_0)\ ,\end{aligned} \tag{121}$$

$$\begin{aligned}\chi_1^{(3)}(\xi_1)=\frac{\pi}{\alpha^{2/3}}\int_{+\infty}^{\xi_1}d\tilde{\xi}_1K_\alpha^-(\xi_1,\tilde{\xi}_1)&\left[f_{10}-h\frac{d}{d\tilde{\xi}_1}\right]\\ &\times\mathrm{Ai}(-\alpha^{2/3}\xi_0)\ ,\end{aligned} \tag{122}$$

where

$$K_\alpha^+(\xi_i,\tilde{\xi}_i)=\mathrm{Bi}(-\alpha^{2/3}\xi_i)\,\mathrm{Ai}(-\alpha^{2/3}\tilde{\xi}_i)\ , \tag{123}$$

$$K_\alpha^-(\xi_i,\tilde{\xi}_i)=\mathrm{Ai}(-\alpha^{2/3}\xi_i)\,\mathrm{Bi}(-\alpha^{2/3}\tilde{\xi}_i)\ . \tag{124}$$

Since $\mathrm{Ai}(-\alpha^{2/}\xi_1)$ is bounded everywhere and $\mathrm{Ai}(-\alpha^{2/3}\xi_1)$ is exponentially smaller than $\mathrm{Ai}(-\alpha^{2/3}\xi_0)$ for $x<x_0$, we have

$$\frac{\chi_1^{(1)}(x)}{\mathrm{Ai}[-\alpha^{2/3}\xi_0(x)]}\approx 0,\quad x\le x_0 \tag{125}$$

$$\alpha^{1/6}\chi_1^{(1)}(x)\approx 0,\quad x>x_0\ . \tag{126}$$

Both $\chi_1^{(2)}$ and $\chi_1^{(3)}$ satisfy equations similar to (125) and (126). We shall give the bound for the second term of $\chi_1^{(2)}$,

$$\tilde{\chi}_1^{(2)}(\xi_1)\equiv-\frac{\pi}{\alpha^{2/3}}\int_{-\infty}^{\xi_1}d\tilde{\xi}_1K_\alpha^+h\frac{d}{d\tilde{\xi}_1}\mathrm{Ai}(-\alpha^{2/3}\tilde{\xi}_0)\ ; \tag{127}$$

the bound for other terms in $\chi_1^{(2)}$ and $\chi_1^{(3)}$ can be obtained similarly. Consider first the region $x\le x_0$. In order to utilize the asymptotic form of $\mathrm{Ai}(-\alpha^{2/3}\tilde{\xi}_0)$ we discuss two cases, $x<x_0^-$ and $x_0^-\le x\le x_0$, separately.

For $x<x_0^-$, using the asymptotic forms of Airy functions, we have

$$\tilde{\chi}_1^{(2)}\approx\frac{i}{4\alpha^{1/6}(-\xi_1)^{1/4}}\exp\left[\alpha\int_x^{x_1}|q_1|dx''\right]\int_{-\infty}^{x}dx'q_0(x')\bar{h}(x')\exp\left[-\alpha\left[\int_{x'}^{x_1}|q_1|dx''+\int_{x'}^{x_0}|q_0|dx''\right]\right]\ , \tag{128}$$

where

$$\bar{h}(x)=\frac{h(x)}{[\xi_1(x)\xi_0(x)]^{1/4}}\ . \tag{129}$$

The integral in Eq. (128) can be written as

$$\int_{-\infty}^{x}dx'\frac{q_0(x')\bar{h}(x')}{-i\alpha[q_0(x')+q_1(x')]}\frac{d}{dx'}\left\{\exp\left[-\alpha\left[\int_{x'}^{x_1}|q_1|dx''+\int_{x'}^{x_0}|q_0|dx''\right]\right]\right\}\ .$$

Performing an integration by parts in this form, we obtain

$$|\tilde{\chi}_1^{(2)}| \le \left| \frac{1}{\alpha^{7/6}[\xi_1(x)]^{1/4}} \frac{q_0\bar{h}(x)}{[q_0(x)+q_1(x)]} \exp\left[-\alpha \int_x^{x_0} |q_0|\, dx'\right] \right| + \left| \frac{1}{\alpha^{7/6}[\xi_1(x)]^{1/4}} \int_{-\infty}^{x} dx' \left[\frac{d}{dx'} \frac{q_0\bar{h}}{q_0+q_1}\right] \exp\left[-\alpha\left[\int_{x'}^{x_1} |q_1|\, dx'' + \int_{x'}^{x_0} |q_0|\, dx'' - \int_x^{x_1} |q_1|\, dx''\right]\right] \right| . \tag{130}$$

Since we have assumed that there is only one classical turning point for each adiabatic potential, the function $\int_x^{x_1} |q_1|\, dx'' + \int_x^{x_0} |q_0|\, dx''$ is monotonically increasing as $x$ moves from $x_0$ to $-\infty$. Hence the exponential term in the integral of Eq. (130) is bounded by

$$\exp\left[-\alpha \int_x^{x_0} |q_0|\, dx''\right] .$$

From this and the assumption about $F_2^{0+}$, it is not difficult to see that

$$|\tilde{\chi}_1^{(2)}| \le \frac{N}{\alpha} \mathrm{Ai}[-\alpha^{2/3}\xi_0(x)], \quad x < x_0^- . \tag{131}$$

For $x_0^- \le x \le x_0$ the asymptotic forms of Airy functions are not valid. However, since both Ai and Bi are bounded, we can estimate the magnitude of the integral easily. In this region the integrand can be bounded as follows:

$$\frac{1}{\alpha^{2/3}} |K_\alpha^+| \le \frac{N}{\alpha} , \tag{132}$$

and

$$\left| \frac{d}{d\xi_1} \mathrm{Ai}(-\alpha^{2/3}\tilde{\xi}_0) \right| \le \alpha^{2/3} N . \tag{133}$$

Since the integration region is only of $O(\alpha^{-2/3})$, the integral is only $O(\alpha^{-1})$. Therefore we conclude that

$$\frac{\tilde{\chi}_1^{(2)}(x)}{\Phi_0(x)} \approx 0, \quad x \le x_0 . \tag{134}$$

For $x > x_0$, $\tilde{\chi}_1^{(2)}$ can be analyzed for regions $x_0 < x < x_1^-$, $x_1^- \le x \le x_1^+$, and $x > x_1^+$ by a similar treatment. We obtain $\alpha^{1/6}\tilde{\chi}_1^{(2)}(x) \approx 0$.

*Proposition 2.* Consider a circle $\Omega_c$ of radius $d_c$ around $z_c$. Assume that $V_1'V_1 + V_2'V_2$ does not vanish at $z_c$ then for sufficiently small $d_c$ and sufficiently large $\alpha$, the general solutions of the Schrödinger equation (23) in $\Omega_c$ is

$$\Psi_0(z) \approx e^{i\alpha q_c \zeta}[a_+ \mathrm{Ai}(\alpha^{2/3}C^{2/3}\zeta) + b_+ \mathrm{Bi}(\alpha^{2/3}C^{2/3}\zeta)] + e^{-i\alpha q_c \zeta}[a_- \mathrm{Ai}(\alpha^{2/3}C^{2/3}\zeta) + b_- \mathrm{Bi}(\alpha^{2/3}C^{2/3}\zeta)] , \tag{135}$$

to the leading order in $\zeta$, where $\zeta$, $q_c$, and $C$ are given by Eqs. (51)–(53), and $a_\pm$ and $b_\pm$ are arbitrary constants.

*Proof.* Eliminating $\Psi_1(z)$ from the Schrödinger equation we obtain the fourth-order differential equation for $\Psi_0(z)$,

$$D\Psi_0(z) \equiv \left[\frac{d^4}{dz^4} + f_3(z)\frac{d^3}{dz^3} + f_2(z)\frac{d^2}{dz^2} + f_1(z)\frac{d}{dz} + f_0(z)\right]\Psi_0(z) = 0 , \tag{136}$$

where

$$f_3 = -2\frac{V_2'}{V_2} , \tag{137}$$

$$f_2 = 2(E - V_0) + \alpha^2\left[-\frac{V_2''}{V_2} + 2\left[\frac{V_2'}{V_2}\right]^2\right] , \tag{138}$$

$$f_1 = -2\alpha^2\left[V_0' + V_1' + \frac{V_2'}{V_2}(E - V_0 - V_1)\right] , \tag{139}$$

$$f_0 = \alpha^4[(E - V_0)^2 V_1^2 - V_2^2] + \alpha^2\left[-(V_0'' + V_1'') + \frac{2(V_2')^2 - V_2V_2''}{V_2^2}(E - V_0 - V_1) + 2\frac{V_2'}{V_2}(V_0' + V_1')\right] . \tag{140}$$

Pulling out a fast oscillating part of $\Psi_0$,

$$\Psi_0(z) = e^{i\alpha q_c \zeta}\chi(\zeta) , \tag{141}$$

the solutions of $\chi(\zeta)$ include two slowly varying solutions (for sufficiently small $|\zeta|$) and two fast-oscillating solutions; we will find the former. The equation for $\chi$ reads

$$\left[\frac{d^4}{dz^4} + g_3(z)\frac{d^3}{dz^3} + g_2(z)\frac{d^2}{dz^2} + g_1(z)\frac{d}{dz} + g_0(z)\right]\chi(z) = 0 , \tag{142}$$

where

$$g_3(z) \approx -4i\alpha q_c , \tag{143}$$

$$g_2(z) \approx 2\alpha^2(E - V_0 - 3q_c^2) , \tag{144}$$

$$g_1(z) \approx 4\alpha^3 i q_c(E - V_0 - q_c^2) - 2\alpha^2\left[V_0' + V_1' + (E - V_0 - V_1 - 3q_c^2)\frac{V_2'}{V_2}\right] , \tag{145}$$

$$g_0(z) \approx \alpha^4[q_c^4 - 2q_c^2(E - V_0) + (E - V_0)^2 - (V_1^2 + V_2^2)] + 2\alpha^3 i q_c \left[ V_1' + V_0' + (E - V_0 - V_1 - q_c^2)\frac{V_2'}{V_2} \right] . \tag{146}$$

Linearizing the potentials at $z_c$ and changing variable from $z$ to $\zeta$ we obtain

$$\left[ \frac{d^4}{d\zeta^4} + \alpha S_3 \frac{d^3}{d\zeta^3} + \alpha^2 S_2 \frac{d^2}{d\zeta^2} + (\alpha^2 S_1 + \alpha^3 T_1 \zeta)\frac{d}{d\zeta} + (\alpha^3 S_0 + \alpha^4 T_0 \zeta) \right] \chi(\zeta) = 0 , \tag{147}$$

where

$$S_3 = -4iq_c , \tag{148}$$

$$S_2 = -4q_c^2 , \tag{149}$$

$$S_1 = -2a_1 - 2a_0 + 2\frac{b_1 a_2}{b_2} + 4q_c^2 \frac{a_2}{b_2} , \tag{150}$$

$$T_1 = -4iq_c a_0 , \tag{151}$$

$$S_0 = -i\frac{2q_c}{b_2}[b_1 a_2 - b_2(a_1 + a_0)] , \tag{152}$$

$$T_0 = -2(a_2 b_2 + a_1 b_1) , \tag{153}$$

with

$$a_i = V_i'(z_c) , \tag{154}$$

$$b_{1,2} = V_{1,2}(z_c) . \tag{155}$$

Making a scale transformation

$$\eta = \alpha^{2/3}\zeta , \tag{156}$$

and assuming that $|d^n\chi/d\eta^n|$ are of the same order as $|\chi|$, Eq. (147) can be reduced to the leading order in $\alpha$,

$$\frac{d^2\chi}{d\eta^2} + C^2\eta\chi + \frac{1}{S_2\alpha^{1/3}}\left[ S_3\frac{d^3\chi}{d\eta^3} + T_1\frac{d\chi}{d\eta} - S_0\chi \right] = 0 . \tag{157}$$

For $\eta > O(\alpha^{-1/3})$ the last term is negligible, and the solutions are the Airy functions. For $\eta < O(\alpha^{-1/3})$ the last term is not smaller than the second term, however, all terms are small; the correction to the Airy functions vanishes in the large-$\alpha$ limit. Hence the slowly varying solutions are

$$\chi(\zeta) \approx a_+ \operatorname{Ai}(\alpha^{2/3}C^{2/3}\zeta) + b_+ \operatorname{Bi}(\alpha^{2/3}C^{2/3}\zeta) , \tag{158}$$

where $a_+$ and $b_+$ are arbitrary constants. This shows that the scaling, Eq. (156), is indeed a correct one. Equations (141) and (158) give one set of solutions. Pulling out another fast-oscillating factor $e^{-i\alpha q_c \zeta}$ [cf. Eq. (141)] we can obtain the other set of solutions in Eq. (135).

*Proposition 3.* Consider the anti-Stokes line $L_1$. Let $z_1$ denote a point at a fixed distance from $z_c$ and let $L_1^-$ denote $L_1$, excluding the segment from $z_c$ to $z_1$. We assume the following conditions to be true. (1) $L_1$ does not pass through singularities of the potentials. (2) The mappings $\xi_i(z) = \int_{z_c}^{z} q_i(z)dz$, $i = 0, 1$, are one to one.[11] (3) $\operatorname{Im}(\xi_i)$ increases monotonically as $z$ moves to the right on $L_1$.[12] If the following functions can be bounded by $N$,

$$F_0(z) = \int_z^\infty (|f_{00}(z)| + |f_{01}(z)|)|q_0(z)dz| , \tag{159}$$

$$F_1(z) = \int_z^\infty (|f_{11}(z)| + |f_{10}(z)|)|q_1(z)dz| , \tag{160}$$

$$F_2^{i\pm}(z) = \int_z^\infty \left| \frac{d}{dz}\left[ \frac{q_i(z)h(z)}{q_0(z) \pm q_1(z)} \right] \right| |dz| , \quad i = 0, 1 \tag{161}$$

where $f_{ij}$ and $h$ are given by Eqs. (167)–(170), then, for $z$ on $L_1^-$, there is a solution of the following form:

$$\Phi_0(z) \approx \Phi_0^+(z, z_c) , \tag{162}$$

$$\frac{\Phi_1(z)}{\Phi_0(x)} \approx 0 , \tag{163}$$

where $\Phi_0^+(z, z_c)$ is defined in Eq. (36).

*Proof.* Defining a new set of variables

$$\chi_i(\xi_i(x)) = \left[ \frac{d\xi_i}{dx} \right]^{1/2} \Phi_i(x), \quad i = 0, 1 \tag{164}$$

the Schrödinger equation (33) can be written as

$$\frac{d^2}{d\xi_0^2}\chi_0 + \alpha^2\chi_0 = f_{00}(\xi_0)\chi_0 + f_{01}(\xi_0)\chi_1 + h(\xi_0)\frac{d}{d\xi_0}\chi_1 , \tag{165}$$

$$\frac{d^2}{d\xi_1^2}\chi_1 + \alpha^2\chi_1 = f_{11}(\xi_1)\chi_1 + f_{10}(\xi_1)\chi_0 - h(\xi_1)\frac{d}{d\xi_1}\chi_0 , \tag{166}$$

where

$$h(\xi_i) = \frac{2\theta'}{(\xi_0'\xi_1')^{1/2}} , \tag{167}$$

$$f_{ii}(\xi_i) = \frac{1}{2}\frac{\xi_i'''}{(\xi_i')^3} - \frac{3}{4}\frac{(\xi_i'')^2}{(\xi_i')^4} + \frac{(\theta')^2}{(\xi_i')^2}, \quad i = 0, 1 \tag{168}$$

$$f_{01}(\xi_0) = \frac{1}{(\xi_0'\xi_1')^{3/2}}(\theta''\xi_1' - \theta'\xi_1'') , \tag{169}$$

$$f_{10}(\xi_1) = \frac{1}{(\xi_0'\xi_1')^{3/2}}(-\theta''\xi_0' + \theta'\xi_0'') . \tag{170}$$

The correspondence between variables $\xi_0$ and $\xi_1$ is one to one. Similar to the proof of proposition 1, we transform (165) and (166) into coupled integral equations,

$$\chi_0(\xi_0) = \chi_0^{(0)}(\xi_0) + \int^{\xi_0} d\tilde{\xi}_0 K_\alpha(\xi_0, \tilde{\xi}_0) \times \left[ f_{00}(\tilde{\xi}_0)\chi_0(\tilde{\xi}_0) + f_{01}(\tilde{\xi}_0)\chi_1(\tilde{\xi}_1) + h(\tilde{\xi}_0)\frac{d}{d\tilde{\xi}_0}\chi_1(\tilde{\xi}_1) \right] , \tag{171}$$

$$\chi_1(\xi_1)=\chi_1^{(0)}(\xi_1)+\int^{\xi_1} d\tilde{\xi}_1 K_\alpha(\xi_1,\tilde{\xi}_1)\times\left[f_{11}(\tilde{\xi}_1)\chi_1(\tilde{\xi}_1)+f_{10}(\tilde{\xi}_1)\chi_0(\tilde{\xi}_0)-h(\tilde{\xi}_1)\frac{d}{d\tilde{\xi}_1}\chi_1(\tilde{\xi}_1)\right], \quad (172)$$

where $\chi_0^{(0)}$ and $\chi_1^{(0)}$ are solutions of the homogeneous equations,

$$\chi_0^{(0)}(\xi_0)=a_0 e^{i\alpha\xi_0}+b_0 e^{-i\alpha\xi_0}, \quad (173)$$

$$\chi_1^{(0)}(\xi_1)=a_1 e^{i\alpha\xi_1}+b_1 e^{-i\alpha\xi_1}, \quad (174)$$

and $K_\alpha$ is the kernel,

$$K_\alpha(\xi_i,\tilde{\xi}_i)=-\frac{\pi}{\alpha}(e^{i\alpha(\xi_i-\tilde{\xi}_i)}-e^{-i\alpha(\xi_i-\tilde{\xi}_i)}) . \quad (175)$$

Choosing the lower bounds of the integrals to be $\xi_i^\infty$, where $z(\xi_i^\infty)=\infty+iy_1$, and choosing

$$\chi_0^{(0)}=e^{i\alpha\xi_0}, \quad (176)$$

$$\chi_1^{(0)}=0 , \quad (177)$$

the integral equations become

$$\chi_0(\xi_0)=e^{i\alpha\xi_0}+\int_{\xi_0^\infty}^{\xi_0} d\tilde{\xi}_0 K_\alpha\left[f_{00}\chi_0+f_{01}\chi_1+h\frac{d}{d\tilde{\xi}_0}\chi_1\right], \quad (178)$$

$$\chi_1(\xi_1)=\int_{\xi_1^\infty}^{\xi_1} d\tilde{\xi}_1 K_\alpha\left[f_{11}\chi_1+f_{10}\chi_0-h\frac{d}{d\tilde{\xi}_1}\chi_0\right] . \quad (179)$$

The first iteration of Eqs. (178) and (179) gives

$$\chi_0(\xi_0)=e^{i\alpha\xi_0}+\int_{\xi_0^\infty}^{\xi_0} d\tilde{\xi}_0 K_\alpha f_{00} e^{i\alpha\tilde{\xi}_0}, \quad (180)$$

$$\chi_1(\xi_1)=\int_{\xi_1^\infty}^{\xi_1} d\tilde{\xi}_1 K_\alpha\left[f_{10}-h\frac{d}{d\tilde{\xi}_1}\right]e^{i\alpha\tilde{\xi}_0} . \quad (181)$$

Equation (180) includes only one channel, which is similar to the ordinary potential scattering problem; the integral is negligible.[10] We will only show the bound for the second term of (181),

$$\chi_1^{(1)}(\xi_1)\equiv-\int_{\xi_1^\infty}^{\xi_1} d\tilde{\xi}_1 K_\alpha h\frac{d}{d\tilde{\xi}_1}e^{i\alpha\tilde{\xi}_0} . \quad (182)$$

Performing an integration by part [which is similar to the step from Eq. (128) to Eq. (130)], we obtain

$$\chi_1^{(1)}=\frac{1}{\alpha}e^{i\alpha\xi_0}(B_1+B_2+B_3+B_4) , \quad (183)$$

where

$$B_1=-\frac{h(z)q_0(z)}{q_0(z)-q_1(z)} , \quad (184)$$

$$B_2=\frac{h(z)q_0(z)}{q_0(z)+q_1(z)} , \quad (185)$$

$$B_3=\int_\infty^z dz'\left[\frac{d}{dz'}\frac{h(z')q_0(z')}{q_0(z')-q_1(z')}\right]e^{i\alpha[\xi_1(z')-\xi_0(z')]} , \quad (186)$$

$$B_4=\int_\infty^z dz'\left[\frac{d}{dz'}\frac{h(z')q_0(z')}{q_0(z')+q_1(z')}\right]\times e^{2i\alpha\{[\xi_1(z')+\xi_0(z')]-[\xi_0(z)+\xi_1(z)]\}} . \quad (187)$$

From the definition of $L_1$, $|e^{i\alpha(\xi_0-\xi_1)}|$ is 1. Therefore $B_1$, $B_2$, and $B_3$ are bounded for $z$ on $L_1^-$. From condition 3 about $L_1$ we see that the real part of the exponent of $B_4$ is always less than 0. Thus $B_4$ is also bounded. Therefore we have

$$\frac{\chi_1^{(1)}(z)}{\Phi_0(z)}\approx 0 . \quad (188)$$

The proof of proposition 4 is similar to what we have just shown. We only give the statement.

*Proposition 4.* Consider the anti-Stokes lines $L_2$. Let $z_2$ denote a point at a fixed distance from $z_c$ and let $L_2^-$ denote $L_2$, excluding the segment from $z_c$ to $z_2$. We assume the following conditions to be true. (1) $L_2$ does not pass through singularities of the potentials. (2) The mappings $\xi_i(z)=\int_{z_c}^z q_i(z)dz$, $i=0,1$, are one to one. (3) $\mathrm{Im}(\xi_i)$ increases monotonically as $z$ moves down to $\bar{x}$ on $L_2$.[13] If the following functions can be bounded by $N$,

$$F_0(z)=\int_{z_2}^z(|f_{00}(z)|+|f_{01}(z)|)|q_0(z)dz| , \quad (189)$$

$$F_1(z)=\int_{z_2}^z(|f_{11}(z)|+|f_{10}(z)|)|q_1(z)dz| , \quad (190)$$

$$F_2^{i\pm}(z)=\int_{z_2}^z\left|\frac{d}{dz'}\left[\frac{q_i(z')h(z')}{q_0(z')\pm q_1(z')}\right]\right||dz'| , \quad i=0,1 \quad (191)$$

where $f_{ij}$, and $h$ are given by Eqs. (167)–(170), then, for $z$ on $L_2^-$, there is a solution of the following form:

$$\Phi_0(z)\approx\Phi_0^+(z,z_c) , \quad (192)$$

$$\Phi_1(z)\approx\Phi_1^+(z,z_c) , \quad (193)$$

where $\Phi_0^+(z,z_c)$ and $\Phi_1^+(z,z_c)$ are defined in Eqs. (36) and (37), respectively.

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[1]For a review on the subject, see B. C. Eu, *Semiclassical Theories of Molecular Scattering* (Springer-Verlag, Berlin, 1984); E. E. Nikitin and S. Ya. Umanskii, *Theory of Slow Atomic Collisions* (Springer-Verlag, Berlin, 1984).

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[12]This condition is not restrictive at all; it is satisfied for all numerical examples presented in Sec. V. A weaker condition is sufficient: there exists a path from $z$ to $\infty$ along which $\mathrm{Im}(\xi_i)$ increases monotonically. (Such a path need not be $L_1$.)
[13]This is also true for our numerical examples. A weaker condition is sufficient: there exists a path from $z_c$ to $z$ along which $\mathrm{Im}(\xi_i)$ increases monotonically.