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Studies of the Potential-Curve-Crossing Problem. II. General Theory and a Model for Close Crossings*

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A unified formal treatment of the two-state potential-curve-crossing problem in atomic collision theory is presented, and the case of close crossings analyzed in detail. A complete solution for this case, including necessary computations, is given using a suitable generalization of the linear model originally suggested by Landau, Zener, and Stueckelberg. Our solution is based upon a hierarchy of approximations concerned with (i) choice of a discrete basis set for electronic coordinates, (ii) semiclassical treatment of the nuclear motion, (iii) an appropriate model for the two-state electronic Hamiltonian, and (iv) a complete solution to that model.

I. INTRODUCTION

This paper is the second in a series concerned with the problem of electronic transitions occurring at a crossing of two electronic potential surfaces during an atomic or molecular collision. Such transitions are usually involved whenever efficient electronic deactivation or energy transfer occurs in collisions of dissimilar atoms. In the first paper of this series[1] we made a detailed analysis of one particular approach to the solution of the crossing problem, viz., that of Stueckelberg.[2] An important conclusion of that analysis is that the precise conditions of validity of the well-known Landau[3a]-Zener[3b]-Stueckelberg (LZS) formula for the transition probability at curve crossings remain unclear; all the derivations of it are valid only under unrealistically stringent conditions, while there is considerable evidence for the *de facto* validity of the formula itself over a rather wider range.

Since the original studies by these three authors in 1932, many treatments of curve crossing, using various assumptions and methods of solution, have appeared in the literature. Most of them can be understood and evaluated within a unified formal theory in a way that sets out clearly the essential assumptions and approximations.

An analysis of the curve-crossing problem is based on a hierarchy of approximations with four basic steps: (i) choice of a suitable truncated discrete basis set for describing the internal (electronic) states, (ii) a semiclassical treatment of the relative (nuclear) motion, (iii) definition of an appropriate explicit model for the projection of the Hamiltonian on the truncated electronic subspace, and (iv) adequate solution of the resulting model problem.

In another series of papers,[4] we have considered in detail the derivations of semiclassical descriptions of inelastic collisions, paying special attention to the precise conditions of validity of the various derivations and to the physical interpretations associated with them. From that analysis we can conclude that inadequacies in previous treatments of the curve-crossing problem have resulted primarily from defects in the construction and solution of curve-crossing models, and not from errors inherent in a semiclassical description.

The major concern of this paper is with the construction and solution of a model for close crossings, in which the crossing point is close to the classical turning point. For completeness, however, we begin with a discussion of the first two approximations in the hierarchy, i.e., the reduction to two states, and the semiclassical treatment of the nuclear motion. The formal properties of the resulting time-dependent equations are discussed, and an important simplification is presented. Finally, a model for the close curve-crossing problem is presented and solved, including the necessary numerical computations for intermediate parameter domains.

The model developed here is a generalization of one due to Bykhovskii, Nikitin, and Ovchinnikova[5] (BNO) and we will use some of their formalism and notation. Both their model and the present one

are extensions of the LZS model of linear potentials, constant coupling, and constant nuclear velocity: The BNO model takes into account the acceleration of the nuclei, while our model also allows for curvature in the potentials and variation in the coupling with internuclear distance. However, our formal analysis of the structure of the curve-crossing problem is more important than the specific model we have employed, because it shows clearly why various approximations, such as the LZS model, are inadequate, and provides criteria and means for systematic model improvements needed to meet actual conditions.

II. GENERAL THEORY

A. Internal States

The description "curve crossing" implies that important features of the problem to be treated are associated with a particular pair of electronic states. The applicability of such an idealization must be decided separately for each system and process in question, and obviously can be appropriate even then for only a limited range of observables. Two general limitations to such a description are inherent in atomic collisions, arising from (i) the tendency of electronic excited states to be nearly degenerate with many others, because of Rydberg convergence on ionization limits, and from (ii) the increasing importance of "direct-impact" excitation with increasing nuclear velocity. These general limitations confine applications of the curve-crossing problem, at least in the detail considered here, to those low-energy collisions that involve as the primary event the excitation of well-isolated (hence, lower-lying[6]) electronic states of the colliding system. To define "low energy" we may take the Massey adiabatic criterion, which confines relative collision energies below 1 keV.

In principle, a curve-crossing theory might be extended to cover the situation where the potential curve for the initial electronic state of a system crosses a sequence of closely spaced curves, and finally moves across the ionization limit of the sequence into a continuum. Some studies of this case have treated it as a multiple-curve-crossing problem.[7,8] While such a formulation may offer useful insight in certain cases, it is important to recognize that this problem also has some fundamentally new features. A highly degenerate manifold of electronic states can never behave adiabatically, because levels less tightly bound than $(m/M)E$ are strongly mixed with the continuum through the nuclear motion.[9] An electron initially translating with one of the nuclei may escape completely during a collision, if it is excited to such a weakly bound state. This effect, and all "direct-impact" effects[10] related to it, cannot be described by the use of Born-Oppenheimer electronic states *or by the use of any unitary transformation upon any finite subspace spanned by Born-Oppenheimer states*. Inclusion of direct-impact effects within the degenerate manifold of final states, which includes a careful account of the electron kinematics, would be necessary before a multiple-crossing model could be properly employed to examine strong coupling of such a manifold to an initial state.

With these restrictions on the generality of the theory, the problem is framed from the outset within a limited electronic subspace which is completely spanned by a finite set of Born-Oppenheimer (BO) or adiabatic electronic states. However, because the BO states obey the noncrossing rule, they may not form the most desirable representation within the subspace; instead it may be desirable to introduce diabatic representations, in which the diagonal matrix elements of the electronic Hamiltonian in the subspace can cross and the off-diagonal interactions appear as scalar coupling potentials. The main aspects of this question have already been discussed by F. T. Smith[11]; our formalism differs from his only in certain details.

A partial-wave analysis is convenient since the choice of electronic representation, etc., may depend on the collision angular momentum (classical impact parameter). Generalizing the definition of "internal state" to include implicit specification of angular momentum state for the collision, and denoting such internal states as a set of kets $\{|n\rangle\}$ which may depend on internuclear distance R as a parameter, we can write the wave function for a single partial wave as a linear combination

$$\Psi_L = R^{-1}\sum_n u_n(R)|n\rangle \quad . \tag{1}$$

Following the general lines indicated in Ref. 11 it is easy to show that the vector $\underline{u}\ (u_1, u_2, \ldots, u_N)$ obeys the coupled equations

$$\{[-i\hbar(d/dR) + \underline{P}(R)]^2 + \underline{H}'(R)\}\underline{u} = E\,\underline{u} \quad , \tag{2}$$

where

$$P_{mn}(R) = \langle m|-i\hbar(d/dR)|n\rangle \quad ; \tag{3}$$

the elements of $\underline{H}'$, $H'_{mn}(R)$, contain all other effects of the Hamiltonian and are simply scalar functions of R.

Only the R component of the nuclear gradient contributes to the nonadiabatic coupling matrix $\underline{P}$. Coriolis forces also appear in the complete Hamiltonian because Born-Oppenheimer states employ a rotating molecular reference frame. These "angular couplings" produce Λ-type doubling and related effects in the electronic spectra of diatomic molecules. They can lead to strong coupling within orbitally degenerate manifolds of the united atom associated with a colliding diatomic system; for

example, they are responsible for the high probability of the Lyman-α excitation process $H^+ + H(1s) \rightarrow H^+ + H(2p)$ at very low energies.[12] On the other hand, the asymptotic significance of the Coriolis forces within orbitally degenerate manifolds of the *separated* atoms can be shown to be trivial.[13] Finally, Coriolis coupling may come into play at an accidental crossing of two BO states whose Λ values differ by ± 1. In any case our formalism includes them in the interaction matrix $\underline{H}'$.

For mathematical simplicity we treat only the two-state case $N = 2$. Even aside from the fundamental problems of such a truncation discussed above, there are cases where a basis with more than two internal states is needed, notably those with angular momentum couplings; however, the important features of curve-crossing problems are present in the two-state case and there are many situations where it should be an adequate model.

The two limiting representations of the internal-state subspace are now easily defined: The "adiabatic" basis is that for which $\underline{H}'$ is made diagonal at each R, and the "diabatic" basis is that for which $\underline{P}$ vanishes. Potential surfaces (diagonal elements H'_{nn}) are usually more readily calculated in the adiabatic basis, though the results of experiments are often more easily interpreted in the diabatic basis. Semiclassical calculations are equally easy in either representation.

Suppose that in the diabatic basis $\underline{H}'$ has the elements

$$H'_{ij} = V_{ij}(R) \quad . \tag{4}$$

Let $\underline{W}$ represent the unitary matrix that renders $\underline{V}$ diagonal,

$$\underline{W}\,\underline{V}\,\underline{W}^\dagger = \underline{\epsilon} \ \text{(diagonal)} \quad , \tag{5}$$

so that in adiabatic representation, $H'_{ij} = \delta_{ij}\epsilon_j(R)$. $\underline{W}$ can be written

$$\underline{W} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \quad , \tag{6}$$

where

$$\sqrt{2}\cos\theta = [1 + t/(1+t^2)^{1/2}]^{1/2}, \qquad \sqrt{2}\sin\theta = [1 - t/(1+t^2)^{1/2}]^{1/2} \quad , \tag{7}$$

and

$$t \equiv [V_{22} - V_{11}]/2V_{12} = \cot 2\theta \quad . \tag{8}$$

The variable t, it will be recalled, plays an important role in Stueckelberg's treatment (cf. our analysis in Ref. 1) and will here also.

For any given state vector, its representative in the diabatic representation $\underline{u}^D$ is related to the corresponding adiabatic representative $\underline{u}^A$ by

$$\underline{u}^A = \underline{W}\,\underline{u}^D \quad . \tag{9}$$

B. Semiclassical Treatment of Nuclear Motion

1. Semiclassical Approximants and Classical Trajectory Equations

A semiclassical treatment is based on the use of asymptotic (WKB) approximants to the channel wave functions adequate to describe elastic propagation in the absence of coupling. The exact wave function for the coupled system is then expanded in terms of these approximants, and coupled equations are obtained for the expansion coefficients. Thus, for the diabatic basis, for example, we write

$$u_j^D = \frac{c_{j+}(R)\exp\{i[\int^R \wp_j(R')dR']/\hbar\} + c_{j-}(R)\exp\{-i[\int^R \wp_j(R')dR']/\hbar\}}{|\wp_j^{1/2}|} \quad , \tag{10}$$

where

$$\wp_j^2(R)/2M + V_{jj}(R) - E = 0 \quad . \tag{11}$$

After deriving first-order coupled equations for $c_{j\pm}(R)$ and making a set of suitable approximations, inherent in the semiclassical theory,[4] we arrive at the equations

$$i\hbar\frac{dc_1}{d\tau} = \left\{V_{12}\exp\left[\frac{i}{\hbar}\int_0^\tau (V_{11} - V_{22})d\tau'\right]\right\}c_2 \quad ,$$
$$i\hbar\frac{dc_2}{d\tau} = \left\{V_{12}\exp\left[-\frac{i}{\hbar}\int_0^\tau (V_{11} - V_{22})d\tau'\right]\right\}c_1 \quad , \tag{12}$$

where τ is a "time" variable related to R by

$$\frac{dR}{d\tau} = \frac{\overline{\wp}}{M} \quad , \tag{13}$$

a quantity subsequently referred to as the "nuclear velocity." Equations (12) are called "the classical-trajectory equations," because they can be obtained by making the heuristic postulate that the nuclei move along a classical trajectory $R(\tau)$ and that the electrons obey the time-dependent Schrödinger equation arising from such a time dependence in the Hamiltonian. However, it has been shown not only that this independent postulate is unnecessary, but that Eqs. (12) are valid much more generally than such an interpretation or postulate allows.[4]

If the inelastic coupling is weak in the adiabatic representation, then the analogous semiclassical solution can be written

$$u_j^A = \frac{\gamma_{j+}(R)\exp[(i/\hbar)\int^R \pi_j\,dR'] + \gamma_{j-}(R)\exp[-(i/\hbar)\int^R \pi_j\,dR']}{|\pi_j^{1/2}|} \quad , \tag{14}$$

where π_j is the adiabatic momentum,

$$[\pi_j^2(R)/2M] + \epsilon_j(R) - E = 0 \quad . \tag{15}$$

By using Eqs. (6)–(9), these forms can be expressed in the *diabatic* representation as

$$\begin{bmatrix} u_1^D \\ u_2^D \end{bmatrix} = \begin{bmatrix} \{1 + t/(1+t^2)^{1/2}\}^{1/2} \\ -\{1 - t/(1+t^2)^{1/2}\}^{1/2} \end{bmatrix} \frac{\gamma_{a+}\exp[(i/\hbar)\int \pi_a\,dR'] + \gamma_{a-}\exp[-(i/\hbar)\int \pi_a\,dR']}{|(2\pi_a)^{1/2}|}$$

$$+ \begin{bmatrix} \{1 - t/(1+t^2)^{1/2}\}^{1/2} \\ \{1 + t/(1+t^2)^{1/2}\}^{1/2} \end{bmatrix} \frac{\gamma_{b+}\exp[(i/\hbar)\int \pi_b\,dR'] + \gamma_{b-}\exp[-(i/\hbar)\int \pi_b\,dR']}{|(2\pi_b)^{1/2}|} \quad , \tag{16}$$

which can be recognized immediately as the asymptotic forms obtained by Stueckelberg[1,2] [cf. Eqs. (14) of Ref. 1]. Stueckelberg's treatment assumes that sufficiently far from a crossing region the coefficients $\gamma_{j\pm}$ are constants and that the relations linking them across the crossing region can be determined by "connection formulas" obtained by examination of Stokes's phenomena associated with the crossing point. In Ref. 1, we showed that this procedure is almost never valid. If the actual variations in $\gamma_{j\pm}(R)$ are considered, we obtain, by methods identical to those for Eqs. (12),

$$\hbar\frac{d\gamma_a}{d\tau} = \left[-\frac{d\theta}{d\tau}\exp\left(-\frac{i}{\hbar}\int^\tau (\epsilon_b - \epsilon_a)\,d\tau'\right)\right]\gamma_b \, ,$$

$$\hbar\frac{d\gamma_b}{d\tau} = \left[\frac{d\theta}{d\tau}\exp\left(\frac{i}{\hbar}\int^\tau (\epsilon_b - \epsilon_a)\,d\tau'\right)\right]\gamma_a \quad ; \tag{17}$$

note that

$$\frac{d\theta}{d\tau} = -\frac{dt}{d\tau}\,[2(1+t^2)]^{-1} \quad .$$

Equations (17) are just the classical-trajectory equations in the *adiabatic* representation [Eqs. (15), Ref. 1].

We wish to emphasize at this point the very general validity of the classical-trajectory equations, especially as investigations of the crossing problem have sometimes focused attention on the applicability of semiclassical methods to the problem. In papers cited in Ref. 4 we have considered the general problem of semiclassical theories of inelastic scattering, paying careful attention to the various derivations of the classical-trajectory equations and the conditions for their validity. In addition to the derivations based on semiclassical approximations in configuration space, we have shown that there exists a derivation based on a momentum-space semiclassical approximation, which complements the one based on configuration space in such a way that Eqs. (12) and (17) can often be valid even to describe coupling in the classical-turning-point region. The general assumptions required for the validity of the classical-trajectory equations are the following:

(i) The semiclassical approximation must be valid to describe elastic scattering for each channel in the absence of coupling.

(ii) The difference between classical trajectories for elastic scattering on potential curves for different channels must be small compared to atomic dimensions.

(iii) The coupling must be negligible near the classical turning points; and/or

(iii′) the forces $-(dV_{jj}/dR)$ must have the same sign near the turning points.

Therefore the classical-trajectory equations are nearly always valid to describe crossing problems. There is only one important case for which they are not applicable: If the crossing point is close to the turning point and the forces $-(dV_{jj}/dR)$ have different signs for the two channels, then a kind of orbiting collision occurs which cannot be described classically. In all other cases Eqs. (12) and (17) are applicable.

Finally we may point out the complete equivalence of Eqs. (12) and (17) within the limits of the semiclassical theory. Sometimes it has been suggested that one form may be more accurate than another. First we may note that if $R(\tau)$ be specified the same in each case, then Eqs. (12) and (17) are merely different types of interaction representations of the same "time-dependent Schrödinger equation." Any argument for the superiority of one form over the other must therefore rest on the claim that one form's choice of mean trajectory $R(\tau)$ is different from and superior to that of another. However, we show in Ref. 4 that if the choice of trajectory

makes much difference, the classical-trajectory formulation itself is not valid. Hence the choice of representation is entirely a matter of convenience insofar as the calculation of the coefficients c_i or γ_j is concerned.

2. Formal Properties

Many results summarized in this section were obtained by Bates, Johnston, and Stewart.[14]

a. Reduction to three real equations. Writing the coefficients $c_{i\pm}$ as a two-vector $\underline{c}(\tau)$, we define the evolution matrix $\underline{G}(\tau, \tau_0)$ such that

$$\underline{c}(\tau) = \underline{G}(\tau, \tau_0)\underline{c}(\tau_0) \quad . \tag{18}$$

$\underline{G}$ obeys the same differential equation as $\underline{c}$ and has the boundary condition

$$\underline{G}(\tau_0, \tau_0) = \underline{1} \quad . \tag{19}$$

It is easy to show that

$$\underline{G}^\dagger \underline{G} = \underline{G}\,\underline{G}^\dagger = \underline{1} \quad , \tag{20a}$$

$$\underline{G}(\tau_0, \tau) = [\underline{G}(\tau, \tau_0)]^{-1} \quad \text{(all } \tau, \tau_0) \quad , \tag{20b}$$

$$\det \underline{G}(\tau, \tau_0) = 1 \quad . \tag{20c}$$

Therefore $\underline{G}$ can be written

$$G(\tau, \tau_0) = \begin{pmatrix} (1-z^2)^{1/2} e^{i\Gamma_1} & -ze^{-i\Gamma_2} \\ ze^{i\Gamma_2} & (1-z^2)^{1/2} e^{-i\Gamma_1} \end{pmatrix}, \tag{21}$$

where z, Γ_1, Γ_2 are real functions of τ and τ_0 satisfying the differential equations

$$\frac{dz}{d\tau} = V_{12}(1-z^2)^{1/2} \sin(\Xi + \Gamma_1 - \Gamma_2) \quad ,$$

$$\frac{d\Gamma_1}{d\tau} = -V_{12} \frac{z}{(1-z^2)^{1/2}} \cos(\Xi + \Gamma_1 - \Gamma_2) \quad , \tag{22}$$

$$\frac{d\Gamma_2}{d\tau} = -V_{12} \frac{(1-z^2)^{1/2}}{z} \cos(\Xi + \Gamma_1 - \Gamma_2) \quad ,$$

with

$$\Xi = \int_{\tau_0}^{\tau} (V_{22} - V_{11}) d\tau'/\hbar \quad , \tag{23}$$

and boundary conditions

$$z(\tau_0, \tau_0) = 0, \quad \Gamma_1(\tau_0, \tau_0) = 0, \quad \Gamma_2(\tau_0, \tau_0) = -\tfrac{1}{2}\pi \quad . \tag{24}$$

In the adiabatic representation the formalism of Eqs. (19)–(24) can be repeated exactly, with the substitutions

$$V_{12} \to \frac{d\theta}{d\tau}, \quad \Xi + \Gamma_1 - \Gamma_2 \to \Xi + \Gamma_1 - \Gamma_2 + \tfrac{1}{2}\pi$$

in Eqs. (22), and with

$$\Xi = \int_{\tau_0}^{\tau} (\epsilon_b - \epsilon_a) d\tau'/\hbar \quad ; \tag{23'}$$

the boundary conditions (24) remain unchanged.

b. Symmetry rules. Let $\tau_0 = 0$ correspond to the "time" at the mean trajectory turning point. Then the classical-trajectory equations have the symmetry properties

$$V_{12}(-\tau) = V_{12}(\tau) = V_{12}^*(\tau) \quad , \quad \Xi(-\tau) = -\Xi(\tau) \quad ,$$
$$\left(\frac{d\theta}{d\tau}\right)_{-\tau} = -\left(\frac{d\theta}{d\tau}\right)_{\tau} \quad . \tag{25}$$

It is easy to show from these equations that $\underline{G}^*(-\tau, 0)$ in either representation obeys the same differential equation and boundary conditions as $\underline{G}(\tau, 0)$, so

$$\underline{G}^*(-\tau, 0) = \underline{G}(\tau, 0) \quad . \tag{26}$$

It follows that

$$\underline{c}(\tau) = \underline{G}(\tau, 0)\underline{c}(0) = \underline{G}(\tau, 0)\underline{G}(0, -\tau)\underline{c}(-\tau)$$

and, using (20a) and (26), we find

$$\underline{c}(\tau) = \underline{G}(\tau, 0)\tilde{\underline{G}}(\tau, 0)\underline{c}(-\tau)$$
$$= \tilde{\underline{G}}(0, -\tau)\underline{G}(0, -\tau)\underline{c}(-\tau) \tag{27}$$

(here $\tilde{\underline{G}}$ is the transpose of $\underline{G}$). Also, we define

$$\underline{c}_\pm = \lim_{\tau \to \pm\infty} [\underline{c}(\tau)] \quad , \tag{28a}$$

$$\underline{G}_+ = \lim_{\tau \to \infty} [\underline{G}(\tau, 0)] \quad , \quad \underline{G}_- = \lim_{\tau \to +\infty} [\underline{G}(0, -\tau)] \quad . \tag{28b}$$

Observables of a collision which can be predicted by the classical-trajectory equations are all incorporated in a matrix $\underline{S}$:

$$\underline{S} = \underline{G}_+\underline{G}_- + \underline{G}_+\tilde{\underline{G}}_+ = \underline{G}_-\tilde{\underline{G}}_- \quad . \tag{29}$$

It is easy to show that $\underline{S}$ is unitary and symmetric, with $\det \underline{S} = 1$. From Eqs. (29) we see that $\underline{S}$ is determined either from $\underline{G}_+$ or from $\underline{G}_-$, requiring integration over only half the "time range" of a collision.

Boundary conditions of $\underline{G}_-$ correspond closely to the physical situation in a collision experiment: The system is initially in one of the two internal states (at $\tau \to -\infty$). Computationally, the boundary conditions are usually applied at some large negative τ and the coupled equations are integrated to $\tau = 0$. However, Lebeda and Thorson[15] showed that the boundary conditions (24) are then not appropriate at any finite starting value of τ, and that using them produces spurious oscillations in z and Γ_2. The corrected boundary conditions obtained by a certain asymptotic device[15] remove these oscillations and lead to a substantial improvement in speed and accuracy of computation.

In the present study, we calculated $\underline{G}_+$ by applying the boundary conditions (24) at the turning point ($\tau = 0$) and integrating to large positive values of τ. The fact that these boundary conditions do not occur in the physical system is unimportant since we can still evaluate the $\underline{S}$ matrix from $\underline{G}_+$ according to (29). This procedure has the advantage that as τ increases, z, Γ_1, and Γ_2 converge to their limits in an oscillatory manner, and by averaging over a few oscillations the asymptotic value is

quickly and accurately obtained. The analogous procedure to obtain $\underline{G}_-$ is not possible in a single computation. This procedure for obtaining $\underline{G}_+$ appears to achieve an improvement in speed and accuracy comparable to that obtained with the Lebeda-Thorson boundary conditions for the $\underline{G}_-$ integration.

Let us further define $z_\pm$, $\Gamma_{j\pm}$ as the values which generate $\underline{G}_\pm$ in Eq. (21); then the $\underline{S}$ matrix can be written

$$S_{11} = (1 - z_+^2)\, e^{2i\Gamma_{1+}} + z_+^2 e^{-2i\Gamma_{2+}} \quad , \qquad (30a)$$

$$S_{21} = +2iz_+(1 - z_+^2)^{1/2} \sin(\Gamma_{1+} + \Gamma_{2+})$$

or

$$S_{11} = (1 - z_-^2)\, e^{2i\Gamma_{1-}} + z_-^2 e^{+2i\Gamma_{2-}} \quad , \qquad (30b)$$

$$S_{21} = -2iz_-(1 - z_-^2)^{1/2} \sin(\Gamma_{1-} - \Gamma_{2-}) \quad .$$

While these forms are a very general result of the symmetry properties of the classical-trajectory equations, they have an especially simple and well-known physical interpretation for the special case of a crossing problem in which the crossing point is well separated from the classical turning point. The probability of making a transition from state 1 to state 2 is

$$P = |S_{21}|^2 = 4z_+^2(1 - z_+^2)\sin^2(\Gamma_{1+} + \Gamma_{2+}) \quad . \qquad (31a)$$

z_+^2 may be considered to be the probability that the system makes a transition in a single passage through the crossing region. Then the probability that after a second passage it remains in state 2 is $z_+^2(1 - z_+^2)$. The factor $4\sin^2(\Gamma_{1+} + \Gamma_{2+})$, with average value 2, takes into account the two possible classical event sequences leading to a transition and the quantal interference between them. The phases Γ_2 and Γ_1 also have an interpretation. Γ_1, which would be zero for zero coupling, represents a reactive response of the initial state on a single passage through the coupling region. Γ_2 contains two terms; one is the phase difference between the two elastic potentials over the "time" interval between turning point ($\tau = 0$) and crossing point [in diabatic representation, $\int_0^{\tau_c} (V_{22} - V_{11})\, d\tau'/\hbar$], but there is also a small inelastic shift associated with the transition. Given this account of the phases, the form of S_{11} also can be interpreted as the sum of amplitudes for the two classical sequences leading to no net transition. In view of these properties $\underline{S}$ can obviously be written

$$\underline{S} = \begin{pmatrix} (1-P)^{1/2} e^{i\Gamma_0} & \pm iP^{1/2} \\ \pm iP^{1/2} & (1-P)^{1/2} e^{-i\Gamma_0} \end{pmatrix} \quad , \qquad (31b)$$

with

$$\Gamma_0 = \tan^{-1} \frac{(1 - z_+^2)\sin 2\Gamma_{1+} - z_+^2 \sin 2\Gamma_{2+}}{(1 - z_+^2)\cos 2\Gamma_{1+} + z_+^2 \cos 2\Gamma_{2+}} \quad , \qquad (31c)$$

so that all results of the scattering could in principle be described by giving the two functions P and Γ_0. However, these quantities vary rapidly, while z_+, Γ_{1+}, and Γ_{2+} are slowly varying, for the crossing problem; it is therefore more convenient to tabulate the latter in this case.

In Ref. 1, we showed that in Stueckelberg's treatment of the crossing problem, which involves a connection-formula technique for solving the classical-trajectory equations in the adiabatic representation [Eqs. (17)], the transition probability [Eq. (51a), Ref. 1] has the form of Eq. (31a), where $\Gamma_{1+} + \Gamma_{2+} = \sigma_0 - \eta$ and σ_0 is the (adiabatic) elastic phase lag associated with the two surfaces. We found that the additional phase $-\eta$ was undetermined in the Stueckelberg connection-formula method, but we were able to determine it by an analytical evaluation of the Stokes's coefficient. We discuss the results of this analytic formula in Sec. III D 5.

3. *Complete Scattering Matrix and Differential Cross Sections*

In a typical scattering experiment the boundary conditions on $u_n(R)$ stipulate incoming waves in a single internal state n'. Let us specifically incorporate this boundary condition by indexing solutions $u_{nn'}(R)$. The $\underline{S}$ matrix of scattering theory is then defined for each partial wave by

$$u_{nn'} \sim \frac{\delta_{nn'} \exp[-i(k_n R - \tfrac{1}{2}L\pi)] - S_{nn'} \exp[+i(k_n R - \tfrac{1}{2}L\pi)]}{k_n^{1/2}} \qquad (32)$$

in the important and common special case where the angular momentum L of the nuclei is essentially conserved and the rotational parts of the kets $\{|n\rangle\}$ are merely spherical harmonics. Comparing this definition with Eq. (10) we find that

$$\lim_{R\to\infty} \sqrt{M}\, c^-_{nn'}(R) = \delta_{nn'} \lim_{R\to\infty} \left(\exp\{i[(\int_{R_{n'}}^{R} \wp_{n'}\, dR'/\hbar) - k_{n'}R + L\pi/2]\}\right) \quad ,$$

$$-S^L_{nn'} = \lim_{R\to\infty} \sqrt{M}\, c^+_{nn'}(R) \times \exp\{+i[(\int_{R_n}^{R} \wp_n dR'/\hbar) - k_n R + L\pi/2]\} \qquad (33)$$

(where R_n is the classical turning point for the nth elastic surface); combining Eqs. (33) with Eqs. (27) and (29) we then find as the final result

$$S^L_{nn'} = S^L_{nn'} \exp[i(\eta_n + \eta_{n'})] \quad , \qquad (34)$$

where η_n is the WKB phase shift for the nth elastic surface

$$\eta_n = \lim_{R\to\infty}\left[\left(\int_{R_n}^{R} \mathcal{P}_n(R')\,dR'/\hbar\right) - k_n R + \tfrac{1}{2}L\pi + \tfrac{1}{4}\pi\right] . \tag{35}$$

[Eqs. (33) and (35) give explicitly the diabatic forms; read π_n for $\mathcal{P}_n$ in the adiabatic case.]

$S_{nn'}$ and η_n can be evaluated using either the diabatic or adiabatic representations; however, consistency is required to obtain the correct scattering matrix elements $S_{nn'}$. This may seem strange in view of our earlier statement (at the end of Sec. II B 1) that Eqs. (12) and (17) are merely "different interaction representations of the same time-dependent Schrödinger equation" [for a given trajectory $R(\tau)$]. The point is that although Eqs. (12) and (17) are so related to a unique wave function in a time-dependent interpretation, the full semiclassical scattering wave functions $\underline{u}^A$ or $\underline{u}^D$ are not calculated via that interpretation, but are related to the coefficients $c_{i\pm}$ or $\gamma_{j\pm}$ through the WKB approximants [cf., respectively, Eqs. (10) and (14)]. It follows that the elements $S_{nn'}$ have the same magnitude, but not quite the same phase, in the two representations; hence the inelastic transition probability, but not the differential-scattering amplitude, is invariant to the representation used. The scattering amplitude is obtained by summing over partial waves with the incident plane-wave boundary condition

$$f_{nn'}(\Theta) = [2i(k_n k_{n'})^{1/2}]^{-1} \times \sum_L (2L+1)\,P_L^0(\cos\Theta)(S_{nn'}^L - \delta_{nn'}) . \tag{36}$$

Equation (34) is especially important, since it implies that the semiclassical solution of the inelastic scattering problem can be separated into two independent parts: first, the calculation of $\underline{S}$ via the classical trajectory equations, and second, the calculation of elastic scattering phase shifts $(\eta_n + \eta_{n'})$ via the WKB approximation and summation over partial waves to obtain differential cross sections. Essentially the same decomposition of results was found by Knudson and Thorson[16] for the special problem of Lyman-α excitation and resonant charge exchange in $H^+ - H(1s)$ collisions.

4. Formal Simplification of Classical-Trajectory Equations

We now obtain an important transformation of the classical-trajectory equations for the two-state case, which provides the formal basis for the unified model analysis of Sec. III. Here we carry out the transformation in the diabatic representation, but an analogous result holds for the adiabatic case.

Let us assume that $V_{12}(\tau)$ does not change its sign as τ varies over the interval of integration $(0 - \pm\infty)$; although, in principle, cases of V_{12} changing sign could occur, we do not in fact know of any in real problems. Noting that $[\int_0^\tau (V_{11} - V_{22})d\tau'/\hbar]$ is a (dimensionless) classical action difference function, we find it convenient to introduce also an "inelastic action function,"

$$s(\tau) = \left[\int_0^\tau V_{12}(\tau')d\tau'/\hbar\right] , \tag{37}$$

which is a monotonic function of τ if V_{12} is of fixed sign. If we then express the diabatic classical-trajectory equations (12) in terms of s as an independent variable, they become

$$\begin{aligned} i\,\frac{dc_1}{ds} &= \exp\left[-i\int^s 2t(s')ds'\right]c_2 , \\ i\,\frac{dc_2}{ds} &= \exp\left[+i\int^s 2t(s')ds'\right]c_1 , \end{aligned} \tag{38}$$

where t, which was defined in Eq. (8), is the inverse of an "effective coupling strength function" and must be expressed as a function of the inelastic action variable s.

Equations (38) show that solutions to the classical-trajectory equations are not sensitive to all the detailed properties of the four functions $V_{11}(R)$, $V_{22}(R)$, $V_{12}(R)$, and $R(\tau)$, but depend only on the behavior of a single function of one variable, $t(s)$. By characterizing models in terms of s vs τ, and t vs s, we can obtain very general results for the matrices $\underline{S}$ which result from particular model assumptions in a computationally concise manner. In the remainder of this paper we develop and solve a model problem appropriate to close crossings.

III. MODEL FOR CLOSE CROSSINGS

A. Properties of $t(s)$ and Close Crossing Concept

The formalism of Sec. II B 4 provides the basis for a unified analysis of all models for the crossing problem.

If $V_{12}(R)$ decreases more rapidly than R^{-1} as $R\to\infty$, Eq. (37) maps the semi-infinite range of the time onto a *finite* range of the variable s $(0 \le s \le s_\infty)$. The fact that this range is finite is relevant to the theory. For crossing problems, $t(s)$ has a fairly simple structure, illustrated in Fig. 1. At the *turning point* $(s=0,\ \tau=0)$, $t(0)$ has some finite negative value, but has *zero slope* because on the trajectory at $\tau = 0$,

$$\left(\frac{dt}{d\tau}\right)_0 = \left(\frac{dt}{ds}\right)_0\left(\frac{ds}{d\tau}\right)_0 = \left(\frac{dt}{dR}\right)_0\left(\frac{dR}{d\tau}\right)_0 = 0$$

and

$$\frac{ds}{d\tau} = V_{12}[R(0)] \neq 0 .$$

At the *crossing point* s_x, $t(s_x) = 0$ but $(dt/ds)_{s_x} \neq 0$. Finally, $t(s)$ is singular at s_∞ $(\tau\to\infty)$. Important limitations on models for the crossing problem are

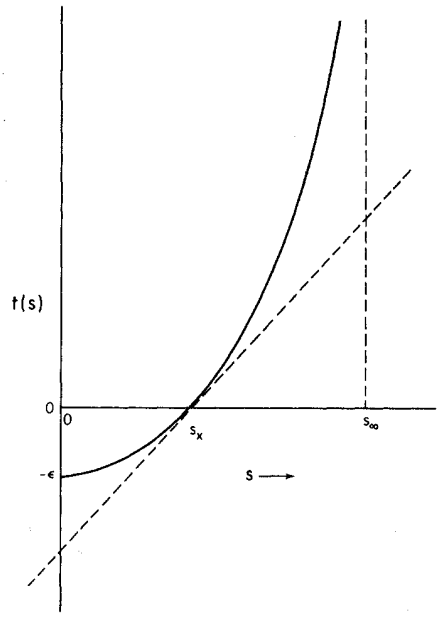

FIG. 1. $t(s)$ vs s for a curve-crossing problem. $S=0$, turning point; $s=s_x$, crossing point; s_∞, finite value of s for $\tau \to \infty$. Solid curve shows the actual behavior of the typical $t(s)$, while the dotted curve represents the linear LZS model. $t(s)$ is singular at s_∞, and has zero slope at $s=0$. Both the BNO model (Ref. 5) and the model of this paper represent $t(s)$ as a suitable quadratic, and are valid if the region near s_∞ does not contribute much to coupling (close crossing case).

associated with this singularity.

We define a *close* crossing model by the assumption that s_∞ and s_x are sufficiently well separated to ensure that the effect of the singularity in $t(s)$ is unimportant. In this case $t(s)$ can be adequately described by a few terms in a Taylor series on the portion of the s axis for which coupling is significant. Conversely, a *distant* crossing is a situation in which s_x is so close to s_∞ that the effect of the singularity is important. We do not treat that case in this paper.

However, there is no exact correspondence between the distance R_x at which a crossing occurs and the applicability of the terms "close" or "distant" crossing in the sense defined above. A given crossing may be considered "distant" for small impact parameters, and "close" for large impact parameters, as the turning point approaches the crossing point. Moreover, since $\int_{R_x}^{\infty} V_{12}\,dR$ is bounded, $|s_\infty - s_x| = O(v^{-1})$ at high velocities; therefore for any system the effect of the singularity increases with increasing velocity (this is what leads to the failure of the LZS formula at high velocities[17]). In general, though, if R_x is small, then the close crossing designation is usually appropriate, while if R_x is large the distant crossing case usually applies, at least over most of the range of impact parameters for which inelastic transitions are important.

B. Discussion of Previous Models

Truncation to a two-state electronic basis and a semiclassical treatment of nuclear motion are features common to all models of the curve-crossing problem. Further, as we have shown above, no model which implies a description of $t(s)$ as an algebraic expansion about $s=0$ or s_x can apply to distant crossings.

The well-known Landau-Zener-Stueckelberg model is characterized by further assumptions: (i) approximate linearity of the diagonal potentials $V_{ii}(R)$ vs R, (ii) approximately constant coupling V_{12}, and (iii) approximately constant nuclear velocity $v=dR/d\tau$. These three assumptions imply that $t(s)$ is linear in s. However, in addition Landau[3a] and Zener[3b] each assumed that (iv) these approximations remain valid in a region about the crossing point which is sufficiently wide that t becomes "infinite" and c_i (or γ_j) reach their asymptotic values before the nonlinear deviations are important. In a less obvious way, Stueckelberg's derivation[1,2] builds on the same assumptions. This model may provide a good first approximation for intermediate energies, but it is bound to fail at high energies because of the singularity at s_∞, and at low energies because of the curvature of $t(s)$ near the turning point.

Bates, Johnston, and Stewart[14] modified the fourth LZS assumption by taking into account the fact that since s_x is finite, $t(0)$ has a finite negative value and therefore $c_i(0)$ does not have the asymptotic limiting value assumed in the Landau-Zener treatment; however they retained the LZS linear approximation for $t(s)$. This model can account for some deviations from the LZS formula for close crossings, but remains inadequate if deceleration effects [which produce the curvature in $t(s)$ at $s=0$] are important in the coupling region.

More recently Heinrichs[18] also employed a modified linear approximation to $t(s)$. However, the essence of his treatment is that transitions always occur within a domain delimited by a fixed critical magnitude of t, $|t| = \hat{t} \simeq 1$. We showed in our analysis of Stueckelberg's method[1] that no energy-independent upper limit can be placed on the t values for which transitions can occur. Effectively Heinrichs set $t(s)$ linear between points $s_x \pm \Delta s$ such that $t(s_x \pm \Delta s) = \pm\hat{t}$, and $t(s) = \pm\infty$ beyond these points. From Fig. 1 we can see that the introduction of a cutoff singularity between $s=0$ and s_x is inappropriate in any case, and while the cutoff at $s_x + \Delta s$ could in some cases simulate effects associated with s_∞, its location on the s axis cannot be determined by presetting a critical value of t.

The idea that the crossing problem can be fully characterized by the value and behavior of $t(R)$ is a tempting one and has a long history, but as Eqs. (38) and Fig. 1 demonstrate, it is entirely misleading because it is $t(s)$ which must actually be considered.

Child[19] has recently presented a general analysis of the curve-crossing problem, and also a treatment of a special model. The general analysis follows an approach by Dubrovskii,[20] in which a form of the classical-trajectory equations is reduced to Weber's equation, and asymptotic properties of the Weber functions are used to obtain Stueckelberg's form of the LZS transition probability, including the associated phases (Zener[3b] solved the LZS-model problem by the same device). Child's analysis is complicated somewhat because not all the mathematical simplifications justified in employing the classical-trajectory equations were utilized from the outset. In the Appendix, we discuss the conditions under which the various forms of the classical-trajectory equations [Eqs. (12) and Eqs. (38)] can be reduced to Weber's equation. The essential requirement is a parabolic approximation to the quantity Ω^2 [cf. Child's Eqs. (7) and (8)] in terms of a suitably defined progress variable x. As we show in the Appendix, this approximation is roughly equivalent to the linear approximation to $t(s)$, and therefore shares the defects of the LZS model both at high and low energies.

Child's special model[19] approximates all elements of the potential-energy matrix $V_{ij}(R)$ by Coulombic forms. This makes $t(R)$ linear and with the constant-velocity approximation leads again to Weber's equation. Although this model may appear to be applicable to distant crossings, this is not so because (a) no system exists in nature for which the true off-diagonal elements of the potential (V_{12}) are Coulombic, and (b) because of the long range of a Coulombic coupling, s_∞ is infinite. As we noted earlier, the difficulty with distant crossings is that the singularity of $t(s)$ at the finite value s_∞ precludes a Taylor-expansion representation based on s_x or $s=0$, and this difficulty is not properly resolved by altering V_{12} so that $s_\infty \to \infty$. The transition probability of Ref. 19 tends to a constant with increasing velocity, instead of following the correct Born behavior ($\sim v^{-2}$) appropriate to finite-range couplings.

Bykhovskii, Nikitin, and Ovchinnikova[5] (BNO) were the first to take into account the correct behavior of $t(s)$ near the turning point. In the BNO model the first two LZS assumptions were retained, but the constant-velocity approximation was replaced (as is consistent with linear V_{ii}) by a constant-acceleration approximation. $t(s)$ is then a quadratic with coefficients coinciding with the Taylor expansion about $s=0$. When s_x is near $s=0$ this expansion will work very well.

The understanding of the curve-crossing problem provided by analysis in terms of $t(s)$ makes it easy to obtain a very simple, yet significant improvement on the BNO model. In the model presented here all the LZS approximations are refined. We may consistently include effects due to variations in V_{12}, curvature in V_{ii}, and acceleration of the nuclei, within a two-parameter model, by obtaining the best possible quadratic approximation to $t(s)$. This model is developed in the following sections.

C. Mathematical Description

The best possible quadratic approximation to $t(s)$ is the one which fits most closely when $|t|$ is smallest.

Consider first the case that the crossing point is in the classically allowed region. We expand $t(s)$ about the crossing point s_x:

$$t(s) = t_1(s - s_x) + \tfrac{1}{2}t_2(s - s_x)^2 \quad . \tag{39}$$

To relate the coefficients t_1 and t_2 to the potentials and the trajectory, we write

$$\begin{aligned} V_{jj}(R) &= -F_j(R - R_x) - \tfrac{1}{2}F_j'(R - R_x)^2 + \cdots \quad , \\ V_{12}(R) &= V_{12} - f(R - R_x) + \cdots \quad , \\ R(\tau) &= R_x + v(\tau - \tau_x) + \tfrac{1}{2}(F/M)(\tau - \tau_x)^2 + \cdots \quad . \end{aligned} \tag{40}$$

Here we have taken $V_{jj}(R_x) = 0$; F_j, F_j', V_{12}, f, v, and F are the (constant) values of the appropriate quantities, evaluated *at the crossing point*. (F is any reasonable average force; in Ref. 4, we argued that if the particular average used makes much difference, then the classical trajectory formulation is itself not valid.) Since the zero of potentials is at R_x, we have $E = \frac{1}{2}Mv^2$. A straightforward calculation then gives

$$\begin{aligned} t_1 &= \hbar v(F_1 - F_2)/2V_{12}^2 \quad , \\ t_2 &= [\hbar^2(F_1 - F_2)F/2MV_{12}^3](1 + 2E/DF) \quad , \end{aligned} \tag{41}$$

where

$$D^{-1} = (F_1' - F_2')/(F_1 - F_2) + 3f/V_{12}$$

(note that $F_1 - F_2 > 0$ by convention, and we assume $F > 0$ for convenience). D (with units of length) carries the effects of the curvature of V_{jj} and inconstancy of $V_{12}(R)$. It is not easy to give an intuitive "physical" explanation of the parameters t_1, t_2; we prefer simply to regard them as the Taylor coefficients of $t(s)$ about s_x.

If R_x is in the classically forbidden region, it is appropriate to expand $t(s)$ about the turning point $s=0$, where t has its minimum (positive) value and zero slope:

$$t(s) = \bar{t}_0 + \bar{t}_2 s^2 \quad . \tag{42}$$

However, we again express the potentials in an ex-

pansion about R_x as in Eqs. (40), while $R(\tau)$ is given by

$$R(\tau) = R_0 + [F(R_0)/M](\tfrac{1}{2}\tau^2) \ , \tag{43}$$

where

$$F(R_0) = \tfrac{1}{2}(F_1 + F_2) + \tfrac{1}{2}(F_1' + F_2')(R_0 - R_x)$$
$$= F + F'(R_0 - R_x) \ . \tag{44}$$

Since the zero of energy is at R_x as before, we take

$$E = \tfrac{1}{2}(V_{22} + V_{11})_{R_0} \quad (<0) \ . \tag{45}$$

After some manipulation one obtains

$$\begin{aligned} \bar{t}_0 &\equiv [(V_{22} - V_{11})/2V_{12}]_{R_0} \\ &= -[E(F_1 - F_2)/2FV_{12}][1 + (2E/dF)] \ , \\ \bar{t}_2 &= [\hbar^2 F(F_1 - F_2)/2MV_{12}^3][1 + f\bar{t}_0/(F_1 - F_2)] \ , \\ d^{-1} &= \tfrac{1}{4}[F'/F - (F_1' - F_2')/(F_1 - F_2) - 2f/V_{12}] \ . \end{aligned} \tag{46}$$

Note that although these expressions give the Taylor coefficients at $s = 0$, the physical parameters in Eq. (46) are those associated with the *crossing point* R_x.

It is convenient to relate the parameters above to those defined by BNO.[5] When R_x is in the classically allowed region, define

$$\beta \equiv (8/t_2)^{1/2} = (4V_{12}/\hbar)[MV_{12}/F(F_1 - F_2)]^{1/2} \times [1 + 2E/DF]^{-1/2} \ , \tag{47a}$$

$$\epsilon \equiv t_1^2/2t_2 = [E(F_1 - F_2)/2FV_{12}][1 + 2E/DF]^{-1} \ . \tag{47b}$$

For the classically forbidden case, define

$$\beta \equiv (8/\bar{t}_2)^{1/2} = (4V_{12}/\hbar)[MV_{12}/F(F_1 - F_2)]^{1/2} \times [1 + f\bar{t}_0/(F_1 - F_2)]^{-1/2} \ , \tag{48a}$$

$$\epsilon \equiv -\bar{t}_0 \tag{48b}$$

[cf. Eqs. (46)]. Equations (48) are not the analytic continuations of (47) because the Taylor series are expanded about different points in the two cases. When the above definitions of ϵ and β are combined with Eqs. (39) or (42), a quadratic expression for $t(s)$ results:

$$t(s) = -\epsilon + 4s^2/\beta^2 \ ; \tag{49}$$

in the classically allowed case, s_x has been eliminated by the requirement that $(dt/ds)_0 = 0$.

In the *diabatic representation*, the classical-trajectory equations then become

$$\begin{aligned} i\frac{dc_1}{ds} &= c_2 \exp[-i(8s^3/3\beta^2 - 2\epsilon s)] \ , \\ i\frac{dc_2}{ds} &= c_1 \exp[+i(8s^3/3\beta^2 - 2\epsilon s)] \ . \end{aligned} \tag{50}$$

This is identical with Eqs. (10) of BNO,[5] since our s corresponds to their $(\frac{1}{2}\tau)$ and our β to their b. The difference between our model and theirs does not lie in the form of Eqs. (50), but entirely in the definitions of ϵ and β and their relationship to the potential parameters and the collision energy. The BNO model requires the first two LZS assumptions (V_{jj} linear and V_{12} constant) and constant acceleration for the nuclear motion, and the nature of their special derivation is such that these assumptions must be strictly maintained. In our formulation, these *a priori* assumptions are not necessary. We have established on very general grounds[4] the validity of the classical-trajectory equations, and the device of a general Taylor expansion of $t(s)$ based on the expansions of $V_{ij}(R)$ and $R(\tau)$, combined with the formal reduction of the classical-trajectory equations [Eqs. (38)], leads to a general theory of close crossings. When at most quadratic terms are retained in $t(s)$, the equations reduce to the BNO form [Eqs. (50)]. Further refinements can be introduced in an obvious way by augmenting the algebraic form of $t(s)$ but this will require the introduction of a third explicit parameter.

The relation between the BNO parameters β_{BNO} and ϵ_{BNO} and ours is mainly an E-dependent deformation, produced by the factors $1 + (2E/DF)$ in Eqs. (47) and by analogous forms in (48). In the BNO model, β_{BNO} is a constant and ϵ is linearly proportional to E. Figure 2 illustrates the behavior of β and ϵ (relative to the BNO parameters) as functions of E; at $E = 0$, $\beta = \beta_{\mathrm{BNO}}$ and $(d\epsilon/dE)_0 = (d\epsilon_{\mathrm{BNO}}/dE)_0$. For most systems, we can see from Eqs. (41) that $DF > 0$; hence as E increases, β decreases and ϵ falls off from a strictly linear behavior. At very large E, ϵ tends to a constant and $\beta \to 0$. For systems with $DF < 0$, ϵ and β become singular at $E = -\frac{1}{2}DF$. In this case, the curvature of V_{jj} and inconstancy of V_{12} offset the deceleration effects, so that the quadratic term vanishes and $t(s)$ is precisely linear. At still higher energies, $t(s)$ would have negative curvature at the crossing point. Obviously, a quadratic approximation to $t(s)$ could never be adequate to describe this situation; the proper procedure is to augment the algebraic form of $t(s)$, if $E > -\frac{1}{2}DF$ for $DF < 0$. Similar behavior of β and ϵ occurs for $E < 0$, but it happens that the transition probabilities in this region are so small that these deformation corrections are quite unimportant. The discontinuity in slopes of β and ϵ at $E = 0$ reflects the fact noted earlier that the Taylor-series representations of $t(s)$ for $E > 0$ and for $E < 0$ are not analytic continuations of each other.

The locus of parameters (β, ϵ), representing a *particular physical system, with fixed potential surfaces* (and a fixed impact parameter), as a func-

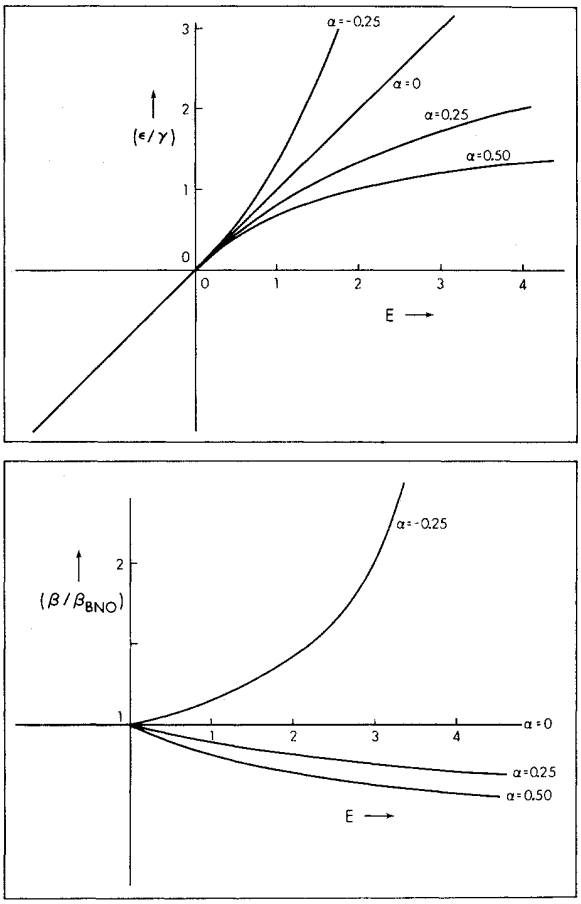

FIG. 2. Energy dependence of the parameters β, ϵ, of the present model, relative to the BNO parameters. (β is a reduced coupling strength and ϵ a reduced collision energy.) α is the parameter $(2/DF)$ appearing in Eqs. (47), and depends only upon the potential curves, as in Eqs. (41).

tion of E, is a curve similar to those shown in Fig. 3. Thus, given characteristic parameters of the potential surfaces, D is determined and the trivial algorithm represented by Figs. 2 and 3 is used to locate the appropriate parameters β, ϵ: Provided that a complete solution of Eqs. (50) for the full range of (β, ϵ) is available, the energy dependence of the scattering amplitude is immediately determined.

It is useful to represent the above model in the *adiabatic representation*, using Eqs. (17); for convenience we use t as the independent variable. From Eqs. (37) and (49) we obtain

$$\frac{dt}{d\tau} = \frac{8V_{12}s}{\beta^2} = \frac{4V_{12}}{\beta}(t+\epsilon)^{1/2} \quad ,$$

while from Eqs. (7) and (8)

$$(\epsilon_b - \epsilon_a) = 2V_{12}(1+t^2)^{1/2} \quad .$$

It follows that

$$\int_0^\tau (\epsilon_b - \epsilon_a)d\tau' = \tfrac{1}{2}\beta \int_{-\epsilon}^{t} [(1+t^2)/(\epsilon+t)]^{1/2} dt \quad , \tag{51}$$

and the classical-trajectory equations in adiabatic representation [Eqs. (17)] take the form

$$\begin{aligned} \frac{d\gamma_a}{dt} &= [2(1+t^2)]^{-1}\gamma_b \exp\left(-i(\tfrac{1}{2}\beta)\right. \\ &\quad \left. \times \int_{-\epsilon}^{t} [(1+t^2)/(\epsilon+t)]^{1/2} dt\right) \quad , \\ \frac{d\gamma_b}{dt} &= -[2(1+t^2)]^{-1}\gamma_a \exp\left(+i(\tfrac{1}{2}\beta)\right. \\ &\quad \left. \times \int_{-\epsilon}^{t} [(1+t^2)/(\epsilon+t)]^{1/2} dt\right) \quad . \end{aligned} \tag{52}$$

Because of the more complicated form of the exponential factor, the adiabatic representation is less convenient for analytical work. However, for numerical work both representations are equally convenient, with the diabatic slightly preferable for weak coupling and high energy, the adiabatic slightly preferable for strong coupling and low energy.

D. Approximate Formulas

In this section we present all of the useful analytical approximations to the G-matrix parameters which are known to us. Some of these are based on the LZS linear model for $t(s)$, and the remainder on the quadratic model; many of the latter were originally obtained by Nikitin and his co-workers, but they remain valid with our general reinterpretation of the parameters β and ϵ.

The first two sets of approximations are simply expressed in the diabatic representation, the last two in adiabatic representation. The general relationship between the forms of solutions in the two representations is given in Sec. III D 3.

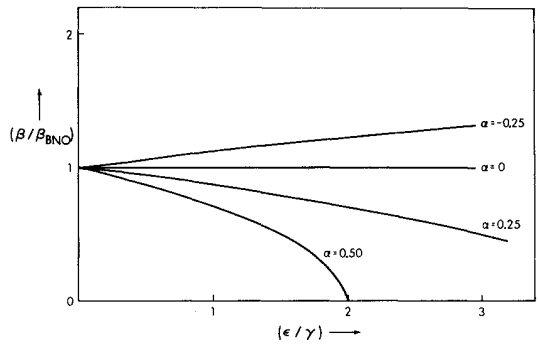

FIG. 3. Typical algorithms showing the locus of points (β, ϵ) associated with E dependence, for a system with various choices of (fixed) α.

Since many of these formulas are closely related, it is difficult to attribute them to specific papers. However, we have tried to do so in a reasonable way, and the numbers in square brackets to the left of equations refer to cited papers in which the formulas appeared. Nontrivial formulas not accompanied by bracketed numbers are, as far as we know, new.

1. Diabatic Perturbation Approximation

Derivation. From Eqs. (50), obtain $c_2(\infty)$ by first-order perturbation theory.

Result. Define $x = \epsilon\beta^{2/3}$. Then

$$[21,5,22]\quad z^D = \tfrac{1}{2}\pi\beta^{2/3}[\mathrm{Ai}^2(-x)+\mathrm{Gi}^2(-x)]^{1/2}\ , \tag{53a}$$

$$[21,5,22]\quad \Gamma_2^D = \tan^{-1}[-\mathrm{Ai}(-x)/\mathrm{Gi}(-x)]\ , \tag{53b}$$

$$\Gamma_1^D = 0\ . \tag{53c}$$

$$[21,5,22]\quad P^D = \pi^2\beta^{4/3}\mathrm{Ai}^2(-x)\ , \tag{53d}$$

$$\Gamma_0^D = 0\ . \tag{53e}$$

[Equations (53c)–(53e) do not preserve the unitarity of $\underline{S}$, a characteristic defect of first-order perturbation approximations.] $\mathrm{Ai}(x)$ and $\mathrm{Gi}(-x)$ are the Airy functions so denoted by Abramowitz and Stegun.[23]

Validity. $\beta \ll 1$; the approximation is more accurate for large $|\epsilon|$.

Asymptotic limits. For large positive ϵ ($\beta \ll 1$, $\epsilon\beta^{2/3} \gg 1$), the above expressions become (Refs. 21, 5, 22)

$$\begin{aligned}
&[21,5,21]\quad z^D = (\pi\beta)^{1/2}/(2\epsilon^{1/4})\ ,\\
&[21,5,21]\quad \Gamma_2^D = -(\tfrac{2}{3}\beta\epsilon^{3/2}+\tfrac{1}{4}\pi)\ ,\\
&\qquad\qquad \Gamma_1^D = 0\ ,\\
&[21,5,21]\quad P^D = (\pi\beta/\epsilon^{1/2})\sin^2\Gamma_2^D\ ,\\
&\qquad\qquad \Gamma_0^D = 0\ ,
\end{aligned} \tag{54}$$

while for large negative ϵ ($\beta \ll 1$, $\epsilon < 0, |\epsilon|\beta^{2/3} \gg 1$)

$$\begin{aligned}
&[21,5,22]\quad z^D = (2|\epsilon|)^{-1}\ ,\\
&[21,5,21]\quad \Gamma_2^D = -\tfrac{1}{2}(\pi\beta|\epsilon|^{3/2})^{1/2}\, e^{-(2/3)\beta|\epsilon|^{3/2}}\ ,\\
&\qquad\qquad \Gamma_1^D = 0\ ,\\
&[21,5,21]\quad P^D = [\pi\beta/(4|\epsilon|^{1/2})]e^{-(4/3)\beta|\epsilon|^{3/2}}\ ,\\
&\qquad\qquad \Gamma_0^D = 0\ .
\end{aligned} \tag{55}$$

2. Zener's Derivation of the LZS Formula

Derivation. Based on a strictly linear approximation to $t(s)$

$$t(s) = [\hbar v(F_1 - F_2)/2V_{12}^2](s - s_x) \equiv T_0^{-1}(s - s_x)\ . \tag{56}$$

Equations (12) or (38) then reduce to Weber's equation, and provided that the effective limits of $(s - s_x)$ are extended to $\pm\infty$ asymptotic properties of the Weber functions can be used to provide the connections between solutions on either side of the crossing point. Obviously the artificial assumptions of the LZS model cannot be applied indiscriminately if an account of the phases as well as the magnitudes of elements in $\underline{G}_+$ is desired (Zener[3b] calculated only the magnitudes). However, provided some care is taken for a consistent physical interpretation of the asymptotic solutions, the elements of $\underline{G}_+$ can be determined in a way which requires reference only to the single LZS parameter T_0 and the relative phase shift between $\tau = 0$ and τ_x associated with the *diabatic* potential curves for the actual system. This result appears at variance with Child,[19] whose essentially similar formula contains instead the *adiabatic* phase difference.

Result.

$$[3(b),19,20]\quad z^D = [2e^{-(\pi T_0/2)}\sinh(\tfrac{1}{2}\pi T_0)]^{1/2}\ ; \tag{57a}$$

$$\Gamma_{2+}^D = \arg[\Gamma(\tfrac{1}{2}iT_0)] + \tfrac{1}{2}T_0 - \tfrac{1}{2}T_0\ln(\tfrac{1}{2}T_0) + \tfrac{1}{4}\pi + \int_0^{\tau_x}\{[V_{22}(\tau) - V_{11}(\tau)]/\hbar\}\,d\tau \tag{57b}$$

[where the true diabatic potentials V_{jj}, not the LZS model forms, are used to evaluate the integral in Eq. (57b)];

$$\Gamma_{1+}^D = 0\ , \tag{57c}$$

$$P^D = 4e^{-\pi T_0}(1 - e^{-\pi T_0})\sin^2(\Gamma_{2+}^D + \Gamma_{1+}^D)\ , \tag{57d}$$

$$\Gamma_0^D = \cot^{-1}\{\cot 2\Gamma_{2+}^D + [e^{-\pi T_0}/(1 - e^{-\pi T_0})]\csc(2\Gamma_{2+})\}\ . \tag{57e}$$

3. Relation between Diabatic and Adiabatic Parameters

The derivation is long and dull. From the general relationship [Eq. (9)] connecting diabatic and adiabatic wave functions, derive the relationship between the coefficients $c_{i\pm}(R)$ and $\gamma_{j\pm}(R)$ of Eqs. (10) and (14). Apply the ± separation and the boundary conditions to relate the $\underline{S}$ and $\underline{G}_+$ matrices in the two representations; then relate z, Γ_{1+}, and Γ_{2+}. The results are as follows. Define

$$\Sigma \equiv \left[\int_{R_a}^{\infty}\pi_a(R')dR' - \int_{R_1}^{\infty}\wp_1(R')dR'\right]/\hbar \tag{58a}$$

$$= \int_0^{s_\infty}\left[\left|(1+t^2)^{1/2}\right| - t\right]ds \tag{58b}$$

$$= \int_{t(0)}^{\infty}\left[\left|(1+t^2)^{1/2}\right| - t\right]T(t)\,dt\ , \tag{58c}$$

where $T(t) \equiv (ds/dt)$ is the quantity so denoted in Ref. 1 [Eq. (26b) ff.]. If the quadratic model for $t(s)$ is used [Eq. (49)],

$$\Sigma = \tfrac{1}{4}\beta\int_{-\epsilon}^{\infty}\{[\,|(1+t^2)^{1/2}| - t]/|(\epsilon+t)^{1/2}|\}\,dt\ . \tag{58d}$$

Further define

$$\underline{M}=\begin{pmatrix} e^{i\Sigma} & 0 \\ 0 & e^{-i\Sigma} \end{pmatrix} \tag{58e}$$

and

$$\underline{W}_0=\underline{W}[t(0)] \ . \tag{58f}$$

Then

$$\underline{S}^D=\underline{M}\underline{S}^A\underline{M} \ , \tag{59a}$$

$$\underline{G}_+^D=\underline{M}\underline{G}_+^A\underline{W}_0 \ , \tag{59b}$$

$$\underline{G}_-^D=\underline{W}_0^{-1}\underline{G}_-^A\underline{M} \ , \tag{59c}$$

so that for the quantities in $\underline{G}_+^D$ and $\underline{G}_+^A$

$$(z^D)^2=(z^A)^2\cos^2\theta_0+[1-(z^A)^2]\sin^2\theta_0 + 2z^A[1-(z^A)^2]^{1/2}\sin\theta_0\cos\theta_0\cos(\Gamma_2^A+\Gamma_1^A) \ , \tag{60a}$$

$$\tan(\Gamma_1^D-\Sigma)=\frac{[1-(z^A)^2]^{1/2}\cos\theta_0\sin\Gamma_1^A+z^A\sin\theta_0\sin\Gamma_2^A}{[1-(z^A)^2]^{1/2}\cos\theta_0\cos\Gamma_1^A-z^A\sin\theta_0\cos\Gamma_2^A} \ , \tag{60b}$$

$$\tan(\Gamma_2^D+\Sigma)=\frac{z^A\cos\theta_0\sin\Gamma_2^A-[1-(z^A)^2]^{1/2}\sin\theta_0\sin\Gamma_1^A}{z^A\cos\theta_0\cos\Gamma_2^A+[1-(z^A)^2]^{1/2}\sin\theta_0\cos\Gamma_1^A} \ , \tag{60c}$$

$$P^D=P^A \ , \tag{60d}$$

$$\Gamma_0^D=\Gamma_0^A+2\Sigma \ , \tag{60e}$$

where $\cos\theta_0$ and $\sin\theta_0$ are given by Eqs. (7) with $t=t(0)$. Except for Eq. (58d), all the above formulas are a perfectly general consequence of the classical-trajectory equations.

4. *Adiabatic Perturbation Approximation*

Derivation. From Eqs. (52), obtain a first-order expression for γ_b. The resulting integral cannot be evaluated in closed form. However, an order-of-magnitude estimate can be obtained by displacing the contour of integration into the upper half-plane so that it passes close to the singular point at $t=i$; the dominant features of the result should then depend on the value of the exponential factor in the integrand, evaluated at $+i$, and the preexponential factors may be determined approximately by calibration with the Landau-Zener formula or another appropriate limiting approximation.

Results. Case (i): $\epsilon>0$. Define

$$\Delta=\tfrac{1}{2}\beta\int_{-\epsilon}^{i}[(1+t^2)/(\epsilon+t)]^{1/2}dt=-\sigma_0^A+i\delta \ ,$$

where σ_0^A is the adiabatic phase lag defined in Eq. (28) of Ref. 1, and

$$i\delta=\tfrac{1}{2}\beta\int_0^i[(1+t^2)/(\epsilon+t)]^{1/2}dt \ .$$

In the limit $\epsilon\gg1$, $\delta=\delta^{(0)}=\frac{1}{2}\pi T_0$ as in Eq. (39a) of Ref. 1. By calibration with the LZS formula in this limit, we find

$$[21,22] \quad z^A=e^{\mathrm{Re}(i\Delta)} \ , \tag{61a}$$

$$[21,22] \quad \Gamma_1^A+\Gamma_2^A=\mathrm{Im}(i\Delta)\pm\pi \ , \tag{61b}$$

$$\Gamma_1^A=0 \ , \tag{61c}$$

$$P^A=4e^{2\mathrm{Re}(i\Delta)}\sin^2[\mathrm{Im}(i\Delta)+\pi] \ , \tag{61d}$$

$$\Gamma_0^A=0 \ . \tag{61e}$$

Validity. The approximation is valid if $\beta\gg1$, $\epsilon<0$. As ϵ increases, (61a) and (61b) becomes more accurate and (61c) less so.

Results. Case (ii). $\epsilon<0$. In this case the first-order perturbation expression for γ_b should be integrated over all positive and negative times. The preexponential factor can be determined by calibration either with the case $\epsilon>0$ or with the Airy formula (Sec. III D 1):

$$[21,22] \quad P=2e^{-2\mathrm{Re}(i\Delta)} \tag{62a}$$

or

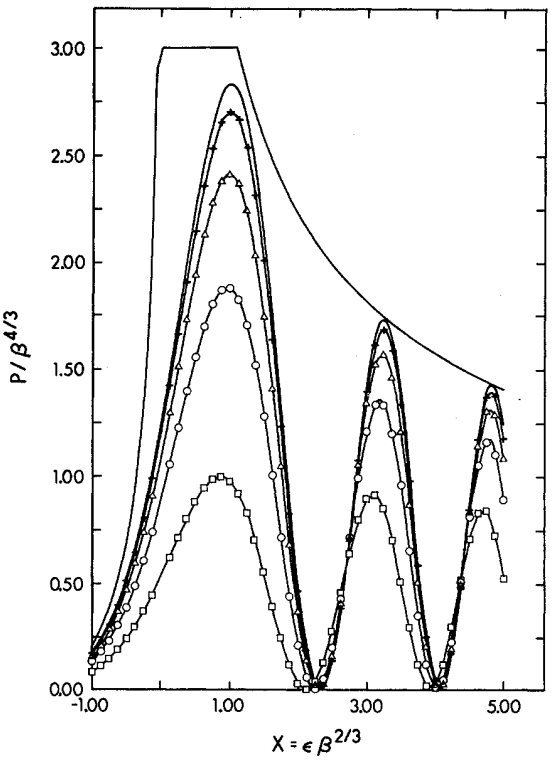

FIG. 4. Excitation probabilities for small β. $(P/\beta^{4/3})$ vs $\epsilon\beta^{2/3}$. Smooth curves are the Airy approximation $\pi^2\,\mathrm{Ai}^2(-\epsilon\beta^{2/3})$ and its envelope, which is $\pi/(\epsilon^{1/2}\beta^{1/3})$ for $\epsilon>0$, and $[\pi/(\epsilon^{1/2}\beta^{1/3})]\exp[-(2/3)\beta|\epsilon|^{3/2}]$ for $\epsilon<0$. □, $\beta=1.00$; ○, $\beta=0.50$; △, $\beta=0.25$; +, $\beta=0.10$.

[21,22] $P=(\pi\beta/4\sqrt{\epsilon})e^{-2\mathrm{Re}(i\Delta)}$, (62b)

$\Gamma_0=0$. (62c)

Validity. The approximation is valid if $\beta\gg1$, $\epsilon<0$ and is better for large $|\epsilon|$. As β decreases and $|\epsilon|$ increases, (62b) becomes better than (62a); however, neither form is very good unless P is very small.

5. Stueckelberg's Formulation

Derivation. See Ref. 1. ($\underline{G}_+$ is the matrix that converts $[\alpha_{a+}, \alpha_{b+}]_{\mathrm{III}}$ to $[\alpha_{a+}, \alpha_{b+}]_{\mathrm{IV}}$.)

Result.

[2,1] $z^A=e^{\mathrm{Re}(i\Delta)}$, (63a)

[2,1] $\Gamma_2^A=\mathrm{Im}(i\Delta)\pm\pi$, (63b)

[1] $\Gamma_1^A=\mathrm{Im}(i\delta)+\eta$. (63c)

Validity. Stueckelberg's derivation can only be justified if neither $(z^A)^2$ nor $[1-(z^A)^2]$ is $\ll1$, i.e., if $(z_A)^2$ has an intermediate value.[1] The quantity η cannot be determined within Stueckelberg's formulation.

In the Appendix of Ref. 1 a direct evaluation of the Stokes's constant needed to determine the Stueckelberg connection formulas was performed. We have since evaluated the infinite-series expression obtained there. However, we find that the magnitude $|B|$ thus obtained for the Stokes's constant does *not* agree with the value obtained from the LZS formula and from Stueckelberg's method [Eq. (A12), Ref. 1]; they agree for small T_0 and for very large T_0, but at intermediate values of T_0 the ratio $|(B_{\mathrm{calc}}/B_{\mathrm{LZS}})|$ reaches a maximum $\simeq1.04$. Since the deviation is largest just when the Stueckelberg procedure is valid, and since we have in any case computed exact numerical phase data for a much more accurate model, we have not shown the phase η given by this calculation (it agrees with the diabatic and adiabatic limiting forms in Secs. III D 2 and III D 4). We do not know why this direct evaluation of B does not agree with the LZS result, which is exact for the strictly linear model. A possible explanation may be associated with a certain nonuniqueness of the set of Stokes's constants for this problem.[24]

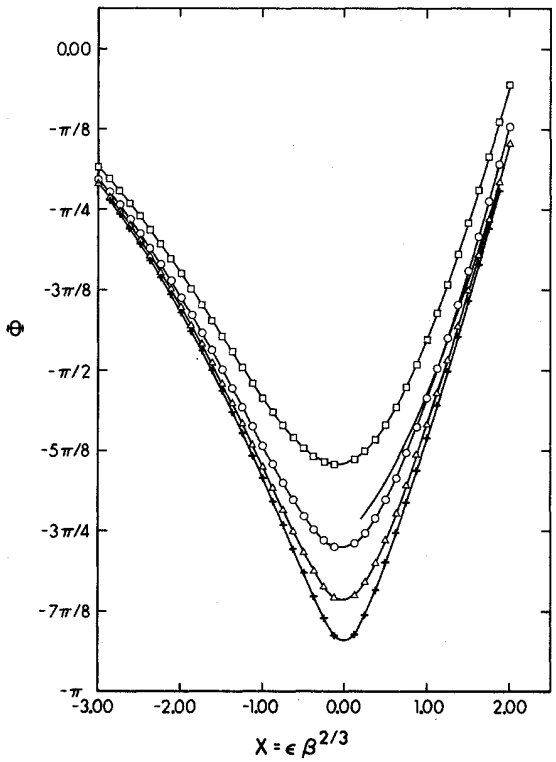

FIG. 5. Phase Φ^A for small β vs $\epsilon\beta^{2/3}$. Smooth curve: diabatic approximation $(\frac{2}{3}\beta\epsilon^{3/2}-\frac{3}{4}\pi)$. Markings of calculated curves correspond to the values of β indicated for Fig. 4.

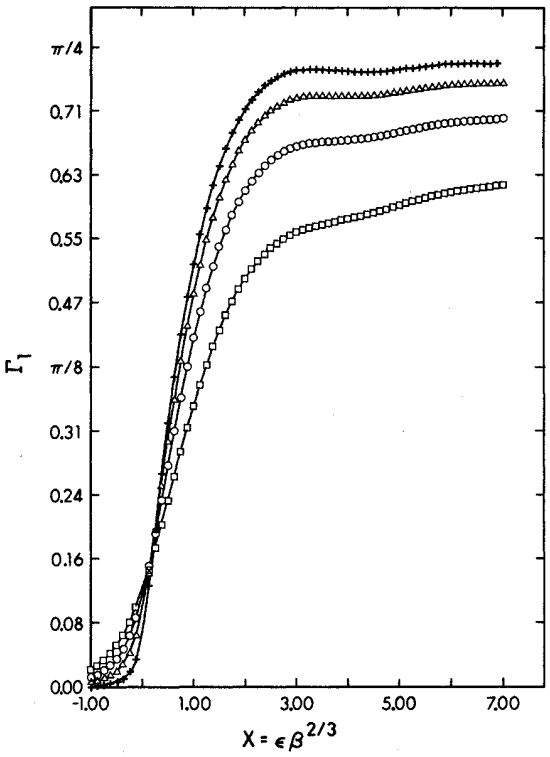

FIG. 6. Phase Γ_1^A for small β vs $\epsilon\beta^{2/3}$. Markings of calculated curves correspond to values of β indicated for Fig. 4.

E. Numerical Results

The approximate formulas of Sec. III D are inadequate in a significant portion of the (β,ϵ) plane, especially when ϵ is not large compared to 1 and $\beta\simeq1$ or larger. Therefore we supplement

these formulas by exact numerical calculations of $\underline{G}_+$ parameters.

Our computations were performed in the *adiabatic* representation, solving Eqs. (52). These can be put in real form as indicated in Eqs. (22)–(24), and the matrices $\underline{S}$ and $\underline{\mathcal{S}}$ obtained using Eqs. (29) and (34). Alternatively, of course, the results could be combined with diabatic phase shifts in Eq. (34) after transformation of $\underline{G}_+^A$ to $\underline{G}_+^D$ via Eqs. (59) and (60).

Figure 4 shows that the Airy approximation to the transition probability is quite good for $\beta \leq 0.1$; it is too large by about a factor of 3 for $\beta = 1$, $\epsilon = 1$, and the approximation improves as ϵ increases for fixed β.

Figure 5 shows calculated values for $\Phi^A = \Gamma_1^A + \Gamma_2^A$. For comparison the diabatic perturbation theory formula is also presented [cf. Eq. (53)]:

$$\Phi^A \simeq \tfrac{2}{3}\beta\epsilon^{3/2} + \tfrac{1}{4}\pi - \pi \quad . \tag{64}$$

The first term in Eq. (64) is the diabatic phase difference; the last term arises from the transformation to adiabatic representation. The additional term $+\frac{1}{4}\pi$ emerges in the asymptotic approximations to the Airy function; it also appears in the exact LZS result [Eq. (57b)] and from the distorted

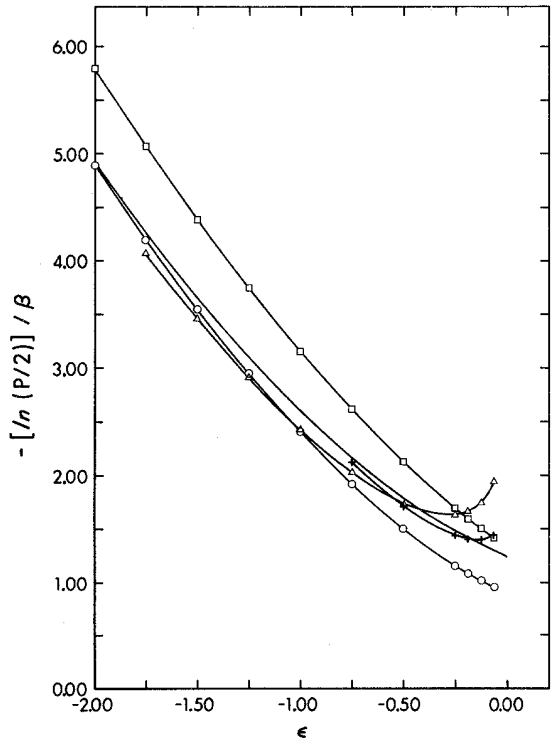

FIG. 7. Excitation probabilities for large β, $\epsilon < 0$: $-\beta^{-1}\ln(\frac{1}{2}P)$ vs ϵ. Smooth curve is the Nikitin approximation [Eq. (62a)]. □, $\beta = 1.00$; ○, $\beta = 2.00$; △, $\beta = 5.00$; +, $\beta = 10.0$.

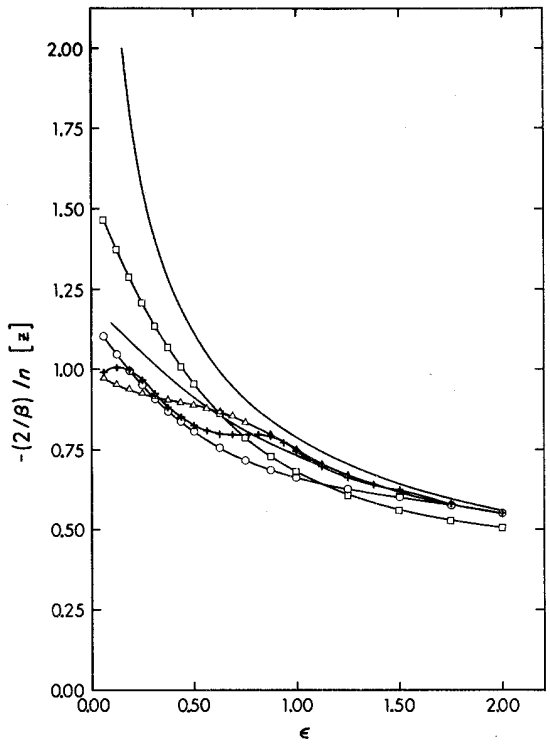

FIG. 8. Exponent for large β, $(-2\beta^{-1}\ln z)$ vs ϵ, $\epsilon > 0$. Smooth curves: upper one, the LZS exponent $= \pi\beta/4\epsilon^{1/2}$; lower one, Nikitin exponent [Eq. (61a)]. Markings on calculated curves correspond to values of β indicated for Fig. 7.

wave approximation to the LZS problem.[1] These additive terms in Φ have caused a great deal of confusion in the past. However, it is now conclusively established that the above form is correct for at least the first few oscillations in the transition probability. For β not too large, it is possible that Eqs. (57b) and (57c) may give a better prediction of Φ^A for $\epsilon > 1$ than does the diabatic perturbation theory, the major improvement being due to an exact evaluation of the diabatic phase difference in Eq. (57b) instead of the estimate based on linear $t(s)$ as in Eq. (64).

Figure 6 shows Γ_1^A for small β. It increases from zero at large negative ϵ to $\pi/4$ at large positive ϵ. This behavior is predicted in Eqs. (53), after conversion to adiabatic representation.

For large β the excitation probability is rapidly oscillatory for positive ϵ, and rapidly decreasing for $\epsilon < 0$. The graphs show the logarithm of P or of z. Figure 7 compares Nikitin's adiabatic formula for negative ϵ [Eq. (62a)], by comparing $-\beta^{-1}\ln(\frac{1}{2}P)$ to $\Delta(\epsilon)$. As mentioned in Sec. III D 4, this formula gives only the correct order of magnitude for P. The deviations at $\epsilon \simeq 0$ for large β result from the behavior of $\Gamma_1^A + \Gamma_2^A$, which passes

through zero in this region.

Figure 8 is a similar test of the Stueckelberg-Nikitin formula [Eqs. (61a) and (63a)]. This is a very substantial improvement upon the LZS formula [Eq. (57a), after transformation], which is also shown; the latter is singular at $\epsilon = 0$. However, even the more accurate formula predicts only the correct order of magnitude.

In Fig. 9, the computed values for $\Phi^A = \Gamma_1^A + \Gamma_1^B$ are compared to Eq. (61b). Finally, Fig. 10 shows the behavior of Γ_1^A for large β.

Data shown in the figures contain only a resumé of the computed results, which are available with a grid size on (β, ϵ) permitting accurate numerical interpolation.

IV. SUMMARY

We have analyzed the potential-curve-crossing problem and solved it for a model of the close crossing case, within a hierarchy of approximations. The first and most severe approximation is that the system can be described by only two electronic states. The second set of approximations, essentially a semiclassical treatment of the nuclear motion, reduces the coupled second-order Schrödinger equations to the first-order "classical-trajectory equations." As we have shown elsewhere, these approximations are valid very generally, in particular, they remain valid even when the crossing point is close to the turning point, provided only that the forces F_{11} and F_{22} have the same sign. For each partial wave the quantal scattering matrix $\underline{S}^L$ can then be factored into an elastic part which contains only the elastic scattering phase shifts for the decoupled potential surfaces, and an inelastic matrix $\underline{S}$, obtained by solving the classical-trajectory equations. The exact solution of the classical trajectory equations has been shown to depend only upon properties of a single function of one variable $t(s)$ whose properties were investigated for the case of curve crossing. The third approximation in the hierarchy replaces the actual $t(s)$ by its Taylor series, including quadratic terms. This approximation is valid for close crossings, a concept definable in terms of the relative spacing (on the s axis) of the points $s = 0$, $s = s_x$, and $s = s_\infty$, corresponding to turning point, crossing point, and the point at infinite separation R where $t(s)$ is singular; distant crossings are those for which the behavior near the singularity in t affects the inelastic scattering. The close crossing model is applicable to a very large portion of curve-crossing problems. The resulting model equations can be

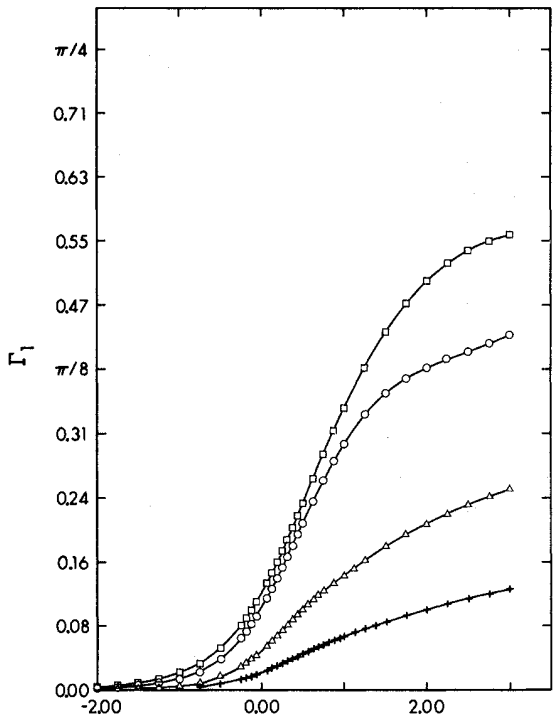

FIG. 10. Phase Γ_1^A for large β vs ϵ. Markings on calculated curves correspond to values of β indicated for Fig. 7.

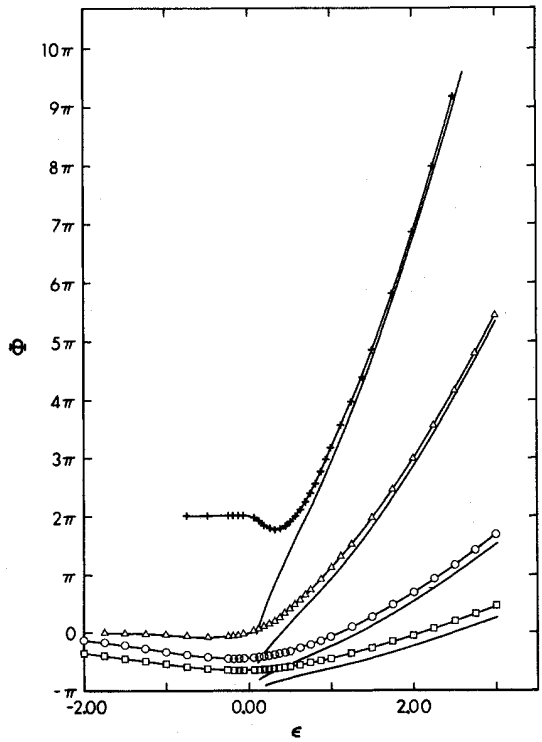

FIG. 9. Phase Φ^A for large β vs ϵ. Smooth curves are the corresponding adiabatic perturbation estimates [Eq. (61b)] but setting $\Delta \simeq \sigma_0^A$. Markings on calculated curves correspond to values of β indicated for Fig. 7.

solved using various limiting approximations in various regions of the (β, ϵ) plane, and numerically everywhere else. A complete grid of these numerical calculations has been done. Within the above hierarchy of approximations, we may regard the problem of close curve crossings as completely solved.

ACKNOWLEDGMENTS

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APPENDIX: REDUCTION TO WEBER'S EQUATION

Under certain circumstances the two-channel classical-trajectory equations can be reduced to Weber's equation.[3b,19,20] The possibility of this reduction is closely connected to the validity of the LZS formula; indeed, Zener's method of solving the LZS model problem relies on just this connection, although to obtain the correct phases [Eqs. (57b) and (57c)] some care must be given to the physical interpretation of the model. We shall briefly investigate the conditions for which reduction to Weber's equation is possible, starting from our Eqs. (12) and (38). In view of the discussion in Secs. III A and III B above we shall use t or s as the progress variable, rather than R or τ.

By starting with Eqs. (12), transformation to t as the independent variable produces the form

$$i\frac{dc_1}{dt} = T(t)\exp[-2i\int^t T(t')t'dt']c_2 \ ,$$
$$i\frac{dc_2}{dt} = T(t)\exp[+2i\int^t T(t')t'dt']c_1 \ , \tag{A1}$$

where $T(t)$ was defined in our study of Stueckelberg's method,[1]

$$T(t) = V_{12}/\hbar\frac{dt}{d\tau} = V_{12}/\hbar v\,\frac{dt}{dR}$$
$$= 2MV_{12}/\hbar(\mathcal{P}_1+\mathcal{P}_2)\frac{dt}{dR} \ . \tag{A2}$$

Recall further that

$$T(t) = \frac{ds}{dt} \ . \tag{A3}$$

The substitution

$$c_1 = y_1(t)[T(t)]^{1/2}\exp[-i\int^t T(t')t'dt'] \tag{A4}$$

into the second-order equation for c_1 leads to the result

$$\frac{d^2y_1}{dt^2} + y_1\left\{T^2(t)(1+t^2) - iT(t) + \left[\frac{d^2\ln T}{dt^2} - \frac{1}{4}\left(\frac{d\ln T}{dt}\right)^2\right]\right\} = 0 \ , \tag{A5}$$

which is essentially the same form as that obtained by Child.[19] If one makes the approximation $T(t) = \text{const} = T_0$, and the scaling substitution $x = (2T_0)^{1/2}t$, the Weber equation results:

$$\frac{d^2y_1}{dx^2} + y_1\left[\tfrac{1}{2}(T_0 - i) + \tfrac{1}{4}x^2\right] = 0 \ , \tag{A6}$$

which is precisely Child's Eq. (9). The derivation requires, as we noted, that $T(t) = T_0$, an assumption also made by Stueckelberg[1,2] and, of course, built into the LZS linear model at the outset.

Starting from Eqs. (38) a very similar procedure leads, with s as independent variable, via the substitution

$$c_1 = \xi(s)\exp[-i\int^s t(s')ds'] \ , \tag{A7}$$

to the equation

$$\frac{d^2\xi}{ds^2} + \xi\left(1 + [t(s)]^2 - i\,\frac{dt}{ds}\right) = 0 \ . \tag{A8}$$

This equation again reduces to (A6) provided t is linear in s, but a quadratic dependence will not permit this.

In summary, if $t(s)$ is truly linear in s over the region of significant coupling, then the LZS transition amplitudes [as given by Eqs. (57)] will result from the asymptotic properties of the parabolic cylinder functions. For *high* energies, the result always breaks down because $t(s)$ cannot remain linear in s as the singularity at s_∞ approaches s_x. For *low* energies it will also fail; it would fail even if $t(s)$ were linear because $|t(0)|$ is finite, and not asymptotically large as turning point $s = 0$ and crossing point s_x draw closer together. However, a much more important effect arises from the fact that $T(s)$ is not constant but becomes *singular* at $s = 0$, i.e., the parabolic dependence of $t(s)$ near $s = 0$ must be considered. The accurate treatment of this effect requires the BNO model or our modification of it, as is clearly demonstrated by our calculations.

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