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Studies of the Potential-Curve Crossing Problem. I. Analysis of Stueckelberg's Method

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A detailed critical analysis is made of Stueckelberg's treatment of inelastic transitions at a crossing of two potential curves. Using an asymptotic method analogous to the WKB approximation, Stueckelberg obtained the well-known Landau-Zener-Stueckelberg (LZS) formula for the inelastic transition probability. His method involved the determination of "connection formulas" linking amplitudes associated with his asymptotic approximants on either side of the crossing-point region. Here we show that (a) Stueckelberg's asymptotic approximants are just the WKB approximants for elastic scattering on the adiabatic (noncrossing) potential curves; (b) Stueckelberg's method for obtaining the connection formulas can be put on a rigorous footing, including sufficient conditions for its validity, using the classical trajectory equations derivable from a general semiclassical theory of inelastic atomic collisions; (c) there is an undetermined phase in the S matrix, which Stueckelberg incorrectly assumed to be zero, and which has the value $\frac{1}{4}\pi$ in the distorted-wave approximation; (d) Stueckelberg's derivation is not valid whenever the inelastic transition probability is small, either in the rapid-passage (diabatic) case or the near-adiabatic limit; (e) for realistic model parameters, the conditions needed for Stueckelberg's derivation to be valid are almost never satisfied. Since the LZS formula is known from numerical computations to be valid under some conditions when the Stueckelberg derivation is not valid, we conclude that analysis via connection-formula methods is not a useful technique for treating the crossing problem. In an appendix we derive an analytical result for the Stokes's constants determining the Stueckelberg connection formulas. The result is an absolutely convergent, infinite series whose numerical evaluation would yield exactly the unknown phase associated with the LZS formula.

I. INTRODUCTION

A problem of fundamental interest in the theory of atomic and molecular collisions is posed by the crossing of two electronic potential surfaces. At such a crossing, electronic transitions between the two states, normally improbable because of the Massey adiabatic criterion, can be important even at low collision velocities. This type of transition is usually involved whenever efficient electronic deactivation or charge transfer is observed between dissimilar atoms. In analyzing such problems, the first and usually the most serious assumption is that a particular process can be isolated and described using only the two electronic states associated with a particular crossing. Then, given the projection of the electronic Hamiltonian on this two-state manifold, the remaining problem is to calculate the transition probability (elastic and inelastic cross sections).

In this series of papers, the potential curve-crossing problem is treated using the "classical trajectory equations" of atomic collision theory. These time-dependent equations governing the electronic degrees of freedom arise if it is assumed that the nuclei move classically in the collision. Previously we have shown[1-4] that these equations are valid much more generally than is the classical picture upon which their intuitive formulation is based. In this paper we use the classical trajectory equations to make a detailed analysis of the solution to the crossing problem given by Stueckelberg in 1932.[5] We will show the relationship between his and other approaches to the problem, and prove that there are extremely severe limitations on the validity of his method.

A. Historical Background

The earliest theoretical work on the crossing problem was done by Landau[6] and Zener,[7] who in-

dependently obtained the well-known formula named after them. Landau used a form of the distorted-wave approximation; a generalization of his approach has been presented recently by Chen and Watson.[8] Zener's derivation was based upon the classical picture of the nuclear motion, and accordingly it ignored the phase coherence between transitions occurring on the incoming and outgoing traversals of the crossing point. Most subsequent studies of the problem have involved extensions of this approach.

Using an extension of the WKB method, Stueckelberg[5] derived a set of "connection formulas" linking the values for certain amplitude parameters of the wave function inside the crossing point to values outside it. By this means he obtained a formula which includes the effects of phase coherence, and which reduces in the appropriate limit to the Landau-Zener formula. We refer to this formula as the Landau-Zener-Stueckelberg (LZS) formula. Unfortunately Stueckelberg was not able to give the conditions for its validity.

Stueckelberg's method is unique and bears no obvious relation to most other work on the crossing problem; furthermore, it appears at first to be based on purely formal arguments whose validity can be guaranteed without reference to specific details of the system considered. To our knowledge there have been only two subsequent studies of Stueckelberg's approach. Rice[9] took a critical perspective based on general considerations of the nature of asymptotic expansions, and his criticisms partially diagnosed the trouble with Stueckelberg's method. However, since Rice did not examine the expansions in detail, he was able only to conclude that Stueckelberg's method is not *necessarily* correct. Furthermore, certain of Rice's criticisms bear on the validity of the classical trajectory equations rather than upon Stueckelberg's method of solving them; in fact, however, the difficulties with the LZS formula arise entirely from the latter. The other analysis of Stueckelberg's approach was briefly reported by Thorson and Boorstein in 1965.[10] Here we will describe their work in detail and also establish definite conditions for the validity of Stueckelberg's derivation.

B. Problem Description

There are four essential steps required in a semiclassical analysis of electronic excitations.

Electronic basis. The first of these steps is the choice of an appropriate electronic basis, $\phi_n(\vec{r}, R)$. A useful choice is the set of Born-Oppenheimer or adiabatic electronic states, which fully diagonalize the electronic Hamiltonian (in the molecular reference frame) at each R. In this representation excitations arise from the so-called "nonadiabatic" couplings via the R dependence of the basis ϕ_n. The adiabatic potential curves $V_{nn}(R)$ do not cross, except when there is no inelastic coupling between the states (noncrossing rule). If two adiabatic curves have such an avoided crossing it is always possible to make a unitary transformation on the adiabatic basis such that the nonadiabatic couplings between this pair of states become negligible. In the resulting "diabatic" representation the diagonal elements of the electronic Hamiltonian cross and coupling results from the off-diagonal element, which is a slowly varying function of R (Fig. 1). A more complete definition of diabatic representations has been given by F. T. Smith.[11] Landau, Aener, Stueckelberg, and most others used a diabatic representation as a starting point, but it is important to recognize that this is purely a matter of convenience; in many modern studies of curve crossings, the adiabatic curves are the more readily available information.

The most serious approximation in the curve-crossing problem is made at this first step of electronic basis choice, i.e., the truncation of the electronic basis to the two states associated with a particular crossing. The validity of this truncation must be examined case by case.

Semiclassical approximants and coupled equations. A semiclassical treatment is based on the use of asymptotic approximants which adequately describe elastic propagation in some fixed electronic representation. When the exact wave function is expanded in terms of these approximants, inelastic scattering is described by coupled equations linking the expansion coefficients. The distinctive feature of semiclassical approximants is that the resulting equations are just the classical trajectory equations.

Selection of any particular set of semiclassical approximants simply amounts to a choice of electronic representation, and the corresponding classical trajectory equations are those appropriate to that representation. For instance, Landau began with the WKB approximants for elastic scattering in the diabatic representation and his solution of the resultant inelastic scattering equations via the distorted-wave approximation is equivalent to the first-order perturbation treatment of the diabatic classical trajectory equations. Zener used the classical trajectory equations for the diabatic representation; this again involves the same WKB approximants. Stueckelberg, on the other hand, starting from the diabatic representation, derived a new set of asymptotic approximants which incorporate some effects of the inelastic coupling. However, it turns out that his approximants are just exactly the elastic scattering WKB approximants for the adiabatic representation, although they are described as two-component vectors in the diabatic basis. The corresponding coupled

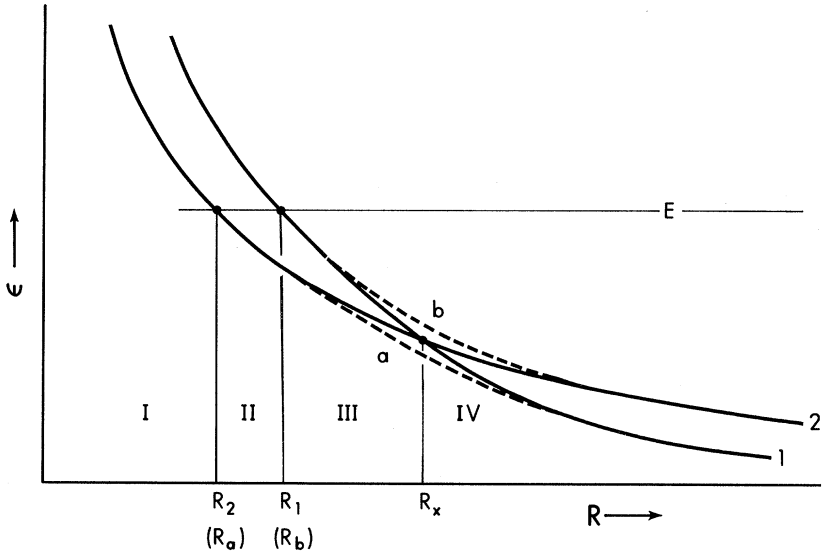

FIG. 1. Potential curve crossing R_x. Solid curves (1, 2), diabatic potentials; dashed curves (a, b), adiabatic potentials. R_2, R_1 (R_a, R_b), classical turning points. Roman numerals indicate distinct asymptotic regions for WKB approximants.

equations, to which Stueckelberg's connection formula technique attempts a solution, are just the classical trajectory equations in the adiabatic representation. Stueckelberg's forms can be derived by methods less tedious than his, which clearly reveal their connection to the adiabatic representation.[2,4,12] In addition, our derivation (in Sec. II) leads to the corresponding coupled equations, which are essential to the analysis of Stueckelberg's method or to any semiclassical treatment (Stueckelberg never consider the equations explicitly).

The classical trajectory equations, which are thus central to all semiclassical treatments of the curve-crossing problem, are valid[1-3] provided only that (a) the WKB approximation would adequately describe elastic scattering in uncoupled channels, (b) differences of elastic momenta in the initial and final electronic states are small in the region of inelastic coupling, and either (c) coupling is negligible in nonclassical and turning-point regions *or* (c′) the two potential curves have slopes of common sign. The significance of the last conditions is discussed in Ref. 3 and in Sec. II.

Model for electronic Hamiltonian. The third step necessary in a semiclassical theory is the selection of a suitable descriptive model for the two-state projection of the electronic Hamiltonian. The LZS model for curve crossings assumes that (in diabatic basis) the diagonal elements H_{11}, H_{22} are sensibly linear, and the off-diagonal element H_{12} sensibly constant, for a sufficiently large distance around the crossing point. As was first shown by Bates,[13] this apparently innocuous assumption can become very restrictive at high energies. In this paper we shall in principle allow for deviations from this model (via Taylor expansions of the matrix elements).

Solution of coupled equations. Finally it is necessary to solve the coupled classical trajectory equations to obtain a formula for the transition probability. The primary objective of this paper is to carry this step out by a rigorous treatment of Stueckelberg's method, and to obtain thereby the conditions of validity for Stueckelberg's derivation of the LZS formula.

II. SEMICLASSICAL TREATMENT OF CROSSING PROBLEM

Using a method similar to that employed in our previous derivations of the classical trajectory equations, we now derive Stueckelberg's asymptotic approximants to the exact radial Schrödinger equation and the corresponding classical trajectory equations for the coefficients. As we derive them, Stueckelberg's forms are just the adiabatic approximants; however, Stueckelberg actually used them in a different representation, discontinuous on the real axis at the crossing point, which we call the "Stueckelberg representation." It differs from the adiabatic representation in the definition of a certain square root (the reader is warned that these definitions must be treated with extraordinary care to avoid error).

A. Derivation of Classical Trajectory Equations in Adiabatic Representation

The Schrödinger equation for radial motion has the solution

$$\Psi_J = R^{-1}[u_1(R)\,\phi_1 + u_2(R)\,\phi_2], \tag{1}$$

where $u_j(R)$ obey the equations

$$\begin{aligned} u_1'' + k_1^2(R)\,u_1 &= U_{12}(R)\,u_2\,, \\ u_2'' + k_2^2(R)\,u_2 &= U_{21}(R)\,u_1 \end{aligned} \tag{2}$$

and

$$k_j^2(R) = 2M[E - H_{jj}(R)] - J(J+1)/R^2 , \tag{3a}$$

$$U_{ij}(R) = 2M H_{ij}(R) . \tag{3b}$$

Define

$$\Delta(R) = k_1^2(R) - k_2^2(R) , \tag{3c}$$

$$t = \Delta/2U_{12} . \tag{3d}$$

Note that, according to Fig. 1, Δ and t are positive for $R > R_x$, zero at R_x, and negative for $R < R_x$; $t \to \infty$ as $R \to \infty$. $H_{ij}(R)$ is the two-state projection of the electronic Hamiltonian in the diabatic or crossing representation.

The adiabatic or noncrossing representation is obtained when the matrix $\underline{U}$ is made diagonal ($U_{jj} = k_j^2$). The adiabatic momenta, which we denote by π_a, π_b, are given by

$$\begin{aligned} \pi_a^2 &= \tfrac{1}{2}[k_1^2(R) + k_2^2(R)] + \tfrac{1}{2}\left|(\Delta^2 + 4U_{12}^2)^{1/2}\right| , \\ \pi_b^2 &= \tfrac{1}{2}[k_1^2(R) + k_2^2(R)] - \tfrac{1}{2}\left|(\Delta^2 + 4U_{12}^2)^{1/2}\right| . \end{aligned} \tag{4}$$

The adiabatic potentials are shown (dashed curves) in Fig. 1. We shall not distinguish between the zeros R_a, R_b of π_a^2, π_b^2 and those of k_2^2, k_1^2, respectively.

Let us now derive the classical trajectory equations in the adiabatic representation. We begin by writing

$$u_j = \sum_{\nu = a,b} (B_{\nu j+} e^{+iS_\nu} + B_{\nu j-} e^{-iS_\nu}), \quad j = 1, 2 \tag{5}$$

where

$$S_\nu = \int \pi_\nu dR' , \quad \nu = a, b . \tag{6}$$

Since only two functions are being determined by eight $B_{\nu j\pm}$'s, we impose two arbitrary conditions

$$u_j' = i \textstyle\sum_\nu \pi_\nu (B_{\nu j+} e^{iS_\nu} - B_{\nu j-} e^{-iS_\nu}), \tag{7a}$$

so that

$$\textstyle\sum_\nu (B_{\nu j+}' e^{iS_\nu} + B_{\nu j-}' e^{-iS_\nu}) = 0 . \tag{7b}$$

Using Eqs. (5) and (7a) in Eqs. (2), two coupled first-order equations for $B_{\nu j\pm}$ are obtained. These can be further reduced by using the four arbitrary constraints still at our disposal to diagonalize the potential matrix $\underline{U}$, i.e., we choose

$$B_{a2\pm} = \gamma B_{a1\pm} , \quad B_{b1\pm} = -\gamma B_{b2\pm} , \tag{8a}$$

where

$$\begin{aligned} \gamma &= +(k_1^2 - \pi_a^2)/U_{12} = -(k_2^2 - \pi_b^2)/U_{12} \\ &= -\left[\left|(1+t^2)^{1/2}\right| - t\right] . \end{aligned} \tag{8b}$$

When these substitutions are made in the coupled equations obtained from (2) and also into Eqs. (7b), we obtain four equations for $B_{a1\pm}$ and $B_{b2\pm}$:

$$\begin{bmatrix} 1 & 1 & -\gamma & -\gamma \\ \pi_a & -\pi_a & -\pi_b\gamma & \pi_b\gamma \\ \gamma & \gamma & 1 & 1 \\ \pi_a\gamma & -\pi_a\gamma & \pi_b & -\pi_b \end{bmatrix} \begin{bmatrix} B_{a1+}' e^{iS_a} \\ B_{a1-}' e^{-iS_a} \\ B_{b2+}' e^{iS_b} \\ B_{b2-}' e^{-iS_b} \end{bmatrix} = \begin{bmatrix} 0 & 0 & -\gamma' & -\gamma' \\ \pi_a' & -\pi_a' & -(\pi_b\gamma)' & (\pi_b\gamma)' \\ \gamma' & \gamma' & 0 & 0 \\ (\pi_a\gamma)' & -(\pi_a\gamma)' & \pi_b' & -\pi_b' \end{bmatrix} \begin{bmatrix} B_{a1+} e^{iS_a} \\ B_{a1-} e^{-iS_a} \\ B_{b2+} e^{iS_b} \\ B_{b2-} e^{-iS_b} \end{bmatrix} \tag{9}$$

The inverse of the coefficient matrix for $B_{\nu j\pm}'$ is

$$(\tfrac{1}{2})/[1+\gamma^2] \begin{bmatrix} 1 & \pi_a^{-1} & \gamma & \gamma\pi_a^{-1} \\ 1 & -\pi_a^{-1} & \gamma & -\gamma\pi_a^{-1} \\ -\gamma & -\gamma\pi_b^{-1} & 1 & \pi_b^{-1} \\ -\gamma & \gamma\pi_b^{-1} & 1 & -\pi_b^{-1} \end{bmatrix} ;$$

multiplying through by it, removing diagonal elements by the substitutions

$$\begin{aligned} B_{a1\pm} &= \alpha_{a\pm}/\left|[\pi_a(1+\gamma^2)]^{1/2}\right| , \\ B_{b2\pm} &= \alpha_{b\pm}/\left|[\pi_b(1+\gamma^2)]^{1/2}\right| , \end{aligned} \tag{10}$$

and noting that

$$1/\left|(1+\gamma^2)^{1/2}\right| = \left|[1 + t/\left|(1+t^2)^{1/2}\right|]^{1/2}\right| , \tag{11}$$

we obtain a system of coupled first-order equations for $\alpha_{\nu\pm}$:

$$\begin{bmatrix} \alpha'_{a+} \\ \alpha'_{a-} \\ \alpha'_{b+} \\ \alpha'_{b-} \end{bmatrix} = \begin{bmatrix} 0 & \left(\frac{\pi'_a}{2\pi_a}\right)e^{-2iS_a} & 0 & \frac{+t'}{4(1+t^2)}\left(\frac{\pi_a+\pi_b}{(\pi_a\pi_b)^{1/2}}\right)e^{-i(S_a-S_b)} \\ \left(\frac{\pi'_a}{2\pi_a}\right)e^{+2iS_a} & 0 & \frac{+t'}{4(1+t^2)}\left(\frac{\pi_a-\pi_b}{(\pi_a\pi_b)^{1/2}}\right)e^{i(S_a+S_b)} & 0 \\ 0 & \frac{-t'}{4(1+t^2)}\left(\frac{\pi_a+\pi_b}{(\pi_a\pi_b)^{1/2}}\right)e^{i(S_a-S_b)} & 0 & \left(\frac{\pi'_b}{2\pi_b}\right)e^{+2iS_b} \\ \frac{+t'}{4(1+t^2)}\left(\frac{\pi_a-\pi_b}{(\pi_a\pi_b)^{1/2}}\right)e^{-i(S_a+S_b)} & 0 & \left(\frac{\pi'_b}{2\pi_b}\right)e^{-2iS_b} & 0 \end{bmatrix} \begin{bmatrix} \alpha_{a+} \\ \alpha_{a-} \\ \alpha_{b+} \\ \alpha_{b-} \end{bmatrix} \tag{12}$$

Equations (12) provide an exact solution to the Schrödinger equation, of the form

$$\Psi = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \alpha_{a+}\chi_a^+ + \alpha_{a-}\chi_a^- + \alpha_{b+}\chi_b^+ + \alpha_{b-}\chi_b^- , \tag{13}$$

where the spinor wave functions $\chi_\nu^\pm$ are given by

$$\begin{aligned} \chi_a^\pm &= \left|(2\pi_a)^{-1/2}\right| \left|\left(1+\frac{t}{|(1+t^2)^{1/2}|}\right)^{1/2}\right| \\ &\quad \times \begin{bmatrix} 1 \\ \gamma \end{bmatrix} \exp\left(\pm i\int^R \pi_a\, dR'\right), \\ \chi_b^\pm &= \left|(2\pi_b)^{-1/2}\right| \left|\left(1+\frac{t}{|(1+t^2)^{1/2}|}\right)^{1/2}\right| \\ &\quad \times \begin{bmatrix} -\gamma \\ 1 \end{bmatrix} \exp\left(\pm i\int^R \pi_b\, dR'\right). \end{aligned} \tag{14}$$

In a previous paper[2] we discussed the conditions under which exact equations of the form (12) can be replaced by simpler approximate forms; to summarize briefly the results, we require the validity of (a) the WKB approximation ($\lambda \ll a_0$), (b) the "$\pm$ separation" ($|\pi_a - \pi_b| \ll |\pi_a + \pi_b|$), and (c) coupling [in this case, equal to $t'/2(1+t^2)$] is negligible near classical turning points. If these approximations are made, we then obtain the equations

$$\begin{bmatrix} \alpha'_{a\pm} \\ \alpha'_{b\pm} \end{bmatrix} = \begin{bmatrix} 0 & \frac{t'}{2(1+t^2)}\, e^{\mp i(S_a-S_b)} \\ -\frac{t'}{2(1+t^2)}\, e^{\pm i(S_a-S_b)} & 0 \end{bmatrix} \times \begin{bmatrix} \alpha_{a\pm} \\ \alpha_{b\pm} \end{bmatrix} ; \tag{15}$$

note that $(\pi_a+\pi_b)/(\pi_a\pi_b)^{1/2}$ has been replaced by 2.

By defining a new independent variable τ having units of time, such that

$$\frac{dR}{d\tau} = \frac{\pm(\pi_a+\pi_b)}{2M} \simeq \frac{\pm(\pi_a\pi_b)^{1/2}}{M} ,$$

Eqs. (15) reduce to the classical trajectory equations in the adiabatic representation. This can be shown by the following argument. In the diabatic representation the classical trajectory equations can be written in the form

$$i\hbar\, \frac{d\underline{C}}{d\tau} = \underline{V}\,\underline{C} , \tag{16}$$

where $d/d\tau$ denotes the time derivative and $\underline{V}$ is the Hamiltonian matrix. Let $\underline{W}$ be the (time-dependent) unitary transformation which renders $\underline{V}$ diagonal; it can always be expressed in terms of an angle θ:

$$\underline{W} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}. \tag{17}$$

Then at each time we have $\underline{W}\underline{V}\underline{W}^{\dagger} = \underline{\epsilon}$ (diagonal), and we define the transformed coefficient matrix $\underline{D} = \underline{W}\underline{C}$; the basis vectors in this transformed representation are the adiabatic eigenvectors of $\underline{V}$, and the new coefficients are therefore the expansion coefficients in the adiabatic representation. They obey the equation

$$i\hbar \frac{d\underline{D}}{d\tau} = \left[\underline{\epsilon} + i\hbar\left(\frac{d\underline{W}}{d\tau}\right)\underline{W}^{\dagger}\right]\underline{D}\,. \tag{18}$$

Defining

$$\gamma_j(\tau) = \exp\left(-\frac{i}{\hbar}\int_0^{\tau}\epsilon_j(\tau')d\tau'\right)D_j(\tau), \quad j = a, b \tag{19}$$

we obtain

$$\begin{aligned} \frac{d\gamma_a}{d\tau} &= -\frac{d\theta}{d\tau}\exp\left(-\frac{i}{\hbar}\int_0^{\tau}(\epsilon_b - \epsilon_a)d\tau'\right)\gamma_b(\tau)\,, \\ \frac{d\gamma_b}{d\tau} &= \frac{d\theta}{d\tau}\exp\left(\frac{i}{\hbar}\int_0^{\tau}(\epsilon_b - \epsilon_a)d\tau'\right)\gamma_a(\tau)\,. \end{aligned} \tag{20}$$

These equations are the classical trajectory equations in the adiabatic representation. Noting that θ satisfies

$$\begin{aligned} &\cot 2\theta = t, \quad \cos\theta = \left(\frac{1 + t/|(1+t^2)^{1/2}|}{2}\right)^{1/2}, \\ &\sin\theta = \left(\frac{1 - t/|(1+t^2)^{1/2}|}{2}\right)^{1/2}, \\ &\frac{d\theta}{d\tau} = -\frac{dt}{d\tau}\Big/ 2(1+t^2), \quad \theta' = \frac{-t'}{2(1+t^2)}\,, \end{aligned} \tag{21}$$

we see that

$$\alpha_a = \gamma_a, \quad \alpha_b = i\gamma_b\,.$$

Thus, the 2 vectors of Eq. (14) are merely the coefficients of the transformation matrix $\underline{W}$, and the asymptotic approximants $\chi_{\nu}^{\pm}$ are just the WKB forms for elastic scattering on the adiabatic potentials. [As such, however, they do not necessarily provide a better description of the scattering problem; the inelastic scattering can only be determined by solving Eqs. (15). If the system truly behaves adiabatically as it traverses the crossing region, then $\alpha_{\nu\pm}$ are constants, $\chi_{\nu}^{\pm}$ are good asymptotic solutions, and there is zero inelastic scattering. Whether Eqs. (15) or the classical trajectory equations in the diabatic representation are used is purely a matter of convenience; the inelastic scattering problem requires the solution of one or the other.]

Since we assume that no coupling occurs near the classical turning-point region, the ordinary WKB connection formulas can be applied to the coefficients $\alpha_{\nu\pm}$ near the turning points:

$$\alpha_{\nu+}(R \simeq R_{\nu}) = -i\alpha_{\nu-}(R \simeq R_{\nu}); \tag{22}$$

+ and − equations then refer, respectively, to outgoing and incoming portions of the classical trajectory.

Bykhovskii, Nikitin, and Ovchinnikova[14] were the first to recognize that under certain circumstances the classical trajectory equations could remain valid even if there is strong coupling in the turning-point region. Their results were extended in Ref. 3. An exactly analogous derivation of classical trajectory equations in the adiabatic representation can be given via the momentum-space semiclassical approximation but for the sake of brevity we will not present it here. In this derivation, the requirement of negligible coupling at the turning points disappears and is replaced by the requirement that both diabatic potentials U_{11}, U_{22} have slopes of common sign. Therefore the classical trajectory equations hold, *except for a situation where there is coupling near a turning point and the forces F_{11}, F_{22} have opposite signs*. Such a situation arises at a crossing between an attractive and a repulsive potential curve, if the energy is such that the turning point is near the crossing point. As described in Ref. 3 there can then occur a peculiar nonclassical "orbiting" effect, in which the particles are temporarily captured into a quasibound state of the two-channel system. A qualitative idea of the nature of these levels can be obtained by considering the noncrossing adiabatic potentials, which can obviously possess quasidiscrete states. A study of the scattering resonances occurring in this case has been done by Levine and co-workers[15] and a different analysis has been given by Child.[16]

In this paper, we do not take advantage of the full range of validity of the classical trajectory equations, but work entirely within the framework of the configuration-space equations (15), as Stueckelberg did. The defects of the LZS formula are not due to inaccuracy of the classical trajectory equations, but to the errors inherent in Stueckelberg's method of solving them.

B. Stueckelberg Approximants and Representation

Comparison of the forms $\chi_{\nu}^{\pm}$ given by Eqs. (14) with the asymptotic forms given by Stueckelberg[5] reveals their similarity; there is a one-to-one equivalence between $\chi_{\nu}^{\pm}$ and the Stueckelberg approximants, on each side of the crossing region $R \simeq R_x$. However, a more careful examination of Stueckelberg's forms shows that his representation is not identical to the adiabatic one, but has a discontinuity on the real axis at R_x. The difference between the two arises from the interpretation given to the quantity $(1+t^2)^{1/2}$. In the adia-

batic basis, as indicated by the absolute value symbols, we take the positive real root, so that π_a^2, π_b^2 are continuous on the real t axis; the solution to the scattering problem is then obtained by integration of Eqs. (15) along the real t axis. This procedure is the one followed in the next paper. Stueckelberg, on the other hand, wishes to follow the solutions from the negative real t axis ($R < R_x$) to the positive real t axis ($R > R_x$) along a path in the complex t plane for which $|t|$ is very large and therefore the coupling in Eqs. (15) is very small; he therefore defines $(1+t^2)^{1/2}$ so that it is analytic in the complex t plane for any path not crossing the branch line between $-i$, 0, and $+i$. In this paper we reserve the symbol "$(1+t^2)^{1/2}$" for Stueckelberg's definition, which has the same characteristics as t for $|t| \gg 1$, and we use $|(1+t^2)^{1/2}|$ to denote the more common usage of the positive real root.

Stueckelberg's asymptotic forms, which we denote $\tilde{\psi}_{j\pm}$, are obtained as follows: We define the Stueckelberg momenta,

$$p_1^2 = \tfrac{1}{2}[k_1^2 + k_2^2] + U_{12}(1+t^2)^{1/2},$$
$$p_2^2 = \tfrac{1}{2}[k_1^2 + k_2^2] - U_{12}(1+t^2)^{1/2}, \tag{23}$$

with related definitions of S_1 and S_2. Following exactly the analog of the method used to derive Eqs. (15), all the equations obtained remain valid, provided $(1+t^2)^{1/2}$ replaces $|(1+t^2)^{1/2}|$ and the indices $j = 1, 2$ replace $\nu = a, b$, respectively. The exact solution Ψ is then given by

$$\Psi = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \tilde{a}_{1+}\tilde{\psi}_{1+} + \tilde{a}_{1-}\tilde{\psi}_{1-} + \tilde{a}_{2+}\tilde{\psi}_{2+} + \tilde{a}_{2-}\tilde{\psi}_{2-}, \tag{24}$$

where the coefficients $\tilde{a}_{j\pm}$ satisfy Eqs. (15) in the complex R plane, with $j = 1, 2$ in place of a, b, and the functions S_j are defined by line integrals in the complex plane. More precisely, the asymptotic forms $\tilde{\psi}_{j\pm}$ for which this analog of Eqs. (15) is valid are given by

$$\tilde{\psi}_{1\pm} = |(p_1)^{-1/2}| \exp\left(\pm i\int_{R_1}^{z} p_1\,dz' - \frac{1}{2}\int_{0^+}^{t} \frac{u}{1+u^2}\,du\right) \begin{bmatrix} \exp(+\frac{1}{2}\int_{0^+}^{t} du/(1+u^2)^{1/2} \\ -\exp(-\frac{1}{2}\int_{0^+}^{t} du/(1+u^2)^{1/2} \end{bmatrix}, \tag{25a}$$

$$\tilde{\psi}_{2\pm} = |(p_2)^{-1/2}| \exp\left(\pm i\int_{R_2}^{z} p_2\,dz' - \frac{1}{2}\int_{0^+}^{t} \frac{u\,du}{(1+u^2)}\right) \begin{bmatrix} \exp(-\frac{1}{2}\int_{0^+}^{t} du/(1+u^2)^{1/2} \\ \exp(\frac{1}{2}\int_{0^+}^{t} du/(1+u^2)^{1/2} \end{bmatrix}, \tag{25b}$$

where the integrals are evaluated along the contours shown in Fig. 2. Care must be taken to include the values of contour integrals from 0^- to 0^+ via such a circumnavigating path if the correct relations between $\tilde{\psi}_{j\pm}$ and $\chi_{\nu}^{\pm}$ are to be obtained on each side of $R = R_x(t=0)$. The quantities $S_j(z)$ can be expressed more usefully as follows:

$$S_j(z) \equiv \int_{R_j}^{z} p_j\,dz' = \int_{R_j}^{R_x^-} p_j\,dR' + \tfrac{1}{2}\int_{R_x^-}^{z} (p_1+p_2)\,dz' \pm \tfrac{1}{2}\int_{R_x^-}^{z} (p_1-p_2)\,dz', \tag{26a}$$

$$\frac{1}{2}\int_{R_x^-}^{z} (p_1-p_2)\,dz' = \frac{1}{2}\int_{R_x^-}^{z} \frac{2U_{12}(1+t^2)^{1/2}}{p_1+p_2}\,dz' = \int_{0^-}^{t_1(z)} T(t)(1+t^2)^{1/2}\,dt = \tfrac{1}{2}\xi(t_1), \tag{26b}$$

where

$$T(t) \equiv U_{12}/(p_1+p_2)\,\frac{dt}{dz}.$$

Since p_1+p_2, U_{12}, and $(dt/dz) = t'$ are analytic everywhere to the right of the classical turning points R_1, R_2, only the contribution of (26b) to S_j depends on the contour in the t plane; the remaining terms are either constants or represent analytic factors common to both $\tilde{\psi}_{1\pm}$ and $\tilde{\psi}_{2\pm}$ near the crossing point. $S_1 - S_2$, which appears in the analog of Eqs. (15), can be written

$$S_1 - S_2 = \sigma_0 + \xi(t), \tag{27}$$

where the "adiabatic phase lag" σ_0 is given by

$$\sigma_0 = \int_{R_1}^{R_x^-} p_1\,dr - \int_{R_2}^{R_x^-} p_2\,dR. \tag{28}$$

According to Eq. (23), σ_0 is negative.

Following Stueckelberg, we define standard real axis forms $\psi_{j\pm}^{\mathrm{III}}$, $\psi_{j\pm}^{\mathrm{IV}}$ for the two regions of the real R axis on either side of R_x (see Fig. 1). These are given by the following equations:

$$\psi_{1\pm}^{\mathrm{III}} = |(2p_1)^{-1/2}| \left|\left(1 + \frac{t}{(1+t^2)^{1/2}}\right)^{1/2}\right| \exp\left(\pm i\int_{R_1}^{R} p_1\,dR'\right) \begin{bmatrix} 1 \\ -[(1+t^2)^{1/2} - t] \end{bmatrix},$$
$$\psi_{2\pm}^{\mathrm{III}} = |(2p_2)^{-1/2}| \left|\left(1 + \frac{t}{(1+t^2)^{1/2}}\right)^{1/2}\right| \exp\left(\pm i\int_{R_2}^{R} p_2\,dR'\right) \begin{bmatrix} (1+t^2)^{1/2} - t \\ 1 \end{bmatrix}, \tag{29}$$

region IV ($R_x < R < \infty$)

$$\psi_{1\pm}^{\mathrm{IV}} = \left|(2p_1)^{-1/2}\right| \left|\left(1+\frac{t}{(1+t^2)^{1/2}}\right)^{1/2}\right| \exp\left(\pm i\int_{R_1}^{R} p_1\,dR'\right) \begin{bmatrix} 1 \\ -[(1+t^2)^{1/2}-t] \end{bmatrix},$$

$$\psi_{2\pm}^{\mathrm{IV}} = \left|(2p_2)^{-1/2}\right| \left|\left(1+\frac{t}{(1+t^2)^{1/2}}\right)^{1/2}\right| \exp\left(\pm i\int_{R_2}^{R} p_2\,dR'\right) \begin{bmatrix} (1+t^2)^{1/2}-t \\ 1 \end{bmatrix}, \tag{30}$$

where

$$\int_{R_j}^{R} p_j\,dR' = \lim_{\epsilon\to 0^+}\left(\int_{R_j}^{R_x-\epsilon} p_j\,dR' + \int_{R_x+\epsilon}^{R} p_j\,dR'\right). \tag{31}$$

By working out the contour integrals in Eqs. (25) it can be shown that in region III the several asymptotic forms are related by

$$\psi_{1\pm}^{\mathrm{III}} = \tilde{\psi}_{1\pm} = +\chi_b^{\pm}, \tag{32a}$$

$$\psi_{2\pm}^{\mathrm{III}} = \tilde{\psi}_{2\pm} = -\chi_a^{\pm}, \tag{32b}$$

while in region IV

$$\psi_{1\pm}^{\mathrm{IV}} = e^{\mp\delta}\tilde{\psi}_{1\pm} = e^{\pm i\sigma_0}\,\chi_a^{\pm}, \tag{33a}$$

$$\psi_{2\pm}^{\mathrm{IV}} = e^{\pm\delta}\tilde{\psi}_{2\pm} = e^{\mp i\sigma_0}\,\chi_b^{\pm}, \tag{33b}$$

where

$$\delta \equiv i\int_{0^-}^{0^+} T(t)(1+t^2)^{1/2}\,dt, \tag{34}$$

evaluated on a contour above $t=+i$ in the upper half-plane.

Equations (32) and (33) provide the connection between any solution to the problem in the adiabatic representation and the equivalent solution in Stueckelberg's representation.

III. ANALYSIS OF STUECKELBERG'S METHOD

A. Stokes's Phenomenon

Stueckelberg's procedure is based on an implicit analogy with the problem of the WKB connection formulas at a classical turning point. We shall make the analogy explicit, following a procedure developed by Zwaan[17] and Kemble[18] which we now review briefly.

If the WKB asymptotic solution is useful, there presumably exist domains on both sides of a classical turning point, in classical and nonclassical regions, where the approximation is valid. However, the WKB forms are singular at the turning point and in that neighborhood make a poor approximation to the exact solution, which of course is not singular. If the Schrödinger equation is extended into the complex R plane, the WKB approximation will be valid at all points far from a turning point. Assume that in a domain on the real axis on one side of the turning point it is known that a particular exact solution is well represented by a given linear combination of WKB approximants with constant coefficients. Suppose now that this solution is analytically continued along a path in the complex plane, circumnavigating the turning point and arriving at the real axis on the other side. Assume that on every point of this path the relative error inherent in the WKB forms is small; then the linear combination of WKB forms matching the same exact solution can also be so continued, to obtain the connection formulas. This idea is due to Stokes, who originally assumed that this implies that the coefficients of the linear combination will remain constant on the path and therefore that the connection formulas are obtained merely by analytic continuation of the WKB forms. This is not correct; Stokes discovered that the coefficients change during the circumnavigation in the complex plane. This happens for the following reason. On a "good path" the error terms neglected in the WKB approximation can be made small, so that some linear combination of the WKB forms (with constant coefficients) provides a good approximation to the exact solution. However, in general the path must traverse regions of the complex plane where the exact solution and one of the WKB approximants are extremely large (Stokes rays). At the same time the other WKB approximant is extremely small—so small that its entire contribution is less than the small relative error in the fit to the exact solution given by the large term. In such a region the coefficient of the subdominant WKB form changes surreptitiously while we are, so to speak, not noticing its contribution. Kemble[18] examined this problem by deriving first-order differential equations for the changes of the coefficients along a "good path" in the complex plane; by this means he obtained an account of the conditions under which discontinuous changes of the coefficients occur (Stokes's phenomenon), and he derived the WKB connection formulas.

In the case of the crossing-point problem, R_x is not itself a singular point for the forms $\tilde{\psi}_{j\pm}$ or $\chi_\nu^{\pm}$; the singularities occur at $t=\pm i$. However, the Stueckelberg approximants are certainly not accurate as one moves along the real axis near $R_x\,(t\simeq 0)$; this is clearly evident in Eqs. (15), which describe the change in the "constant" coefficients. Stueckelberg's procedure was to connect the approximate solution in region III to that in

region IV by taking account of changes in coefficients, due to Stokes's phenomenon, on a "good" path in the complex t plane, circumnavigating the singular points at $t=\pm i$. The resulting connection formulas would then describe the effects of inelastic transitions. Like Zwaan's treatment of the turning-point case, Stueckelberg's method assumes a "good path" exists and he gives no explicit consideration to the equations for the changes of the coefficients along such a path.

These equations are of course the complex t-plane analogs of the classical trajectory equations (15). Using them we can obtain explicit and rigorous conditions for the validity of Stueckelberg's derivation of the LZS formula.

B. Conditions for a "Good Path"

We proceed by exact analogy with Kemble,[18] whose lucid account for the WKB turning point case will serve as background for our brief summary.

As a necessary, but not sufficient, condition for the validity of Stueckelberg's method, we require the validity of the classical trajectory equations (15) in regions III and IV. In this paper we have obtained these with the assumptions that inelastic coupling in the turning-point region can be neglected; as shown in Paper III of this series, this assumption is not necessary in many cases. Therefore it is possible that Eqs. (15) will be valid even though the coefficients $\alpha_{\nu\pm}$ determined by them cannot be assumed to be constants anywhere in region III ($R_1 < R < R_x$). Stueckelberg, however, requires that there exist a region on the real R axis in region III where $\alpha_{\nu\pm}$ are essentially constants, an assumption which is consistent with our present derivation of Eqs. (15).

In the Stueckelberg representation [Eq. (24)] the analog of Eqs. (15) can be represented in terms of t as the independent (complex) variable; defining $\beta_{1\pm}=\bar{a}_{1\pm}e^{\pm i\sigma_0/2}$, $\beta_{2\pm}=\bar{a}_{2\pm}e^{\mp i\sigma_0/2}$, we find

$$\frac{d\beta_{1\pm}}{dt}=\frac{1}{2(1+t^2)}\,e^{\mp i\xi(t)}\,\beta_{2\pm}(t), \tag{35a}$$

$$\frac{d\beta_{2\pm}}{dt}=-\frac{1}{2(1+t^2)}\,e^{\pm i\xi(t)}\,\beta_{1\pm}(t). \tag{35b}$$

These equations specify precisely how the "constants" change on any path in the complex t plane.

For a path Λ in the complex plane we can define an "index of quality," μ_Λ:

$$\mu_\Lambda=\int_\Lambda \frac{|dt|}{|(1+t^2)|}\,. \tag{36}$$

A "good path" is one for which μ_Λ is sufficiently small. A path of interest to us in the upper half-circle with radius $\hat{t}$; for this path, $\mu_\Lambda \simeq \pi/\hat{t}$.

It is useful to describe regions in the complex plane by their properties with respect to $|e^{i\xi}|$. Regions where $|e^{i\xi}|\leq 1$ are called "mountains," those where it is less than 1, "valleys." A path segment is "uphill" if along it $|e^{i\xi}|$ monotonically increases.

Consider the changes in the + coefficients on an arbitrary uphill path segment with endpoints t_0 and t_1. Assume that $|e^{-i\xi(t_0)}|\leq 1$; then by integrating Eqs. (35) we obtain

$$\beta_{1+}(t)=\beta_{1+}(t_0)+\beta_{2+}(t_0)\int_{t_0}^{t}dt'\,e^{-i\xi(t')}\,\theta'(t')$$

$$+\int_{t_0}^{t}dt'\int_{t_0}^{t'}dt''\,[\theta'(t')\,\theta'(t'')e^{i[\xi(t'')-\xi(t')]}\beta_{1+}(t'')], \tag{37a}$$

$$\beta_{2+}(t)=\beta_{2+}(t_0)-\int_{t_0}^{t}dt'\,\theta'(t')\,\beta_{1+}(t')e^{i\xi(t')}, \tag{37b}$$

where $\theta'(t)=1/2(1+t^2)$. Because of the limits of integration in (37a), along an uphill path we have

$$\left|e^{-i[\xi(t')-\xi(t'')]}\right|\leq 1$$

and

$$\left|e^{-i\xi(t')}\right|\leq 1\,.$$

Therefore we can bound the change in β_{1+},

$$\left|\beta_{1+}(t)-\beta_{1+}(t_0)\right|\leq \tfrac{1}{2}\mu_\Lambda\left|\beta_{2+}(t_0)\right|+\tfrac{1}{8}\mu_\Lambda^2\left|\beta_{1+}^{\max}\right|,$$

where $|\beta_{1+}^{\max}|$ is the maximum magnitude of $\beta_{1+}(t)$ on the path segment. It follows that $|\beta_{1+}(t)|$ differs from $|\beta_{1+}(t_0)|$ by a quantity at most of order μ_Λ, at any point on such an uphill path in the mountains [we assume a normalized choice of coefficients such that $|\beta_{2+}(t_0)|\leq 1$]. Thus, on an uphill path in the mountains we can say that to within errors of order μ_Λ, relative to the larger of $|\beta_{1+}|$, $|\beta_{2+}|$,

$$\beta_{1+}(t_1)\simeq \beta_{1+}(t_0), \tag{37c}$$

$$\beta_{2+}(t_1)\simeq \beta_{2+}(t_0)-\beta_{1+}(t_0)\int_{t_0}^{t_1}\theta'(t')e^{i\xi(t')}\,dt'. \tag{37d}$$

By an extension of this argument, it is now easy to show that for any path entirely in the mountains, beginning at a level line where $|e^{i\xi(t_0)}|=1$, going uphill over a mountain ridge where $|e^{i\xi}|$ has a maximum, and going down the other side to the next level line where $|e^{i\xi(t_2)}|=1$, the change in β_{1+} is less than $\frac{1}{2}\mu_\Lambda[\,|\beta_{2+}(t_0)|+|\beta_{2+}(t_2)|\,]$, and β_{2+} changes by some coefficient times the (constant) value of β_{1+}. Similarly, for any path entirely in a valley leading from one level line to the next, the same statement can again be made with the roles of β_{1+} and β_{2+} reversed. This set of relationships is Stokes's phenomenon.

Rice[9] criticized Stueckelberg's method on the

grounds that (a) it was not clear whether the relations (37c) and (37d) should involve + and − coefficients separately, and (b) Stueckelberg described the changes as discontinuities associated with the Stokes rays (mountain ridges and valley bottoms). These criticisms miss the point. First, the ± separation is valid if Eqs. (15) are valid, i.e., if the crossing point is sufficiently far from the turning points that coupling there is negligible; the need for this assumption was explicitly stated by Stueckelberg.

Second, it is quite true that the coefficients do not change discontinuously at Stokes rays, but this is irrelevant to the argument above. For $T(t)=T_0=\text{const}$, we have been able to evaluate the integral appearing in Eq. (37d) (to within errors of about μ_Λ) on the quarter circle of radius $|t|\to\infty$ associated with the mountain region surrounding the Stokes ray labeled B in Fig. 2 (see Appendix). We find that contributions from every point within the region are important; for example, methods using steepest-descents or stationary-phase asymptotic approximations, which would be valid if the contributions were localized at Stokes rays, give divergent results. It is never the case that the changes occur discontinuously at the Stokes rays. However, the argument of Stueckelberg does not require this assumption; it is only required as shown above that the region of significant change be topologically distinct (alternate mountain and valley regions). *To within the stated error bounds of order* μ_Λ, the changes in the coefficients depend only upon the topological arrangement of mountain ridges and valley floors along the good path Λ. The major defect in the Stueckelberg method, as we will show in Sec. V, arises from the fact that there are conditions for which these error bounds are far too large to be of any use because they greatly exceed the quantities being estimated.

IV. STUECKELBERG'S DERIVATION OF LZS FORMULA

Figure 2 is a map of the complex t plane, showing the topography of mountain ridges and valley floors with respect to $e^{i\xi}|$. The branch cut for $(1+t^2)^{1/2}$ is drawn between $-i$ and $+i$ as shown. Two types of contours are shown: The large-radius outer curve (dashed) represents a hypothetical "good path" circumnavigating the singularities at $t=\pm i$; the contour from 0^- to 0^+ and return is used to calculate δ[cf. Eq. (34)].

$(1+t^2)^{1/2}$ can be represented in terms of a redundant pair of complex numbers,

$$t-i=\rho e^{i\phi},\quad t+i=\sigma e^{i\theta},$$

where

$$-\tfrac{1}{2}\pi<\phi<\tfrac{3}{2}\pi,\quad -\tfrac{1}{2}\pi<\theta<\tfrac{3}{2}\pi\ .$$

It is not hard to show that with these conventions $(1+t^2)^{1/2}$ has the correct mapping characteristics previously assigned. Moreover, assuming that the analytic function $T(t)$ can be expanded in a Maclaurin series about $t=0$,

$$T(t)=T_0+T_1t+\tfrac{1}{2}T_2t^2+\tfrac{1}{6}T_3t^3+\cdots\ , \tag{38}$$

we can determine the topological arrangement of mountain ridges and valley floors issuing forth from $t=\pm i$. For large $|t|$ the higher-order terms in $T(t)$ will deform the topography to some extent, but this is irrelevant, as shown in Sec. III. As represented in Fig. 2, $e^{+i\xi}$ *is dominant* for a ridge from $+i$ at $\phi=\frac{5}{6}\pi$, one from $-i$ at $\theta=-\frac{1}{6}\pi$, and on the 0^+ side of the branch cut; $e^{-i\xi}$ *is dominant* for a valley from $+i$ at $\phi=\frac{1}{6}\pi$, one from $-i$ at $\theta=\frac{7}{6}\pi$, and on the 0^- side of the branch cut.

Finally, we will need to work out the value of the integral δ, which is done on the contour shown connecting 0^- and 0^+. The leading term is given by Stueckelberg:

$$\delta^{(0)}=\tfrac{1}{2}\pi T_0\ ; \tag{39a}$$

including the higher-order terms we find the expansion

$$\delta=\tfrac{1}{2}\pi\left[T_0+i(4/3\pi)T_1-\tfrac{1}{4}T_2-i(8/15\pi)T_3+\tfrac{1}{8}T_4+\cdots\right]. \tag{39b}$$

By the same means we can also evaluate (on the lower contour) the integral

$$+i\int_{0^-}^{0^+}T(t)(1+t^2)^{1/2}dt=-\delta^*. \tag{40}$$

Associated with each of the four dominance lines crossed by the "good path" in Fig. 2 is an unknown proportionality constant, which we have labeled A, B, C, D as indicated in the figure. It is not hard to show from Eqs. (35) that β_{2-} behaves like β_{1+} and β_{1-} like β_{2+}, except that the constants are $-A$, $-B$, $-C$, $-D$, respectively.

We now carry out an excursion on the "good path," starting at $P_{\rm IV}$ and going counterclockwise. Let the values of $\beta_{j\pm}$ at $P_{\rm IV}$ be $\beta_{j\pm}^{(0)}$. On passing line A, we have

$$\beta_{1+}\to\beta_{1+}^{(0)}+A\beta_{2+}^{(0)},\quad \beta_{2-}\to\beta_{2-}^{(0)}-A\beta_{1-}^{(0)}; \tag{41a}$$

on passing line B, we have

$$\beta_{2+}\to\beta_{2+}^{(0)}+B[\beta_{1+}^{(0)}+A\beta_{2+}^{(0)}]=(1+AB)\beta_{2+}^{(0)}+B\beta_{1+}^{(0)},$$

$$\beta_{1-}\to(1+AB)\beta_{1-}^{(0)}-B\beta_{2-}^{(0)}. \tag{41b}$$

Equations (41a) and (41b) give the values of $\beta_{j\pm}$ on arrival at $P_{\rm III}$.

Conditions on the unknown constants can be obtained by returning from $P_{\rm III}$ to $P_{\rm IV}$ via the lower half-plane. On passing line C the coefficients β_{1+}, β_{2-} again alter, while at D β_{2+} and β_{1-} change. In the meantime, on completing the counterclockwise circuit from 0^+ to 0^- and back the asymptotic

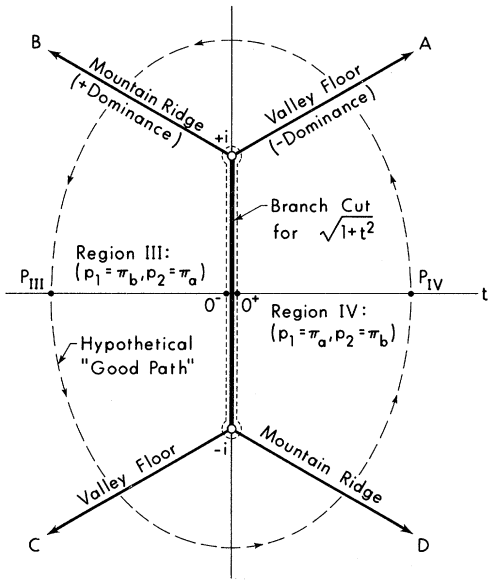

FIG. 2. Complex t plane near R_x, showing regions of dominance for $|e^{\pm i\xi(t)}|$. Branch cut connects $-i$ and $+i$. Inner contour is used to evaluate δ.

functions $\tilde{\psi}_{1+}$ and $\tilde{\psi}_{2-}$ alter by the factor $e^{-\delta-\delta^*} = e^{-2\mathrm{Re}(\delta)}$, while ψ_{2+} and ψ_{1-} change by $e^{+2\mathrm{Re}(\delta)}$. However, the full wave function must return to its original value. This leads to four equations connecting the constants A, B, C, D:

$$A+C+ABC=0\,,\quad B+D+BCD=0\,,$$
$$(1+BC)\,e^{-2\,\mathrm{Re}(\delta)}=1\,, \tag{42}$$
$$[(1+AB)(1+CD)+AD]\,e^{+2\,\mathrm{Re}(\delta)}=1\,.$$

However, Eqs. (42) yield only three independent relations:

$$1+AB=e^{-2\,\mathrm{Re}(\delta)}\,,$$
$$1+CD=e^{-2\,\mathrm{Re}(\delta)}\,, \tag{43}$$
$$1+BC=e^{+2\,\mathrm{Re}(\delta)}\,.$$

To determine the connection formulas we need only know A and B, but Eqs. (43) do not determine these independently. We must therefore seek additional relations.

One more condition is provided by the probability conservation property of Eqs. (15),

$$|\alpha_{1\pm}|^2+|\alpha_{2\pm}|^2=\mathrm{const.} \tag{44}$$

Since Ψ in regions III and IV can be expressed in terms of the standard real-axis forms [Eqs. (29) and (30)],

$$\Psi^{III}=a^{III}_{1+}\psi^{III}_{1+}+a^{III}_{1-}\psi^{III}_{1-}+a^{III}_{2+}\psi^{III}_{2+}+a^{III}_{2-}\psi^{III}_{2-}\,,$$
$$\Psi^{IV}=a^{IV}_{1+}\psi^{IV}_{1+}+a^{IV}_{1-}\psi^{IV}_{1-}+a^{IV}_{2+}\psi^{IV}_{2+}+a^{IV}_{2-}\psi^{IV}_{2-}\,, \tag{45}$$

and Eqs. (32) and (33) connect these to $\chi^{\pm}_{\nu}$, it follows that

$$|a^{III}_{1\pm}|^2+|a^{III}_{2\pm}|^2=|a^{IV}_{1\pm}|^2+|a^{IV}_{2\pm}|^2=\mathrm{const.} \tag{46}$$

However, via the connection formulas, Eqs. (41), and the relations given by (32) and (33) between the standard real axis forms and $\tilde{\psi}_{j\pm}$, we can express a^{III}_{j-} in terms of a^{IV}_{j-} and the unknown constants A, B; without loss of generality we can take $a^{IV}_{2-}=0$, $a^{IV}_{1-}=1$. Then the connection formulas are

$$a^{III}_{1-}=(1+AB)\,e^{+\delta}=e^{-\delta *}\,,$$
$$a^{III}_{2-}=-Ae^{+\delta}\,e^{-i\sigma_0}\,, \tag{47}$$

and using Eq. (46) we find

$$e^{-2\,\mathrm{Re}(\delta)}+|A|^2\,e^{+2\,\mathrm{Re}(\delta)}=1\,,$$

or

$$|A|^2=e^{-2\,\mathrm{Re}(\delta)}(1-e^{-2\,\mathrm{Re}(\delta)})\,. \tag{48}$$

The same relation is recovered from the other possible boundary condition, $a^{IV}_{1-}=0$, $a^{IV}_{2-}=1$.

The constants A, B are now determined to within an unknown phase factor $e^{i\eta}$. If we define $P_0^2=e^{-2\,\mathrm{Re}(\delta)}$ and note that $0\leq P_0\leq 1$ since $\mathrm{Re}(\delta)\geq 0$ if $T(t)$ is positive definite, then

$$A=|A|\,e^{i\eta}, \qquad B=-|B|\,e^{-i\eta},$$
$$|A|=P_0(1-P_0^2)^{1/2},\quad |B|=(1-P_0^2)^{1/2}/P_0\,. \tag{49}$$

The transition probabilities can now be evaluated from the application of the connection formulas (41) to a^{III}_{j+} and a^{IV}_{j+}:

$$a^{IV}_{2+}=a^{III}_{2+}\,e^{-\delta}-Be^{-\delta}\,e^{i\sigma_0}a^{III}_{1+}\,,$$
$$a^{IV}_{1+}=a^{III}_{1+}\,e^{-\delta *}-Ae^{+\delta}\,e^{-i\sigma_0}\,a^{III}_{2+}\,. \tag{50}$$

When the WKB turning-point connection formulas are employed,

$$a^{III}_{j+}=-ia^{III}_{j-}\,,$$

then with the boundary condition $a^{IV}_{2-}=0$, $a^{IV}_{1-}=1$, we obtain

$$|a^{IV}_{2+}|^2=4P_0^2(1-P_0^2)\sin^2\sigma\,, \tag{51a}$$
$$|a^{IV}_{1+}|^2=1-4P_0^2(1-P_0^2)\sin^2\sigma\,, \tag{51b}$$

where $\sigma=\sigma_0-\eta$ is an undetermined phase. This is the LZS formula, given the definition of P_0^2 in terms of δ.

Equations (51) differ from the results cited by Stueckelberg in two ways. He approximated $\mathrm{Re}(\delta)$ by $\delta^{(0)}$ [Eq. (39a)], while it is clear that in some cases there may be small effects due to the higher-order terms in the series for $T(t)$. Second, he assumed $\eta=0$, while we find it is not determined by the above arguments. Furthermore, no other

general constraints (unitarity, symmetry, etc.) can determine η.

However, there is a limiting case in which η is determined.[10,19] In the "diabatic limit," where U_{12} is small and the velocity suitably large, the distorted-wave approximation gives $\eta = \frac{1}{4}\pi$. Exact calculations, reported in a subsequent paper, show that the exact phase usually does not differ too greatly from this.

We have been able to evaluate analytically the constant B appearing in Eqs. (42) ff., for the case that $T(t) = T_0$, and obtain as the result an absolutely convergent infinite series closely related to Bessel functions I_ν of complex orders $\nu = \pm\frac{1}{2} + \frac{1}{2}iT$. Unfortunately the phase η does not seem to be expressible in simple form. The derivation of this new result for B is given in the Appendix.

In connection with the indeterminate value for σ found here, we note that Rice[9] also found connection formulas to be inadequate for a complete determination of the scattering parameters. In Rice's case the determination is even less complete because he chose to follow the more rigorous method of circumnavigating not only the crossing point but also the classical turning points, in his analytic continuation procedure. As a result he was able only to establish that the cross sections are of the form of Eqs. (51), but P_0^2 and σ are both undetermined. However, it is easy to show that this form is guaranteed simply by the symmetry and unitarity of the $\underline{S}$ matrix and is valid regardless of the nature of the potential curves and their interaction. Stueckelberg's procedure, when valid, has permitted us to determine one of the two parameters characterizing the $\underline{S}$ matrix, but not the other.

V. VALIDITY OF LZS FORMULA

As pointed out in the Introduction, derivation of the LZS formula requires that we make assumptions at several levels. The first of these is the use of the two-state model, perhaps the most restrictive in relation to real systems. The second approximation is to treat the system by a semiclassical method, using the classical trajectory equations. This is valid very generally and is of course not limited to the case of two states. The third approximation is what we have called the "LZS model": essentially linear diagonal elements (H_{11}, H_{22}) and essentially constant coupling element (H_{12}). As given in Sec. IV, Stueckelberg's treatment of the problem allows to some extent for deviations from this model by means of Taylor expansions about R_x. In the second paper of this series we present a computational study of the crossing problem in the same modified LZS model framework and discuss the effect of including these deviations from the simple LZS model. As shown there, certain of these deviations are important to a correct treatment. Finally, there are approximations and assumptions made in deriving the LZS formula as the solution to Eqs. (15). It is mainly this last set of approximations, rather than the LZS model, which is the source of errors in the LZS formula. We shall confine the discussion here to an examination of the validity of Stueckelberg's derivation of the LZS result.

Stueckelberg[5] emphasizes that the crossing point and the two classical turning points must be well separated from each other, but he does not explain why this matters. Our analysis shows that if elastic coupling occurs at the turning points, the reduction of Eqs. (12) to Eqs. (15) cannot be justified and there are no points (P_{III}) in region III where the coefficients $\alpha_{\nu\pm}$ are essentially constants. In such a case no reasonable upper limits can be placed on μ_Λ, i.e., no "good path" connecting any point in region III to a point in IV can exist.

While the requirements for the validity of Eqs. (15) [and their analogs in Stueckelberg's representation, Eqs. (35)] may be satisfied for a wide range of conditions, this does not necessarily imply that the connection formulas obtained in Sec. IV offer an accurate solution. That is, there can exist paths in the complex plane along which Eqs. (35) are valid, but such that the approximate integration of these equations represented in the connection formulas is uselessly inaccurate. An accurate integration of Eqs. (35) would give the correct result, but in such a case it would differ from the LZS formula.

The procedure of Kemble, which we adapted to this problem in Sec. III, is rigorously correct to within the error limits stated, i.e., to within errors of order μ_Λ with respect to a typical coefficient. However, there is an important difference between the classical turning-point problem treated by Zwaan and Kemble, and the problem we are considering. For the crossing-point case, under certain conditions the amplitudes being determined by connection relations have greatly disparate magnitudes: One of them may be $\simeq 1$, while the other is very small, but not exactly zero. But since at least one of the coefficients β_j has magnitude $\simeq 1$, Eqs. (37c) and (37d) are valid only to errors of absolute magnitude μ_Λ. Therefore the Stueckelberg connection formulas are useless if an estimated amplitude is of order μ_Λ or less. It is not hard to show that such errors accumulate for the inelastic cross section whenever it is small, i.e., whenever the quantity P_0 [cf. Eq. (49)], or the quantity $(1 - P_0^2)^{1/2}$, is much less than 1. Only if neither P_0 nor $(1 - P_0^2)^{1/2}$ is small can the derivation be valid without requiring unattainably small μ_Λ. Therefore the Stueckelberg derivation of the LZS formula certainly breaks down either for rapid passage (diabatic limit) or for slow passage (adia-

batic limit).

This result removes an inconsistency between apparent implications of Stueckelberg's method and other studies of the LZS formula and its validity. If we used the path quality index μ_A as the criterion for validity, as Stueckelberg's work implies we should, we would conclude that the LZS formula can be justified on a basis that is independent of the collision energy: Since $\mu_A \simeq \pi/|t|$, and t depends only upon the potentials and not upon the kinetic energy, it would appear that an energy-independent width of the coupling region could be defined. This, however, is not consistent with the facts. At high velocities, the LZS formula reduces to the Landau-Zener result. Some years ago it was shown by Bates[13] that the Landau-Zener formula is certainly not correct at high velocities (it does not even agree with the Born approximation). The reason, Bates showed, is that the width of the coupling region actually becomes infinite and is not sharply localized as Landau and Zener both assumed. Likewise, our arguments in the previous paragraph show that an energy-independent bound on μ_A is not sufficient to ensure the validity of Stueckelberg's derivation.

It is useful to make some numerical estimates of the conditions of validity in a typical system. We must consider the possible size of μ_A and the conditions under which either P_0 or $(1-P_0^2)$ become small. If the Stueckelberg derivation is ever to be valid we certainly should put $\mu_A \leq 0.1$. Assuming that crossing point R_x and classical turning points are separated by a distance D_0, we have

$$\mu_A = \pi |H_{12}| \Big/ \left(D_0 \left| \frac{d}{dR} (H_{11} - H_{22}) \right| \right). \tag{52a}$$

A reasonable upper limit for $D_0 |(d/dR)(H_{11} - H_{22})|$ is about 0.4 a.u. (10 eV) if the two-state approximation is to be justified. This gives us

$$\mu_A \simeq 10 |H_{12}| , \tag{52b}$$

i.e., in no case can the Stueckelberg derivation be valid if H_{12} exceeds 0.01 a.u. ($\sim$0.25 eV).

In the near-adiabatic case, we have $P_0 \simeq e^{-\delta^{(0)}} \ll 1$. $\delta^{(0)}$ can be approximated by

$$\delta^{(0)} \simeq \mu_A H_{12} D_0 / 2v , \tag{52c}$$

where v is the nuclear speed in a.u. Large $\delta^{(0)}$ can be achieved by large H_{12} or by small v, but there is a lower limit $\simeq 1 \times 10^{-3}$ on v if the WKB approximation and hence Eqs. (15) are to be valid. With these constraints we find that $\delta^{(0)}$ can never become large enough to reach the near-adiabatic limit $P_0 \lesssim \mu_A$, for any H_{12} less than the above upper bound of 0.25 eV; that is, the adiabatic limits of the Stueckelberg derivation are sufficiently contained by the limits on H_{12} expressed in Eq. (52b).

In the diabatic limit we have $(1-P_0^2)^{1/2} \simeq \delta^{(0)} \ll 1$, which requires [using Eq. (52c)] the constraint

$$\frac{\delta^{(0)}}{\mu_A} \simeq H_{12} D_0 / 2v \geq 10. \tag{52d}$$

Again taking a reasonable maximum value of $D_0 \sim 4$ a.u., and the smallest possible value of v consistent with the WKB approximation, we see that condition (52d) cannot be met if $|H_{12}| \lesssim 5 \times 10^{-3}$ a.u., i.e., about 0.1 eV.

We have established that Stueckelberg's derivation of the LZS formula can be valid only if (a) $|H_{12}| \lesssim 0.25$ eV and (b) the transition probability is substantial. This latter requirement (together with the requirement that the semiclassical approximation be valid) implies that (b′) $|H_{12}| \gtrsim 0.1$ eV. These restrictions are rather severe.

Numerical computations and experimental results indicate that the LZS formula itself is probably valid much more generally than this derivation would indicate. The cause of this is that μ_A is often a gross overestimate of the errors resulting from changes of the "constant" coefficients β_j [Eqs. (37)]. The driving terms in Eqs. (35) may oscillate rapidly and this can reduce the actual change in β_j relative to the estimate μ_A. However, any systematic attempt to more accurately bound the error by asymptotic approximations to the integrals of Eq. (37) is fraught with uncertainties. It is easier in the long run to solve the problem using numerical integration of Eqs. (15) in the modified LZS model, and these computations are described in the next paper.

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APPENDIX: ANALYTICAL EVALUATION OF THE STOKES CONSTANT B

According to Eq. (37d) of Sec. III, we can evaluate the coefficient B appearing in Eqs. (41b) ff., by evaluating the integral

$$B = -\frac{1}{2} \int_{t_1}^{t_2} \frac{dt}{1+t^2} e^{i\xi(t)} , \tag{A1}$$

where the evaluation is made along a "good path" entirely confined to the mountain region surrounding the ridge at Stokes ray B (Fig. 2). We assume $T(t) = T_0 = \text{const}$ and take as our good path the quarter circle $t = \rho e^{i\theta}$, $\rho = \text{const} = |t| \to \infty$, $\frac{1}{2}\pi \leq \theta \leq \pi$. We shall calculate B to errors of order $\mu_A = \pi/|t|$.

$\xi(t)$ can be evaluated analytically by simple methods. It is convenient to transform to the complex variable

$$u = (1+t^2)^{1/2} + t .$$

$\xi(t)$ can then be written

$$\xi(t)=\frac{T_0}{4}\left(u^2-\frac{1}{u^2}\right)+T_0\ln u+2T_0\int_{0^-}^{0^+}(1+t^2)^{1/2}\,dt\ , \tag{A2}$$

and this gives

$$B=-e^{\pi T_0}\int_{re^{i\pi/2}}^{re^{i\pi}}u^{\gamma}(u^2+1)^{-1}\,e^{i\alpha(u^2-1/u^2)}\,du\ , \tag{A3}$$

$r=\text{const}\to\infty$, and $\gamma=iT_0$, $\alpha=\frac{1}{4}T_0$. Differentiating with respect to α and expanding $e^{-i\alpha/u^2}$ in power series, we obtain

$$\frac{\partial B}{\partial\alpha}=-\frac{1}{2}\,e^{-i\pi(1+iT_0)/4}\sum_{n=0}^{\infty}\frac{\alpha^n\gamma^{\gamma+1-2n}}{n!}\times[F(a;b^0-n)-ir^{-2}F(a;b^0-n-1)]\ , \tag{A4}$$

where $a=\alpha r^2$, $b^0=\frac{1}{2}(1+iT_0)$, and

$$F(a;b)=\int_{-\pi/2}^{\pi/2}e^{ae^{i\phi}+ib\phi}\,d\phi\ . \tag{A5}$$

The properties of $F(a;b)$ as $r\to\infty$ are such that every term in the series (A4) contributes to the result. Using integration by parts and differentiation of Eq. (A5) with respect to a, we find the recurrence relation

$$F(a;b+1)+(b/a)F(a;b)=-(i/a)(e^{i(a+b\pi/2)}-e^{-i(a+b\pi/2)}) \tag{A6}$$

and the differential equation

$$\frac{\partial F(a;b)}{\partial a}+\frac{b}{a}F(a;b)=-\frac{i}{a}(e^{i(a+b\pi/2)}-e^{-i(a+b\pi/2)})\ . \tag{A7}$$

Equation (A7) can be solved exactly for $b=b^0-1$, with the result (as $a\to\infty$)

$$F(a\to\infty;-\tfrac{1}{2}+\tfrac{1}{2}iT_0)=-2a^{1/2-iT_0/2}\cosh(\tfrac{1}{2}\pi T_0)\Gamma(-\tfrac{1}{2}+\tfrac{1}{2}iT_0)\ ; \tag{A8}$$

the leading term in $F(a;b^0-n)$ (to errors of approximately $\sim\mu_\Lambda$) is then

$$F(a\to\infty;b^0-n)=2(-1)^n a^{n-b^0}\cosh(\tfrac{1}{2}\pi T_0)\Gamma(b^0-n),\qquad n=0,1,2\ldots\ . \tag{A9}$$

After some manipulation of the Γ products one obtains

$$\frac{\partial B}{\partial\alpha}=-\pi e^{-i\pi(1+iT_0)/4}\times\sum_{n=0}^{\infty}\frac{\alpha^{2n-b^0}}{n!}\left(\frac{1}{\Gamma(b^0+n+1)}-\frac{i\alpha}{\Gamma(b^0+n+2)}\right)$$
$$=-\pi\,e^{-i\pi/4}\,e^{+\pi T_0/4}[I_{-1/2-iT_0/2}(2\alpha)-iI_{1/2-iT_0/2}(2\alpha)]\ . \tag{A10}$$

Since it can easily be shown that $B(0;\beta)\simeq\mu_\Lambda$, we obtain the absolutely convergent series

$$B=-\pi e^{-i\pi/4}e^{\pi T_0/4}\sum_{n=0}^{\infty}\frac{\alpha^{2n+1/2-iT_0/2}}{n!\,\Gamma(n+\frac{1}{2}-\frac{1}{2}iT_0)}\times\{[2n+\tfrac{1}{2}-\tfrac{1}{2}iT_0]^{-1}-i\alpha/[(n+\tfrac{3}{2}-\tfrac{1}{2}iT_0)\times(2n+\tfrac{3}{2}-\tfrac{1}{2}iT_0)]\}\ , \tag{A11}$$

where $\alpha=\frac{1}{4}T_0$.

We have so far not been able to express this result in closed form, nor in particular to prove using (A11) that $|B|$ has the value obtained in Eq. (49) which is (to errors μ_Λ)

$$|B|=e^{\pi T_0/4}[2\sinh(\tfrac{1}{2}\pi T_0)]^{1/2}\ ; \tag{A12}$$

little information is available about Bessel functions of complex order.

While the unknown phase η associated with B has also not been obtained from (A11) in analytical closed form, Eq. (A11) does provide an exact expression by which it can easily be evaluated. In the next paper of the series we use it to compute B for comparison with exact numerical solutions of the LZS problem.

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Calculations of Stopping Cross Sections for 0.8- to 2.0-MeV Alpha Particles*

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Calculations of α-particle stopping cross sections based on the theories of Lindhard *et al.* using the Hartree-Fock-Slater atomic-charge distribution provide generally good agreement with previously obtained experimental results. In particular, the calculations are helpful in understanding the structure which results when, for fixed energy of the α particle, the stopping cross section is plotted against the atomic number of the stopping medium.

I. INTRODUCTION

It is plausible to assume that physical properties related to the distribution of the atomic electrons will have a periodic nature due to the shell structure of the atomic electrons. In 1906 Crowther[1] measured the mass absorption coefficient for Pa^{234} β rays and found the absorption to be a periodic function of the atomic number. In 1933 Bothe[2] suggested that Crowther's finding might be due to a periodicity in the characteristic frequencies in the Bohr stopping theory. The first computation to show the periodic structure in the stopping power was made by Westermark,[3] who calculated the energy loss of charged relativistic particles (184 GeV/amu) using the Bethe-Bloch formula and obtained a periodic dependence on the atomic number.

The stopping powers of 23 metallic elements for 19.8-MeV protons were measured by Burkig and MacKenzie.[4] Anomalies were noted from Ca to Fe and from Ta to Th, and the first anomaly was associated with the number of electrons in the $3d$ shell. Recently, Chu and Powers[5] measured α-particle stopping cross sections $\epsilon_\alpha(E_\alpha)$ in 17 solid elements from 400 keV to 2 MeV. An anomalous structure in $\epsilon_\alpha(E_\alpha)$ vs target element Z_2 was observed in the region of the first transition series ($Z_2 = 22$--29), and the amplitude of the anomalous structure was more pronounced at low energy. They attributed this finding to a correlation with the Hartree-Fock-Slater potential. White and Mueller[6] measured the electronic stopping cross section of H^1 and He^4 particles in five solid elements at energies near 100 keV, and an anomalous structure was also obtained. All of the above-mentioned experiments were performed using a given projectile (proton or α particle) to study the Z_2 dependence of ϵ_p or ϵ_α. Numerous experiments have also been performed by using a given target with different ion beams at a fixed velocity to study the Z_{ion} dependence of ϵ_{ion}. In 1963 Ormrod and Duckworth[7] noticed that the electronic stopping cross section has an oscillating dependence on Z_{ion}. This oscillatory dependence (or periodic structure) of ϵ_{ion} on Z_{ion} has been verified in boron, carbon, and aluminum thin films[8–11] and in gaseous targets[12,13] and also has been verified in the channeling of heavy ions in W crystals,[14] Si crystals,[15] and gold crystals.[16] Evidence of an oscillatory behavior of the excitation potential was observed by Andersen *et al.*[17]

Several calculations were made in 1968–69 to explain the above-mentioned experimental results of the oscillation dependence of ϵ_{ion} on Z_{ion}. Most of the calculations were based on the Firsov[18] model or uniform electron-gas model with modification to include an effective atomic number,[19] an ion-size effect,[20,21] or both.[22] Harrison[23] indicated that the periodic dependence of ϵ_{ion} on Z_{ion} was contained in the electron density of the moving ions when the density is determined from the Hartree-Fock-Slater wave function. Chu and Powers[5] indicated that the anomalous structure of ϵ_α vs Z_2 is indirectly related to the Hartree-Fock-Slater atomic potential.

With the above as background, one is encouraged to look for an explanation of the salient structure of the atomic stopping process in terms of the particular electronic structure of the target atoms. In the present paper, the stopping cross section is computed from the spherically averaged electronic charge density obtained from Hartree-Fock-Slater wave functions. The calculation is based on the theories of Lindhard, and co-workers[24–26] and Bonderup.[27]

II. REVIEW OF BASIC THEORY

At sufficiently high energies, the energy loss of a heavy charged particle in matter can be computed using the familiar Golden rule of second-order