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"Semiclassical Theory of Electronic Transitions in Low Energy Atomic and Molecular Collisions Involving Several Nuclear Degrees of Freedom"

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ABSTRACT

A semiclassical theory is developed for describing electronic transitions in low energy atomic and molecular collisions, such as $A + BC$, that involve quantized nuclear degrees of freedom (i.e., rotation and vibration) as well as translation. The principal physical idea is that in this low energy regime the dynamics is essentially classical motion of the nuclei on electronically adiabatic potential energy surfaces, with transitions between surfaces being events which are localized in space and time. The quantum principle of superposition is incorporated in the formulation in that classical dynamics is used to construct the classical limit of amplitudes (i.e., S-matrix elements) for transitions from a specific initial electronic-rotational-vibrational state of $A + BC$ to a specific final electronic-rotational-vibrational state of $A + BC$ or $AB + C$, etc. Approximate and "exact" versions of the theory are developed, and in the "exact" version it is seen clearly that electronic transitions are inherently a "classically forbidden" process in that the classical action along the trajectories appropriate for such transitions has an imaginary contribution.

I. Introduction

There has recently been considerable interest and development in understanding the various ways in which classical mechanics can be used to describe atomic and molecular collisions¹⁻⁴. For the collision of two molecular species, such as an atom A and a diatomic molecule BC, on a single electronically adiabatic potential energy surface, for example, it has been seen that the primary role of quantum mechanics is often simply to superpose probability amplitudes corresponding to different classical contributions to a particular transition. A quantum formulation of the scattering problem is thus employed so as to incorporate quantum superposition properly, but all dynamical parameters in the scattering amplitude (i.e., the S-matrix elements) are evaluated by the appropriate use of classical mechanics⁴. This "classical S-matrix" approach has been seen in several applications to be an accurate description of molecular collision dynamics.

Although quantum superposition and classical dynamics can be easily combined (as noted above), it is in general more difficult to mix classical and quantum dynamics per se. For the electronically adiabatic A + BC collision, for example, one can treat the quantized internal degrees of freedom (i.e., rotation and vibration of BC and the orbital angular momentum of A relative to BC) and the translational degree of freedom both quantum mechanically (a coupled-state expansion and numerical solution of the coupled radial Schrodinger equations) or both classically (the use of numerically computed classical trajectories to construct the "classical S-matrix"), and in either of these approaches the formulation of the scattering calculation is a straight-forward matter. If one mixes classical

and quantum dynamics explicitly, however - such as a coupled-state expansion of the internal degrees of freedom with a classical treatment of the radial motion² - it is difficult to make progress unless dynamical approximations (such as the sudden approximation) are incorporated in the approach.

When electronic transitions are possible, however, one cannot proceed completely classically - i.e., it is clear that electronic degrees of freedom must be handled in a quantum framework. To exploit the fact that dynamics of the nuclear degrees are described well classically, therefore, one cannot avoid dealing with an explicit mixture of classical and quantum dynamics. The plan is to state-expand in the electronic degrees of freedom, but to treat all nuclear dynamics classically; quantum superposition is incorporated within the spirit of the "classical S-matrix" approach, and quantization of rotation and vibration accomplished, as before³⁻⁴, with action-angle variables.

For the simpler case of electronic transitions in atom-atom collisions, $A + B$, the only nuclear degree of freedom (once the conserved orbital angular momentum is taken account of) is translation itself, and this leads to the well-known Landau-Zener-Stuckelberg problem^{5,6}. Section II summarizes Stuckelberg's general results⁶ which, with minor modifications, we refer to as the "exact" semiclassical solution to this atom-atom problem. (Approximations to Stuckelberg's primary results lead to the popular Landau-Zener formula⁵; see Section II.) The goal of this paper is to construct an analogous "exact" semiclassical theory for the multi-electronic state problem for a system, such as $A + BC$, which has internal nuclear degrees of freedom in addition to translation⁷. In view of Stuckelberg's solution for the atom-atom case Section II discusses the general properties and requirements one expects of such a theory.

Before attempting the "exact" semiclassical solution of the problem of electronic transitions in complex (e.g., A + BC) collisions, Section III presents an approximate version. This approximate scheme is seen to have much in common with the recent work by Tully and Preston⁸ and in some sense may be viewed as a justification and extension of some of their procedures. Section IV develops the "exact" semiclassical solution to the problem; it is seen that an electronic transition between two adiabatic electronic states is in general a classically forbidden process and must be treated as such if a consistent theory is to result.

In concluding this Introduction it should be pointed out that there may be cases for which no semiclassical treatment ("exact" or otherwise) of the electronic transition is useful. A primary requirement for a semiclassical description of such processes appears to be that the transition be localized in space and time. This will obviously fail to be true at sufficiently high collision energies (many electron volts), but there may also be low energy situations for which the possibility of transition is delocalized. The very division between "high" and "low" collision energy is also indefinite and may depend on the nature of the potential energy surfaces.

II. Summary of Stuckelberg's Solution for Electronic Transitions in Atom-Atom Collisions.

There have been several recent extensive studies of the Landau-Zener-Stuckelberg problem⁹, and here we wish only to summarize the results to emphasize those features that motivate our treatment of the more general collision system. Once the relative orbital angular momentum of the two

atoms is separated (i.e., a partial wave expansion), an expansion of the total wavefunction in electronic states leads to the standard coupled-channel equations for the radial functions:

$$\left[\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \underset{\sim}{V}(R) - \underset{\sim}{E} \right] \cdot \underset{\sim}{u}(R) = 0 \quad , \quad (2.1)$$

where R is the radial (translational) coordinate, $\underset{\sim}{V}(R)$ is the matrix of the total potential energy in the basis of the electronic states, $\underset{\sim}{E}$ is the diagonal matrix $(E - \epsilon_i)\delta_{i,j}$, ϵ_i being the electronic energy of state i and E the total energy, and $\underset{\sim}{u}(R)$ is the matrix of radial functions which is to be determined by solving Equation(2.1); for simplicity the centrifugal potential $\hbar^2 \ell(\ell+1)/2\mu R^2$ has been omitted, and no index ℓ is attached to $\underset{\sim}{u}(R)$.

The general WKB-like solution to Equation (2.1) is quite simple¹⁰. If $\underset{\sim}{U}(R)$ is the unitary matrix that diagonalizes $\underset{\sim}{\epsilon} + \underset{\sim}{V}(R)$ at each inter-nuclear distance R ,

$$\underset{\sim}{U}(R) \cdot \left[\underset{\sim}{\epsilon} + \underset{\sim}{V}(R) \right] \underset{\sim}{U}(R)^+ = \underset{\sim}{W}(R) \quad , \quad (2.2)$$

where $W_{i,j}(R) = W_i(R)\delta_{i,j}$ are the adiabatic potential curves, then the WKB solution for $\underset{\sim}{u}(R)$ is

$$\underset{\sim}{u}(R) = \underset{\sim}{U}(R)^+ \cdot \underset{\sim}{v}(R) \quad , \quad (2.3)$$

where $v_{i,j}(R) = v_i(R)\delta_{i,j}$ is the ordinary one-dimensional WKB wavefunction for the potential $W_i(R)$.

Important point No. 1: The general WKB solution for the multi-channel problem is elastic scattering on the adiabatic potential curves. Even though one does not begin with adiabatic electronic states, therefore, it is the adiabatic potentials which emerge naturally as the ones fundamental to a semiclassical description of the multi-channel problem. Stuckelberg's⁶ radial functions are simply the two-channel case of Equation (2.3).

The multi-channel WKB solution is thus very disappointing, for it gives no inelastic transitions.

Important point No. 2: All inelastic processes result from a breakdown of the WKB solution. In general, therefore, one would expect the WKB solution to be rather worthless, for everything of interest is contained in its breakdown. One can make progress semiclassically, however, if the breakdown is local. In practice this is fairly easy to identify, for the breakdown is typically associated with two adiabatic potential curves whose difference goes through a minimum as a function of R ; i.e., $\frac{d}{dR} [W_i(R) - W_j(R)] = 0$ for $R = R_0$, say. The problem is thus reduced to that of deriving connection formulas that join the WKB solution valid for $R \ll R_0$ to that valid for $R \gg R_0$. Stuckelberg⁶ has derived such connection formulas for the two-state problem, but they apply, of course, to any such local breakdown that involves only two electronic states at a time. Since one expects (or hopes) this to be the case, Stuckelberg's connection formulas provide the general solution to the problem, no matter how many such local two-state breakdowns occur.

If there is only one region of breakdown, then there will be two "crossing encounters" due to the fact that the radial coordinate R_0 is passed twice, once on the way in and once on the way out. The S-matrix is

given in this case by

$$S_{i,j} = (P_{i,j}^I)^{\frac{1}{2}} e^{i\phi_{i,j}^I} + (P_{i,j}^{II})^{\frac{1}{2}} e^{i\phi_{i,j}^{II}}, \quad (2.4)$$

for $i, j = 1, 2$, where $W_1(R)$ is chosen to be the lower adiabatic potential curve ($W_1(R) < W_2(R)$ for all R), the ϕ 's are WKB phase integrals (i.e., classical action integrals), the P 's are transition probabilities; the Roman numerals I and II refer to the two crossing encounters and thus to the two different classical trajectories that contribute to each transition:

$$\phi_{1,1}^I = \lim_{R \rightarrow \infty} 2 \left[\frac{\pi}{4} - k_1 R + \int_{R_1}^R dR' k_1(R') \right] \quad (2.5a)$$

$$\phi_{1,1}^{II} = \lim_{R \rightarrow \infty} 2 \left[\frac{\pi}{4} - k_1 R + \int_{R_2}^{ReR_*} dR' k_2(R') + \int_{ReR_*}^R dR' k_1(R') \right] \quad (2.5b)$$

$$\begin{aligned} \phi_{1,2}^I = \phi_{2,1}^I = \lim_{R \rightarrow \infty} & \left[\frac{\pi}{4} - k_1 R - k_2 R + \int_{ReR_*}^R dR' k_1(R') \right. \\ & \left. + \int_{ReR_*}^R dR' k_2(R') + 2 \int_{R_2}^{ReR_*} dR' k_2(R') \right] \quad (2.5c) \end{aligned}$$

$$\begin{aligned} \phi_{1,2}^{II} = \phi_{2,1}^{II} = \lim_{R \rightarrow \infty} & \left[-\frac{\pi}{4} - k_1 R - k_2 R + \int_{ReR_*}^R dR' k_1(R') \right. \\ & \left. + \int_{ReR_*}^R dR' k_2(R') + 2 \int_{R_1}^{ReR_*} dR' k_1(R') \right] \quad (2.5d) \end{aligned}$$

$$\phi_{2,2}^I = \lim_{R \rightarrow \infty} 2 \left[\frac{\pi}{4} - k_2 R + \int_{R_2}^R dR' k_2(R') \right] \quad (2.5e)$$

$$\phi_{2,2}^{II} = \lim_{R \rightarrow \infty} 2 \left[\frac{\pi}{4} - k_2 R + \int_{R_1}^{\text{Re}R_*} dR' k_1(R') + \int_{\text{Re}R_*}^R dR' k_2(R') \right] \quad (2.5)$$

$$P_{1,1}^I = P_{2,2}^I = (1-p)^2 \quad (2.6a)$$

$$P_{1,1}^{II} = P_{2,2}^{II} = p^2 \quad (2.6b)$$

$$P_{1,2}^I = P_{1,2}^{II} = P_{2,1}^I = P_{2,1}^{II} = p(1-p) \quad (2.6c)$$

where $p = e^{-2\delta}$ (2.7)

and
$$\delta = i \int_{R_*}^{R_*} dR [k_2(R) - k_1(R)]$$

$$= 2i \int_{\text{Re}R_*}^{R_*} dR [k_2(R) - k_1(R)] . \quad (2.8)$$

The local momenta $k_i(R)$ refer to the adiabatic potential curves

$$k_i(R) = \left\{ 2\mu \left[E - W_i(R) \right] / \hbar^2 \right\}^{\frac{1}{2}}$$

$$k_i = k_i(\infty) ,$$

R_1 and R_2 are the turning points on the adiabatic potentials, and R_* is the "complex crossing point", i.e., that value of R for which

$$W_1(R_*) = W_2(R_*) ; \quad (2.9)$$

since $W_1(R)$ and $W_2(R)$ do not cross for any real R , it is clear that R_*

must be complex¹¹. [One must thus be able to analytically continue $W_1(R)$ and $W_2(R)$ to complex R in order to find R_* and evaluate the phase integral for δ in Equation (2.8).] Equations (2.5c) and (2.5d) are not precisely the ones given by Stueckelberg in that the constant phases $+\frac{\pi}{4}$ and $-\frac{\pi}{4}$ are not the ones he obtains; it is clear now, however, that the phases given in Equation (5) are the more desirable ones⁹.

Important point No. 3: All the quantities in the S-matrix in Equation (2.5) are classical action integrals that refer only to the adiabatic potential curves; i.e., there is no reference whatever to any "diabatic" potential curves and off-diagonal interaction which, when diagonalized, give the adiabatic curves. Within this "exact" semiclassical treatment, therefore, all necessary knowledge of the non-adiabatic coupling is contained implicitly in the structure of the adiabatic potential curves. If one expands the phase integral for δ in Equation (2.8) to lowest order in $1/v_0$ (v_0 = local velocity at R_0), then a Landau-Zener-like expression is obtained for δ :

$$\delta = C/v_0 ,$$

where C is a constant which depends on the shape of the potentials at the "avoided crossing". If one furthermore assumes that $W_1(R)$ and $W_2(R)$ result from diagonalizing a 2×2 diabatic potential matrix $\tilde{V}(R)$, where $V_{11}(R)$ and $V_{22}(R)$ are linear about R_0 ($V_{11}(R_0) = V_{22}(R_0)$) and $V_{12}(R)$ is constant near R_0 , then the Landau-Zener expression is obtained for the constant C :

$$C = \frac{2\pi}{\hbar} |V_{12}(R_0)|^2 / |V_{11}'(R_0) - V_{22}'(R_0)|.$$

It should be emphasized, however, that this familiar Landau-Zener formula for δ is a $1/v_0$ expansion of the phase integral in Equation (2.8); the well-known failure of the Landau-Zener formula

near threshold¹², for example, is a failure of this approximate way of evaluating the phase integral in Equation (2.8) and is not necessarily an inherent failure of the general semiclassical theory.

From the above summary of Stueckelberg's solution to the problem of electronic transitions in slow atom-atom collisions one can attempt to "guess" the type of solution expected for the case of electronic transitions in, for example, A + BC collisions. Thus we expect the dynamics to be classical motion on the adiabatic potential surfaces with the possibility of transitions between surfaces localized to certain regions of configuration space (the "surfaces of avoided intersection"). To effect such a solution one needs (1) a criterion for deciding at what locations a transition from one surface to another should be permitted; (2) an expression for the probability of changing surfaces at a given transition region; this probability should depend only on local structure of the adiabatic potential surfaces; (3) a prescription for assigning initial conditions for the classical motion on the new potential surface. In the atom-atom case point (3) is no problem, for total energy conservation fixes the initial radial momentum on the new potential curve; for the A + BC case, however, there are not enough constants of the motion to determine initial values for all the momenta on the new surface. (The coordinates are assumed to be conserved at the instant of transition; this is in the spirit of the Franck-Condon principle.)

Assuming that such a form of the solution exists (it will be seen in Section IV that the general situation is actually considerably more complicated), it is easy to see how classical S-matrix elements are constructed. If (n, q) denote collectively the action-angle variables of all

the internal nuclear degrees of freedom and (R,P) the translational coordinate and momentum, then one starts a classical trajectory on potential surface 1 (i.e., electronic state 1) with initial values (n_1, q_1, R_1, P_1) . Integration of Hamilton's equation of motion is continued on potential surface 1 until a transition region is encountered (if no such region is encountered, then there is no electronic transition); this is designated crossing encounter number I, and the probability of changing to the new surface, p_I , is calculated. From this time on one follows two trajectories - the one beginning on the new surface with probability p_I associated with it, and the one remaining on the original surface with probability $(1-p_I)$ associated with it. If either of these trajectories encounters a transition region II, say, then it splits into two branches, one with probability p_{II} and the other with probability $(1-p_{II})$. This procedure continues, with branching at each transition region, until the radial coordinate of all branches of the trajectory is sufficiently large.

The final nuclear "quantum number" $n_2^\gamma(q_1, n_1)$ is thus a multivalued function, where γ labels the multiplicity, namely the particular branch of nuclear trajectory. To construct the classical S-matrix element for the transition $1n_1 \rightarrow 2n_2$ (where Arabic numerals label the electronic states, and n_1 and n_2 the quantum numbers of the internal nuclear degrees of freedom), one must find roots of the classical trajectory relation

$$n_2^\gamma(q_1, n_1) = n_2 \quad , \quad (2.10)$$

where n_2 is a set of integers, for all branches γ that end up on potential surface 2. The S-matrix element is then given by

$$S_{2n_2, 1n_1} = \sum_{\gamma} P_{\gamma}^{\frac{1}{2}} \left[2\pi\hbar \left(\frac{\partial n_2^{\gamma}}{\partial q_1} \right)_{n_1} \right]^{-\frac{1}{2}} \exp \left[i\phi^{\gamma}(n_2, n_1)/\hbar \right], \quad (2.11)$$

where $\phi^{\gamma}(n_2, n_1)$ is the classical action along the particular trajectory γ ,

$$\phi^{\gamma}(n_2, n_1) = - \int_{-\infty}^{\infty} dt R(t) \dot{p}(t) + q(t) \dot{n}(t), \quad (2.12)$$

and the sum in Equation (2.11) is over all values of q_1 which satisfy Equation (2.10) and also a sum over all branches of the trajectory that end on potential surface 2. P_{γ} is the probability that the particular branch γ of the trajectory is followed; i.e., P_{γ} is the product of N probability factors, where N is the number of transition regions that that particular branch of the trajectory experiences, for example,

$$P_{\gamma} = (p_I)(1-p_{II})(p_{III})(p_{IV})\dots \quad (2.13)$$

III. General Formulation and Approximate Solution.

A. General Formulation

An extremely convenient way of setting up the problem of electronic transitions in atom-diatom collisions is the path integral formulation of Feynman; one proceeds along the lines of Feynman's discussion of "the path integral as a functional"¹³. This is also the framework in which Pechukas discusses the semiclassical theory of electronic transitions in atom-atom collisions.^{2a}

The total Hamiltonian for the system is

$$H = T_q + T_x + V(x,q) \quad (3.1)$$

$$= T_q + h(x,q) \quad , \quad (3.2)$$

where x and q denote all electronic and nuclear coordinates, respectively, T_q and T_x are the kinetic energies of nuclei and electrons, $V(x,q)$ is the total potential energy, and $h(x,q) \equiv T_x + V(x,q)$ is the electronic Hamiltonian for fixed nuclei. The path integral representation for matrix elements of the propagator is¹³

$$\begin{aligned} \langle q_2 x_2 | e^{-iH(t_2-t_1)/\hbar} | q_1 x_1 \rangle & \quad (3.3) \\ &= \int_{q_1}^{q_2} Dq \int_{x_1}^{x_2} Dx \exp \left\{ i\phi[q(t),x(t)]/\hbar \right\} , \end{aligned}$$

where the path integral is over all nuclear and electronic paths with double-ended boundary conditions (q_2, q_1) and (x_2, x_1) , respectively; ϕ is the classical action functional,

$$\phi[q(t),x(t)] = \int_{t_1}^{t_2} dt T_q + T_x - V(x,q). \quad (3.4)$$

Following Feynman, one imagines performing the electronic path integral first, whereby Equation (3.3) becomes

$$\begin{aligned} \langle q_2 x_2 | e^{-iH(t_2-t_1)/\hbar} | q_1 x_1 \rangle &= \int_{q_1}^{q_2} Dq \langle x_2 | K[q(t)] | x_1 \rangle \\ &\times \exp \left\{ \frac{i}{\hbar} \int_{t_1}^{t_2} dt T_q \right\} \end{aligned} \quad (3.5)$$

with the "electronic propagator" $\langle x_2 | K[q(t)] | x_1 \rangle$ defined as

$$\langle x_2 | K[q(t)] | x_1 \rangle = \int_{x_1}^{x_2} Dx \exp \left\{ \frac{i}{\hbar} \int_{t_1}^{t_2} dt \left[T_x - V(x, q) \right] \right\}. \quad (3.6)$$

Equation (3.6) is the electronic transition amplitude for the system with time-dependent electronic Hamiltonian $h(x, q(t))$, the time-dependence coming from the fixed nuclear path $q(t)$; it is this sense in which the electronic propagator is a functional of the nuclear path.

As Pechukas has noted,^{2a} one actually requires matrix elements of the total propagator of Equation (3.3) with respect to initial and final electronic states of the asymptotic electronic Hamiltonian $h_0(x) = \lim_{q \rightarrow \infty} h(x, q)$. If $\phi_1(x)$ and $\phi_2(x)$ are such electronic states, then this "reduced propagator" is defined as

$$\begin{aligned} \langle 2, q_2 | e^{-iH(t_2-t_1)/\hbar} | 1, q_1 \rangle &\equiv \int dx_2 \int dx_1 \quad (3.7) \\ \phi_2(x_2)^* \langle q_2 x_2 | e^{-iH(t_2-t_1)/\hbar} | q_1 x_1 \rangle &\phi_1(x_1) \quad ; \end{aligned}$$

i.e., one is simply changing from an electronic coordinate representation to an electronic representation in the eigenstates of h_0 . If Equation (3.5) is used for the propagator in the integral of Equation (3.7), then this takes the form

$$\begin{aligned} \langle 2, q_2 | e^{-iH(t_2-t_1)/\hbar} | 1, q_1 \rangle \\ = \int_{q_1}^{q_2} Dq K_{21}[q(t)] \exp \left\{ \frac{i}{\hbar} \int_{t_1}^{t_2} dt T_q \right\}, \quad (3.8) \end{aligned}$$

where $K_{21}[q(t)]$ is the matrix element of Equation (3.6) with the electronic wavefunctions $\phi_i(x)$; i.e., $K_{21}[q(t)]$ is the transition amplitude for the $1 \rightarrow 2$ electronic transition with the nuclei constrained to follow the path $q(t)$.

Equation (3.8) is a fundamental and important relation, giving the following prescription for constructing the amplitude for propagation from nuclear positions q_1 and electronic state 1 to nuclear positions q_2 and electronic state 2: one first solves the time-dependent electronic problem for the fixed nuclear path $q(t)$ and then, after supplying the phase factor that is the action due to nuclear kinetic energy, path-integrates over all nuclear paths $q(t)$ with boundary conditions (q_1, q_2) . This has two important interpretations. First, it places in an exact framework the various approximate time-dependent models often used in scattering problems¹⁴. In such procedures one usually chooses a nuclear trajectory $q(t)$ determined by some "distorting potential" (which is often set to zero) and then solves the time dependent electronic problem (often within the sudden approximation) for transitions between electronic states. Equation (3.8) shows that this would actually be exact if one then path-integrated over all possible nuclear paths. Second, Equation (3.8) has a "dynamic Born-Oppenheimer" interpretation analogous to the Born-Oppenheimer solution for bound state problems. For bound states, for example, one first fixes the positions of the nuclei and solves for electronic eigenvalues, whereas in Equation (3.8) one fixes the trajectory of the nuclei and solves for electronic transition amplitudes; in the former case the electronic eigenvalues are functions of the nuclear positions, and in Equation (3.8) the electronic transition amplitude is a functional

of the nuclear path. In the bound state problem one then takes account of nuclear kinetic energy, deriving a Schrodinger equation which leads to the total eigenvalues, and in Equation (3.8) one adds in the factor due to the action associated with nuclear kinetic energy and integrates over all nuclear paths to obtain the total transition amplitude.

All the above equations of this section are exact quantum mechanical relations. As discussed in the Introduction, however, one wishes to treat the nuclear dynamics classically; this means that the path integral in Equation (3.8) will be evaluated in a stationary phase-like approximation, which will lead to classical trajectories on some effective potential. One can then proceed in the same manner as in constructing classical S-matrix elements for A + BC collisions with only one potential energy surface⁴. Thus one would replace the propagator by the S-operator

$$e^{-iH(t_2-t_1)/\hbar} \rightarrow e^{iH_0 t_2/\hbar} e^{-iH(t_2-t_1)/\hbar} e^{-iH_0 t_1/\hbar},$$

where $H_0 = T_q + h_0(x)$, and change from a nuclear coordinate representation to a momentum representation of the action-angle variables for the nuclear degrees of freedom. The S-matrix elements $S_{2n_2, 1n_1}$ would be constructed by finding those classical trajectories that begin on potential surface 1 with nuclear quantum numbers n_1 (i.e., integer values of the action variables) and end on potential surface 2 with quantum numbers n_2 (also integer values of the action variables); the initial and final integer values of the nuclear action variables — the rotation and vibrational quantum numbers — replace q_1 and q_2 as the double-ended boundary conditions that determine the nuclear trajectory. Since the details of this aspect of the problem are identical to those for the classical S-matrix with just one electronic

potential energy surface, there is no need to go more explicitly into them.

Consider now the electronic transition amplitude $K_{21}[q(t)]$; its construction is a two-state time-dependent electronic problem. Anticipating the fact that an adiabatic representation is the one fundamental to semi-classical theory, we introduce the adiabatic (i.e., Born-Oppenheimer) electronic states $\psi_i(x;q)$ which become the electronic states $\phi_i(x)$ in the asymptotic regions; i.e.,

$$h(x,q) \psi_i(x;q) = W_i(q) \psi_i(x;q) \quad , \quad (3.9)$$

where $W_i(q)$ are the adiabatic electronic eigenvalues which are the potential energy surfaces for nuclear motion. The time-dependent electronic wavefunction $\Psi(x,t)$ satisfies the time-dependent electronic Schrödinger equation

$$i\hbar \frac{d}{dt} \Psi(x,t) = h(x,q) \Psi(x,t) \quad , \quad (3.10)$$

where $q \equiv q(t)$ is a fixed nuclear path; Ψ is expanded in the adiabatic basis

$$\Psi(x,t) = c_1(t) \psi_1(x;q) + c_2(t) \psi_2(x;q) \quad , \quad (3.11)$$

and this leads to coupled equations for the coefficients⁷:

$$i\hbar \dot{c}_1(t) = W_1(q) c_1(t) - i\hbar \langle \psi_1 | \frac{\partial \psi_2}{\partial t} \rangle c_2(t) \quad (3.12a)$$

$$i\hbar \dot{c}_2(t) = W_2(q) c_2(t) - i\hbar \langle \psi_2 | \frac{\partial \psi_1}{\partial t} \rangle c_1(t) \quad , \quad (3.12b)$$

where the dots denote time derivatives. One solves Equations (3.12) with initial conditions $c_1(t_1) = 1$, $c_2(t_1) = 0$, and the electronic transition amplitudes are easily shown to be given by

$$K_{21}[q(t)] = c_2(t_2) \quad (3.13a)$$

$$K_{11}[q(t)] = c_1(t_2) \quad (3.13b)$$

It is interesting to note the solution for $c_1(t)$ in the one-channel case; the equation is

$$i\hbar \dot{c}_1(t) = c_1(t) W_1(q) \quad ,$$

with solution

$$c_1(t) = \exp \left\{ \frac{-i}{\hbar} \int_{t_1}^t dt' W_1(t') \right\} \quad , \quad (3.14)$$

where $W_i(t') \equiv W_i(q(t'))$, so that

$$K_{11}[q(t)] = \exp \left\{ \frac{-i}{\hbar} \int_{t_1}^t dt W_1(t) \right\} \quad . \quad (3.15)$$

This is the usual phase factor due to the potential energy contribution to the classical action; thus if Equation (3.15) is substituted into the one-channel version of Equation (3.8), one has

$$\langle 1, q_2 | e^{-iH(t_2-t_1)/\hbar} | 1, q_1 \rangle = \int_{q_1}^{q_2} Dq \exp \left\{ \frac{i}{\hbar} \int_{t_1}^{t_2} dt [T_q - W_1(q)] \right\},$$

the standard path integral expression for nuclear motion on the potential energy surface $W_1(q)$.

Finally, rather than using Equation (3.12) directly, one usually⁷ takes account of the diagonal time dependence of Equation (3.14) and subtracts this out by defining the coefficients $a_i(t)$;

$$a_i(t) = c_i(t) \exp \left\{ \frac{i}{\hbar} \int_{t_1}^t dt' W_i(t') \right\}, \quad (3.16)$$

which are found to satisfy the equations

$$\dot{a}_1(t) = -a_2(t) \langle \psi_1 | \frac{\partial \psi_2}{\partial t} \rangle \exp \left\{ \frac{-i}{\hbar} \int_{t_1}^t dt' \Delta W(t') \right\} \quad (3.17a)$$

$$\dot{a}_2(t) = -a_1(t) \langle \psi_2 | \frac{\partial \psi_1}{\partial t} \rangle \exp \left\{ \frac{+i}{\hbar} \int_{t_1}^t dt' \Delta W(t') \right\} \quad (3.17b)$$

where

$$\Delta W(t) = W_2(t) - W_1(t) \quad (3.18)$$

The electronic transition amplitudes are given in terms of $a_i(t)$ by

$$K_{21}[q(t)] = a_2(t_2) \exp \left\{ \frac{-i}{\hbar} \int_{t_1}^{t_2} dt W_2(t) \right\} \quad (3.19a)$$

$$K_{11}[q(t)] = a_1(t_2) \exp \left\{ \frac{-i}{\hbar} \int_{t_1}^{t_2} dt W_1(t) \right\} \quad (3.19b)$$

B. Approximate Solution.

Before pursuing an "exact" semiclassical solution for the electronic transition problem [Equation (3.17)], it is illustrative to consider the first-order perturbation solution¹⁵; this gives

$$a_2(t_2) = - \int_{t_1}^{t_2} dt \langle \psi_2 | \frac{\partial \psi_1}{\partial t} \rangle \exp \left\{ \frac{i}{\hbar} \int_{t_1}^t dt' \Delta W(t') \right\}, \quad (3.20)$$

which can be combined with Equation (3.19) to give

$$K_{21}[q(t)] = - \int_{t_1}^{t_2} dt \langle \psi_2 | \frac{\partial \psi_1}{\partial t} \rangle \exp \left\{ \frac{-i}{\hbar} \int_{t_1}^t dt' W_1(t') - \frac{i}{\hbar} \int_t^{t_2} dt' W_2(t') \right\}. \quad (3.21)$$

Equation (3.21) has an interesting interpretation: the integrand is a magnitude times a phase; recalling from Equation (3.15) that the phase of $K_{21}[q(t)]$ is the classical action due to nuclear potential energy, one sees that the phase of the integrand is precisely that appropriate to a nuclear trajectory which propagates on potential energy surface 1 from time t_1 to t and then on potential surface 2 from t to t_2 . The integrand of Equation (3.21), therefore, is the transition amplitude for the case that the electronic transition takes place at time t . Since the transition can take place at any time between t_1 and t_2 (with varying probability), the net transition amplitude is a "sum" over all possible transition times; this is another instance of quantum superposition.

To proceed semiclassically one considers evaluation of the time integral in Equation (3.21) by stationary phase; the requirement that t be

a point of stationary phase for the integral is that

$$0 = \frac{d}{dt} \left[\int_{t_1}^t dt' W_1(t') + \int_t^{t_2} dt' W_2(t') \right] ,$$

or

$$0 = - \Delta W(t) \quad , \quad (3.22)$$

i.e., that the nuclear configuration $q(t)$ be a point in configuration space where the potential surfaces are degenerate. If the potential surfaces $W_i(q)$ are functions of f independent variables (e.g., $f = 3$ for the A + BC case), however, their "surface of intersection" for real values of q is of dimension $f-2$ or less¹⁶. Thus even if such a "conical intersection" exists, there is zero probability of a trajectory passing through it.

[If the electronic states are of different symmetry, however, they can of course intersect in an $(f-1)$ dimensional surface; one would then need to consider interactions (such as spin-orbit coupling) that couple the two electronic states on their surface of intersection.]

Failing to find a solution to Equation (3.22), one thus looks for a time at which the phase of the integrand of Equation (3.21) is least rapidly varying¹⁷, i.e., a value of t satisfying

$$0 = \frac{d^2}{dt^2} \left[\int_{t_1}^t dt' W_1(t') + \int_t^{t_2} dt' W_2(t') \right]$$

or

$$0 = - \frac{d}{dt} \Delta W(t) \quad . \quad (3.23)$$

Let t_0 be a solution of Equation (3.23); i.e., t_0 is a time for which $\Delta W(t)$ passes through a local minimum. The phase is expanded in a Taylor's series about t_0

$$\int_{t_1}^t dt' W_1(t') + \int_t^{t_2} dt' W_2(t') = \tau - (t-t_0) \Delta W_0 + 0 - \frac{1}{6}(t-t_0)^3 \ddot{\Delta W}_0 \quad (3.24)$$

where

$$\tau = \int_{t_1}^t dt W_1(t) + \int_{t_0}^{t_2} dt W_2(t)$$

$$\Delta W_0 = \Delta W(t_0)$$

$$\ddot{\Delta W}_0 = \frac{d^2}{dt^2} \Delta W(t) \quad , \quad t = t_0 \quad ,$$

and t_0 is the root of $\dot{\Delta W}(t) = 0$. Taking the magnitude of the integrand to be constant at t_0 Equation (3.21) becomes

$$K_{21}[q(t)]' = - \langle \psi_2 | \frac{\partial \psi_1}{\partial t} \rangle_{t_0} e^{-i\sqrt{\hbar} \int_{-\infty}^{\infty} dt} \exp \left\{ i \frac{\Delta W}{\hbar}(t-t_0) + i \frac{\ddot{\Delta W}}{6\hbar}(t-t_0)^3 \right\} \quad , \quad (3.25)$$

where the t -limits are extended to $\pm \infty$ since it is the region about t_0 that dominates the contribution. The integral over t in Equation (3.25) is recognized as the integral representation of the Airy function¹⁸, and invoking its asymptotic form gives

$$\begin{aligned}
 K_{21}[q(t)] = & - \langle \psi_2 | \frac{\partial \psi_1}{\partial t} \rangle_{t_0} \left[2\pi\hbar / (2\Delta W_0 / \dot{\Delta W}_0)^{\frac{1}{2}} \right]^{\frac{1}{2}} \\
 & \times \exp \left\{ - \frac{2}{3} \frac{\Delta W_0}{\hbar} (2\Delta W_0 / \dot{\Delta W}_0)^{\frac{1}{2}} - \frac{i}{\hbar} \int_{t_1}^{t_0} dt W_1(t) \right. \\
 & \left. - \frac{i}{\hbar} \int_{t_0}^{t_2} dt W_2(t) \right\} \quad (3.26)
 \end{aligned}$$

The exponential part of Equation (3.26) is actually quite similar to the "exact" semiclassical solution of Section IV; the pre-exponential factor obtained via this perturbation approximation, however, is essentially meaningless. The "exact" result most closely corresponds to Equation (3.26) if the pre-exponential factor is set to 1, which we now do:

$$\begin{aligned}
 K_{21}[q(t)] = & \exp \left[- \frac{2}{3} \frac{\Delta W_0}{\hbar} (2\Delta W_0 / \dot{\Delta W}_0)^{\frac{1}{2}} \right] \exp \left\{ \frac{-i}{\hbar} \int_{t_1}^{t_0} dt W_1(t) \right. \\
 & \left. - \frac{i}{\hbar} \int_{t_0}^{t_2} dt W_2(t) \right\} \quad (3.27)
 \end{aligned}$$

In light of the discussion at the beginning of this section it is seen that Equation (3.27) implies that the $1 \rightarrow 2$ electronic transition takes place at t_0 , the time at which $\Delta W(t)$ goes through a local minimum. Although all times t contribute as transition times in Equation (3.21), the stationary phase approximation singles out this particular time t_0 as the dominate one; this is a typical semiclassical approximation to quantum mechanics. The probability of the $1 \rightarrow 2$ transition is

$$P_{21} = |K_{21}[q(t)]|^2 = \exp \left[- \frac{4}{3} \frac{\Delta W_0}{\hbar} (2\Delta W_0 / \dot{\Delta W}_0)^{\frac{1}{2}} \right] \quad (3.28)$$

Equations (3.27) and (3.28) have an even more suggestive form. It was noted that $\Delta W(t) \neq 0$ for any real t ; one can easily see, however, that there are complex times at which $\Delta W(t) = 0$. Expanding about t_0 ,

$$\Delta W(t) = \Delta W_0 + 0 + \frac{1}{2}(t-t_0)^2 \ddot{\Delta W}_0, \quad (3.29)$$

one sees that

$$\Delta W(t) = 0 \text{ at } t_*, \text{ where}$$

$$t_* = t_0 + i (2\Delta W_0 / \ddot{\Delta W}_0)^{\frac{1}{2}}. \quad (3.30)$$

The action integral between t_* and its complex conjugate is

$$\begin{aligned} \int_{t_*}^{t_*} dt \Delta W(t) &= 2 \int_{t_0}^{t_*} dt \Delta W(t) = 2 \int_{t_0}^{t_*} dt [\Delta W_0 + \frac{1}{2}(t-t_0)^2 \ddot{\Delta W}_0] \\ &= i \frac{4}{3} \Delta W_0 (2\Delta W_0 / \ddot{\Delta W}_0)^{\frac{1}{2}} \end{aligned} \quad (3.31)$$

so that the electronic transition amplitude of Equation (3.27) is equivalently written

$$K_{21}[q(t)] = e^{-\delta} \exp \left\{ -\frac{i}{\hbar} \int_{t_1}^t dt W_1(t) - \frac{i}{\hbar} \int_{t_0}^{t_2} dt W_2(t) \right\}, \quad (3.32a)$$

where

$$\delta = -\frac{i}{\hbar} \int_{t_0}^{t_*} dt \Delta W(t), \quad (3.32b)$$

or even more compactly as

$$\begin{aligned}
 K_{21}[q(t)] &= \exp \left\{ -\frac{i}{\hbar} \int_{t_1}^{t_0} dt W_1(t) - \frac{i}{\hbar} \int_{t_0}^{t_*} dt W_1(t) \right. \\
 &\quad \left. - \frac{i}{\hbar} \int_{t_*}^{t_2} dt W_2(t) - \frac{i}{\hbar} \int_{t_0}^{t_2} dt W_2(t) \right\} \\
 &= \exp \left\{ -\frac{i}{\hbar} \int_{t_1}^{t_*} dt W_1(t) - \frac{i}{\hbar} \int_{t_*}^{t_2} dt W_2(t) \right\} \quad (3.33)
 \end{aligned}$$

From Equation (3.33) one may say that the transition actually takes place at the complex time t_* where the potentials cross (i.e., $\Delta W(t_*) = 0$); the electronic transition amplitude is the negative exponential of the time integral of the effective potential energy for this trajectory from t_1 to t_* on potential surface 1 and from t_* to t_2 on potential surface 2. If there are several solutions to the equation determining t_* , then one chooses the root for which P_{21} of Equation (3.32) is largest; this will normally be the one for which $|\text{Im}t_*|$ is smallest¹¹.

Equations (3.32) and (3.33) are more fundamental (as will be seen in Section IV) and accurate than those of Equations (3.27) and (3.28) which are based on a quadrate approximation to $\Delta W(t)$ about t_0 . In practice, for example — after Equation (3.33) is substituted into Equation (3.8) and the nuclear path integral evaluated by stationary phase — one will be computing a classical trajectory on potential surface $W_1(q)$ until a time t_0 at which $\Delta W(t)$ is observed to go through a minimum; here the trajectory is allowed to branch, and one then follows two trajectories. In calculating

these trajectories one will have the function $\Delta W(t)$ at fairly closely spaced time intervals. It would thus be a simple matter to fit $\Delta W(t)$ to an accurate interpolation formula (e.g., a spline fit) and find t_* , the root of $\Delta W(t) = 0$, quite accurately; similarly, the time integral of $\Delta W(t)$ required for δ in Equation (3.32b) could be computed from this accurate fit to $\Delta W(t)$. The probability associated with the branch of the trajectory originating on surface 2 is $P_{21} \equiv e^{-2\delta}$, and $(1-P_{21})$ is the probability associated with the branch of the trajectory remaining on surface 1. An interesting point is that, just as with Stuckelberg's solution for the atom-atom case summarized in Section II, $K_{21}[q(t)]$ is given in Equations (3.33) in terms of classical action integrals on the adiabatic potential surfaces.

Finally, we note that either of the two branches of the trajectory may come to another time at which $\Delta W(t)$ goes through another local minimum, and one would then allow for a further branching. It is also easy to see how many electronic states can be incorporated into the theory. As the trajectory propagates on the initial potential surface 1, say, one monitors the difference between $W_1(q(t))$ and all other potential surfaces $W_i(q(t))$; if $|W_i(q(t)) - W_1(q(t))|$ is observed to go through a minimum at some time, then the trajectory starts a branch on surface i with probability P_{i1} [of the same form as above with $\Delta W \rightarrow \Delta W_i = W_i - W_1$] associated with it. This branching process continues in the obvious fashion and the overall S-matrix element is constructed in the manner discussed at the end of Section II.

C. Initial Conditions on the New Potential Surface.

The results presented in the previous section lack only one

element in order to be a workable solution: one needs an unambiguous procedure for assigning initial values for the coordinates and momenta on the new potential surface. Since $W_2(q(t_0)) \neq W_1(q(t_0))$, it is clear that the coordinates and momenta at t_0 on the new potential surface 2 cannot all be the same as those on potential surface 1 at t_0 . In this section we present a solution to this aspect of the problem that is valid, however, only for a special case of the general situation. It was consideration of these "switching conditions", in fact, that necessitated the more general attack on the problem presented in Section IV.

As noted in the previous section, potential surfaces 1 and 2, functions of f independent variables, can intersect for real coordinates only on a surface of dimension $f-2$ or less¹⁶. They may, however, have a surface of avoided intersection of dimension $f-1$. If, for example, the potential surfaces were functions of two variables (i.e., $f = 2$), then their graphical representation would actually be a surface in three-dimensional space; a "surface of avoided intersection" of dimension 1 could exist, this being a line in three dimensions. The highest dimension in which the surfaces could actually intersect would be a point, this being Teller's¹⁹ "conical intersection".

Assuming that such an $(f-1)$ dimensional surface of avoided intersection exists, a crossing from surface 1 to surface 2 takes place (with some probability) at the time t_0 that the trajectory, initially on surface 1, crosses the surface of avoided intersection. To describe the branch of the classical trajectory that crosses onto surface 2, we consider the effective potential surface $W(q)$,

$$W(q) = W_1(q)h[f(q)] + W_2(q)h[-f(q)] \quad , \quad (3.34)$$

where $f(\underline{q})$ is some function of coordinates that is positive (negative) for points \underline{q} on the initial (final) side of the surface of avoided intersection (i.e., $f(\underline{q}) = 0$ defines this surface of avoided intersection), and $h(x)$ is the usual step function

$$\begin{aligned} h(x) &= 1, \quad x > 0 \\ &= 0, \quad x < 0 \end{aligned}$$

The potential surface $W(\underline{q})$ of Equation (3.34) corresponds to a "sudden approximation" for the electronic transition (i.e., the electronic transition is a "Franck-Condon transition").

The plan is to integrate the classical equations of motion for a short time interval about t_0 with the potential surface $W(\underline{q})$; this will give the initial values for all the coordinates and momenta on surface 2 in terms of their values on surface 1. Since the effective potential $W(\underline{q})$ of Equation (3.34) does not involve the time, total energy will be conserved. (This is why the "switching condition" had to be specified in a time-independent manner.) Furthermore, any other conserved quantities, such as total angular momentum, will also be automatically conserved. To see this last point, consider the atom-diatom case, A + BC: There are six coordinates for this system (with its overall center of mass motion eliminated), but the potential surfaces actually depend on only three, namely any three coordinates that specify the size and shape of the A-B-C triangle (e.g., the three interparticle distances), and the potentials are independent of the three Euler angles that orient the A-B-C triangle in space; it is this fact, of course, that leads to conservation of total angular momentum. Since $W_1(\underline{q})$ and $W_2(\underline{q})$ are independent of the Euler angles,

the surface of avoided intersection of W_1 and W_2 is also independent of them, so that the function $f(\underline{q})$ in Equation (3.34) also is, or finally, one sees that the effective potential $W(\underline{q})$ of Equation (3.34) is independent of the Euler angles. Therefore, any trajectories determined by the potential surface $W(\underline{q})$ will conserve total angular momentum as well as total energy.

The effective Hamiltonian for the crossing trajectory is

$$H(\underline{p}, \underline{q}) = \frac{1}{2} \underline{p} \cdot \underline{M}^{-1} \cdot \underline{p} + W(\underline{q}) \quad , \quad (3.35)$$

where \underline{M} is the "mass matrix"; for simplicity, and with no loss of generality, we have taken \underline{p} and \underline{q} to be Cartesian variables, and \underline{M} is thus diagonal.

Let $\underline{q}^{(1)}$ and $\underline{p}^{(1)}$ be the coordinates and momenta on surface 1 at time t_0 (i.e., "just before" the transition) and $\underline{q}^{(2)}$ and $\underline{p}^{(2)}$ the coordinates and momenta on surface 2 at time t_0 (i.e., "just after" the transition); $\underline{q}^{(1)}$ and $\underline{p}^{(1)}$ are known, and $\underline{q}^{(2)}$ and $\underline{p}^{(2)}$ are to be determined. It is easy to see that the coordinates are conserved at the instant of transition, for the equations of motion are

$$\dot{q}_i = \frac{\partial H}{\partial p_i} = p_i / M_i \quad ,$$

and integrating from $t_0 - \epsilon$ to $t_0 + \epsilon$ gives

$$q_i^{(2)} - q_i^{(1)} = \int_{t_0 - \epsilon}^{t_0 + \epsilon} dt \dot{q}_i = \mathcal{O}(\epsilon) \rightarrow 0 \quad . \quad (3.36)$$

as $\epsilon \rightarrow 0$. The RHS of Equation (3.36) is zero because the integrand is

bounded and the range of integration is infinitesimal.

For the momenta, on the other hand, the equations of motion give

$$\dot{p}_i = - \frac{\partial H}{\partial q_i} = \frac{\partial W_1}{\partial q_i} h[f(q)] + \frac{\partial W_2}{\partial q_i} h[-f(q)] + [W_1(q) - W_2(q)] \times \frac{\partial f}{\partial q_i} \delta[f(q)] \quad , \quad (3.37)$$

where we have used the facts that $h'(x) = \delta(x)$ and $\delta(-x) = \delta(x)$. The first two terms in Equation (3.37) are bounded and will not contribute when integrating Equation (3.37) over the infinitesimal time interval $(t_0 - \epsilon, t_0 + \epsilon)$. Since the coordinates are conserved at t_0 , integration of Equation (3.37) gives

$$p_i^{(2)} - p_i^{(1)} = -\Delta W_0 \left(\frac{\partial f}{\partial q_i} \right)_{q_0} \int_{t_0 - \epsilon}^{t_0 + \epsilon} dt \delta[f(q)] \quad , \quad (3.38)$$

where q_0 is the common value of $q^{(1)}$ and $q^{(2)}$. For t near t_0 , $f(q)$ may be expanded as

$$f(q) = f(q_0) + \sum_i \left(\frac{\partial f}{\partial q_i} \right)_{q_0} M_{ii}^{-1} [p_i^{(1)} h(t_0 - t) + p_i^{(2)} h(t - t_0)] (t - t_0) \quad ; \quad (3.39)$$

since $f(q_0) = 0$ (i.e., q_0 is a point on the surface of avoided intersection), $f(q)$ is of the form

$$f(q) = a h(t_0 - t)(t - t_0) + b h(t - t_0)(t - t_0) \quad .$$

By using some convenient form of the step-function, one can show that

$$\int_{-\epsilon}^{\epsilon} dt \delta[a h(t)t + b h(-t)t] = \frac{2}{a+b} \quad , \quad (3.40)$$

so that Equation (3.38), with Equations (3.39) and (3.40), becomes

$$p_i^{(2)} = p_i^{(1)} + 2\Delta W_o \left(\frac{\partial f}{\partial q_i} \right)_{q_o} \left[\sum_i \left(\frac{\partial f}{\partial q_i} \right)_{q_o} M_{ii}^{-1} \right. \\ \left. \times \left(p_i^{(1)} + p_i^{(2)} \right) \right]^{-1} \quad , \quad (3.41)$$

or if we define the vector \tilde{v} by

$$v_i = \left(\frac{\partial f}{\partial q_i} \right)_{q_o} \quad ,$$

Equation (3.41) is

$$\tilde{p}^{(2)} = \tilde{p}^{(1)} - A \tilde{v} \quad , \quad (3.42)$$

where

$$A = 2 \Delta W_o \left[\tilde{v} \cdot \tilde{M}^{-1} \cdot \tilde{p}^{(1)} + \tilde{v} \cdot \tilde{M}^{-1} \cdot \tilde{p}^{(2)} \right]^{-1} \quad . \quad (3.43)$$

Equation (3.42) is not a solution for $\tilde{p}^{(2)}$ since the constant A depends on $\tilde{p}^{(2)}$. If $\tilde{p}^{(2)}$ from Equation (3.42) is substituted into Equation (3.43), however, one obtains a quadratic equation for A, the solution of which is

$$A = \left(\frac{a}{b} \right) \left\{ 1 - \left[1 - 2\Delta W_o b/a^2 \right]^{\frac{1}{2}} \right\} \quad ,$$

where

$$a = \tilde{v} \cdot \tilde{M}^{-1} \cdot \tilde{p}^{(1)} \quad , \quad b = \tilde{v} \cdot \tilde{M}^{-1} \cdot \tilde{v}$$

Thus the explicit expression for the momenta $\underline{p}^{(2)}$ in terms of $\underline{p}^{(1)}$ is

$$\underline{p}^{(2)} = \underline{p}^{(1)} + \hat{n} \frac{(\hat{n} \cdot M^{-1} \cdot \underline{p}^{(1)})}{\hat{n} \cdot M^{-1} \cdot \hat{n}} \times \left\{ 1 - \left[1 - \frac{2\Delta W_0 (\hat{n} \cdot M^{-1} \cdot \hat{n})}{(\hat{n} \cdot M^{-1} \cdot \underline{p}^{(1)})^2} \right]^{\frac{1}{2}} \right\}, \quad (3.44)$$

where \hat{n} is the unit vector along \underline{y} .

Finally, it is easy now to give a clearer interpretation of the vector \underline{y} and the unit vector \hat{n} . Since the surface of avoided intersection is defined by the equation $f(\underline{q}) = 0$, it follows that the vector $\underline{v}_i \equiv \left(\frac{\partial f}{\partial q_i} \right)_{\underline{q}_0}$ is a vector that is normal to this surface, and thus \hat{n} is the unit vector normal to the surface of avoided intersection. Equation (3.44) says, therefore, that all of the correction to the momenta is normal to the surface of avoided intersection and, thus, that the component of \underline{p} parallel to this surface is conserved at the instant of transition. This "switching condition" is essentially the one used by Tully and Preston⁸ and justified by numerical studies. This section has shown that the switching conditions in Equation (3.44) are a direct result of the assumption of a well-defined surface of avoided intersection and that it automatically conserves all constants of the motion (e.g., energy and total angular momentum).

IV. "Exact" Semiclassical Solution.

A. Electronic Transition Amplitude.

First we consider the coupled equations [Equations(3.17)] that

define the electronic transition amplitude. The two first order equations for $a_1(t)$ and $a_2(t)$ are equivalent to one second order equation; if $a_2(t)$ is expressed in terms of $a_1(t)$, for example,

$$a_2(t) = - \frac{\dot{a}_1(t)}{B(t)} \exp \left\{ \frac{i}{\hbar} \int_{t_1}^t dt' \Delta W(t') \right\} , \quad (4.1)$$

where $B(t)$ is the non-adiabatic coupling function

$$B(t) = \langle \psi_1 | \frac{\partial \psi_2}{\partial t} \rangle , \quad (4.2)$$

then the second order equation for $a_1(t)$ is

$$\ddot{a}_1(t) + \left[\frac{i}{\hbar} \Delta W(t) - \dot{B}(t)/B(t) \right] \dot{a}_1(t) + |B(t)|^2 a_1(t) = 0 . \quad (4.3)$$

The term in Equation (4.3) involving the first derivative can be eliminated by defining the function $f(t)$ by

$$f(t) = a_1(t) B(t)^{-\frac{1}{2}} \exp \left\{ \frac{i}{2\hbar} \int_{t_1}^t dt' \Delta W(t') \right\} , \quad (4.4)$$

and $f(t)$ is found to satisfy the equation

$$\ddot{f}(t) + k(t)^2 f(t) = 0 , \quad (4.5)$$

where

$$k(t)^2 = \left[\frac{\Delta W(t)}{2\hbar} \right]^2 + |B(t)|^2 + \frac{i}{2\hbar} \left[-\Delta \dot{W}(t) + \Delta W(t) \dot{B}(t)/B(t) \right] + \frac{1}{2} \frac{d}{dt} \left[\dot{B}(t)/B(t) \right] - \left[\frac{1}{2} \dot{B}(t)/B(t) \right]^2 . \quad (4.6)$$

Equation (4.5) looks formally like a one-dimensional Schrodinger equation, and since $\Delta W(t)/\hbar$ is expected to be a large slowly varying function of time we solve it within a WKB-like approximation. Thus the general solution to Equation (4.5) is

$$f(t) = c_+ f_+(t) + c_- f_-(t) \quad , \quad (4.7)$$

where the WKB approximation for the functions $f_{\pm}(t)$ gives

$$f_{\pm}(t) = 2^{-\frac{1}{2}} k(t)^{-\frac{1}{2}} \exp \left\{ \pm i \int_{t_0}^t dt' k(t') \right\} \quad , \quad (4.8)$$

with $k(t)$ as defined by Equation (4.6); t_0 is any convenient lower limit in Equation (4.8), the factor $2^{-\frac{1}{2}}$ has been inserted for later convenience, and the constants c_{\pm} in Equation (4.7) are as yet arbitrary.

To lowest order in \hbar^{-1} the function $k(t)$ is

$$k(t) \approx \Delta W(t)/2\hbar \quad , \quad (4.9)$$

so that the WKB solutions in Equation (4.8) become invalid in any region where $\Delta W(t)$ goes to zero or becomes small. If t_0 is a time at which $\Delta W(t)$ has a minimum, therefore, the interval about t_0 is a region where the WKB solution is poor. Thus one is faced with the usual problem of determining the coefficients c'_{\pm} that are valid for $t \gg t_0$ in terms of the coefficients c_{\pm} that are valid for $t \ll t_0$. This failure of the WKB approximation due to a minimum in $k(t)$, however, is identical to the one-dimensional barrier transmission-reflection problem for the case that the energy of the particle is greater than the barrier maximum²⁰.

Thus one may use the connection formula derived by Fröman and Fröman²¹ for the barrier problem to relate the coefficients c_{\pm} and c'_{\pm} of Equation (4.7),

$$\begin{pmatrix} c'_+ \\ c'_- \end{pmatrix} = \begin{pmatrix} (1 + e^{2\theta})^{\frac{1}{2}} & -ie^{\theta} \\ ie^{\theta} & (1 + e^{2\theta})^{\frac{1}{2}} \end{pmatrix} \begin{pmatrix} c_+ \\ c_- \end{pmatrix} \quad (4.10)$$

where θ is the "barrier penetration integral"

$$2\theta = i \oint dt k(t) \quad , \quad (4.11)$$

with the contour integral in the complex t -plane enclosing the two branch points of $k(t)$.

In Appendix I we show that for $t \gg t_0$ or $t \ll t_0$, the WKB solutions in Equation (4.8) become

$$f_+(t) = B(t)^{-\frac{1}{2}} \exp \left\{ \frac{i}{2\hbar} \int_{t_0}^t dt' \Delta W(t') \right\} \quad (4.12a)$$

$$f_-(t) = \frac{\hbar B(t)^{\frac{1}{2}}}{\Delta W(t)} \exp \left\{ \frac{-i}{2\hbar} \int_{t_0}^t dt' \Delta W(t') \right\} \quad (4.12b)$$

Equations (4.4) and (4.1) can be used to express $a_1(t)$ and $a_2(t)$ in terms of $f(t)$:

$$a_1(t) = B(t)^{\frac{1}{2}} \exp \left\{ \frac{-i}{2\hbar} \int_{t_1}^t dt' \Delta W(t') \right\} f(t) \quad (4.13a)$$

$$a_2(t) = -B(t)^{-1} \exp \left\{ \frac{i}{\hbar} \int_{t_1}^t dt' \Delta W(t') \right\} \\ \times \frac{d}{dt} \left[B(t)^{\frac{1}{2}} \exp \left\{ \frac{-i}{2\hbar} \int_{t_1}^t dt' \Delta W(t') \right\} f(t) \right] \quad (4.13b)$$

and with $f(t)$ given by Equations (4.7) and (4.12) one has for $t \ll t_0$

$$a_1(t) = c_+ \exp \left\{ \frac{-i}{2\hbar} \int_{t_1}^t dt \Delta W(t) \right\} \quad (4.14a)$$

$$a_2(t) = ic_- \exp \left\{ \frac{i}{2\hbar} \int_{t_1}^t dt \Delta W(t) \right\} ; \quad (4.14b)$$

for $t \gg t_0$ Equation (4.14) is modified only in that $c_{\pm} \rightarrow c'_{\pm}$. [The c_- term in the expression for $a_1(t)$ was dropped in writing Equation (4.14a) since the coefficient has a factor of \hbar multiplying it.] It is physically correct that the functions $\{a_i(t)\}$ in Equation (4.14) are constant in time for t not near t_0 , for the WKB solution is valid in the limit of zero non-adiabatic coupling, and it is clear from Equation (3.17) that $\{a_i(t)\}$ will be constant in any region for which $B(t)$ is negligible.

One now chooses c_{\pm} from Equation (4.14) so that $a_1(t) = 1$, $a_2(t) = 0$ for $t \ll t_0$ - i.e.,

$$c_+ = \exp \left\{ \frac{i}{2\hbar} \int_{t_1}^0 dt \Delta W(t) \right\} \quad (4.15a)$$

$$c_- = 0 , \quad (4.15b)$$

and then uses the connection formula [Equation (4.10)] to determine the

coefficients c_{\pm}^i and thus $\{a_i(t)\}$ for $t \gg t_0$ from Equation (4.14); this gives

$$a_1(t_2) = (1 + e^{2\theta})^{\frac{1}{2}} \exp\left\{\frac{-i}{2\hbar} \int_{t_1}^{t_0} dt \Delta W(t)\right\} \quad (4.16a)$$

$$a_2(t_2) = -e^{\theta} \exp\left\{\frac{i}{2\hbar} \int_{t_1}^{t_0} dt \Delta W(t)\right\} \quad (4.16b)$$

Equation (3.19) gives the electronic amplitudes in terms of these final values of $\{a_i(t)\}$, and with Equation (4.16) this is

$$K_{11}[q(t)] = (1 + e^{2\theta})^{\frac{1}{2}} \exp\left\{\frac{-i}{\hbar} \int_{t_1}^{t_2} dt W_1(t)\right\} \quad (4.17a)$$

$$K_{21}[q(t)] = -e^{\theta} \exp\left\{\frac{-i}{\hbar} \int_{t_1}^{t_0} dt W_1(t) - \frac{i}{\hbar} \int_{t_0}^{t_2} dt W_2(t)\right\} \quad (4.17b)$$

To conclude the solution we consider the contour integral of Equation (4.11) which defines θ . If $k(t)$ is expanded in powers of \hbar ,

$$k(t) \approx \frac{\Delta \dot{W}(t)}{2\hbar} + \frac{i}{2} \left[\frac{-\Delta \dot{W}(t)}{\Delta W(t)} + \frac{\dot{B}(t)}{B(t)} \right] + o(\hbar) \quad (4.18)$$

then

$$2\theta = \frac{i}{2\hbar} \oint dt \Delta W(t) + \frac{1}{2} \oint dt \frac{\Delta \dot{W}(t)}{\Delta W(t)} + o(\hbar) \quad (4.19)$$

where the term involving the non-adiabatic coupling function has been discarded. If t_* and its complex conjugate are the zeros of $\Delta W(t)$, then

the first term in Equation (4.19) is

$$\frac{i}{2\pi} \oint dt \Delta W(t) = \frac{i}{\pi} \int_{t_*}^{t_*} dt \Delta W(t) \equiv -2\delta, \quad (4.20)$$

where δ is real and positive. The second term in Equation (4.19) can be evaluated by writing $\Delta W(t)$ in an approximate form that has the correct branch point character

$$\Delta W(t) \approx \text{constant} [(t-t_0)^2 + s^2]^{\frac{1}{2}},$$

where $t_* = t_0 + is$. Thus

$$\frac{\dot{\Delta W}(t)}{\Delta W(t)} \approx \frac{t-t_0}{(t-t_0)^2 + s^2},$$

and the second term of Equation (4.19) is

$$\frac{1}{2} \oint dt \frac{\dot{\Delta W}(t)}{\Delta W(t)} \approx \frac{1}{2} \oint \frac{t-t_0}{(t-t_0)^2 + s^2} = i\pi$$

so that Equation (4.19) is

$$2\theta = -2\delta + i\pi, \quad (4.21)$$

and in Equation (4.17) one has

$$(1 + e^{2\theta})^{\frac{1}{2}} = (1 - e^{-2\delta})^{\frac{1}{2}} \quad (4.22a)$$

$$-e^{\theta} = -ie^{-\delta} \tag{4.22b}$$

The amplitudes in Equation (4.17), with the probability factors given by Equation (4.20) and (4.22), are identical to the ones suggested in Section IIIb, and this present derivation thus gives a more rigorous justification of the result discussed there.

It is interesting that $K_{21}[q(t)]$ of Equation (4.17b) and (4.22b) is given directly in the form of the exponential of the classical action²², the imaginary part of the time integral providing the probability factor $e^{-\delta}$. The probability factor $(1 - e^{-2\delta})^{\frac{1}{2}}$ for $K_{11}[q(t)]$, however, is of a more indirect form, essentially a renormalization factor to account for the fact that some probability has been lost to the new branch of the trajectory. It is also interesting (and reassuring) that this same probability factor for K_{11} is obtained by invoking the unitary relation for the full S-matrix; Appendix II shows the details of the procedure.

Finally, it is important that within this WKB approximation for Equation (4.5) the electronic transition amplitudes in Equation (4.17) depend only on the adiabatic potential surfaces and do not involve the non-adiabatic coupling function $B(t)$ defined in Equation (4.2). [If the adiabatic potentials $W_1(q)$ and $W_2(q)$ are of different symmetry and actually do cross, then of course the results do depend on $B(t)$; the discussion in Appendix I includes this possibility as well.]

B. Switching Conditions; Complex Time and Complex Surfaces of Intersection.

One now substitutes the electronic transition amplitude given by Equations (4.17) and (4.22) into the nuclear path integral of

Equation (3.8). The result of evaluating this path integral by stationary phase (or actually by a steepest decent method since the phase of $K_{21}[q(t)]$ is complex) is that one computes classical trajectories that start on potential surface 1 and branch onto various other surfaces i when times are passed for which $|W_i(t) - W_1(t)|$ has a local minimum. There remains, however, the problem of how in general to specify the initial conditions for the new branch of the trajectory beginning on surface i ; Section IIIc gave the solution only for a special (although probably common) situation.

The point of view adopted here is that of the discussion following Equation (3.33) of Section IIIB, namely that the transition actually takes place at t_x , the (complex) time at which $\Delta W(t) = 0$. Thus the transition from one surface to another occurs at a position $q_x \equiv q(t_x)$ for which the potential surfaces are degenerate; i.e., q_x satisfies the equation $W_2(q_x) = W_1(q_x)$, which defines a surface of dimension $(f-1)$ (where the potential surfaces are functions of f independent variables). These remarks are entirely consistent with the "non-crossing rule"¹⁶ which says that the real surface of intersection must be of dimension $(f-2)$ or less; if complex coordinates are admitted, however, it is clear that the complex surface of intersection is of dimension $(f-1)$. For the one-dimensional case ($f=1$), for example, potential curves cannot intersect for any real R (since $f-2 = -1$), but there can be complex points (a surface of dimension $f-1 = 0$) of intersection as discussed in Section II.

Since the electronic states are degenerate at t_x , all the coordinates and momenta are conserved at time t_x . One thus imagines performing the calculation as follows: the trajectory propagates on potential surface 1 until time t_0 at which $\Delta W(t)$ is observed to go through a minimum; this is

the "signal" that "close by" there is a complex time t_* (the real part of which is approximately t_0) at which $\Delta W(t_*) = 0$. One then allows the time (and therefore the coordinates and momenta) to become complex as one integrates Hamilton's equations to this time t_* . At t_* the trajectory branches and the numerical integration of Hamilton's equations for the two branches continues. For the branch remaining on surface 1 the time is incremented from t_* back to t_0 where the coordinates and momenta all become real again, equal in fact to their previous values at t_0 ; time is further incremented in the real time direction and the trajectory on surface 1 continues as though there had never been this "side-track" to $t_0 \rightarrow t_* \rightarrow t_0$ (except for the probability factor $(1 - e^{-2\delta})^{\frac{1}{2}}$ that is acquired). For the branch of the trajectory beginning on surface 2 at t_* , the initial values of the coordinates and momenta are simply the same values as those on surface 1 at time t_* (to emphasize again, this is possible only because the potential surfaces intersect at t_*); time is incremented back toward t_0 and then in the real time direction as this branch of the trajectory propagates on surface 2.

For the new branch of the trajectory beginning on surface 2 one would like to be able to increment the time from t_* to a value t_0' at which all the coordinates and momenta on surface 2 become real, and then to add only real increments to the time so that the coordinates and momenta would all remain real (at least until another crossing encounter). For N nuclear coordinates and momenta, however, it is not possible in general to find one time t_0' for which $\{q_i(t), p_i(t)\}$, $i = 1 \dots N$, all become real. Only for the case $N = 1$ (i.e., there is only one nuclear degree of freedom, namely translation) it is possible to find such a t_0' : one

chooses t_0' so that $q_1(t)$ (the translation coordinate) is real, and since the potential $W_2(q_1)$ is then real, the momentum p_1 is forced by total energy conservation to be real also. This case $N = 1$, in which there are no internal nuclear degrees of freedom, is the original Stueckelberg problem discussed in Section II, and one can quite easily show that the procedure outlined in the previous paragraph exactly reproduces Stueckelberg's formula for a single crossing encounter. It is also easy to see that t_0' , the time at which the radial coordinate on the new potential becomes real, is not a real value of time; this is clear on physical grounds since the trajectory from R_0 to R_* (the radial coordinates corresponding to t_0 and t_*) on potential $W_1(R)$ requires a different amount of time than the trajectory from R_* to R_0 on potential $W_2(R)$:

$$t_* - t_0 = \int_{R_0}^{R_*} dR \left\{ 2[E - W_1(R)]/\mu \right\}^{-\frac{1}{2}}$$

$$t_0' - t_* = \int_{R_*}^{R_0} dR \left\{ 2[E - W_2(R)]/\mu \right\}^{-\frac{1}{2}},$$

so that

$$t_0' - t_0 = \frac{i\hbar}{2} \frac{d}{dE} \delta(E),$$

with δ given by Equation (2.8). This last equation is an example of the general relation between "time delays" and the energy derivative of the classical action.²³ It may seem strange that t_2 , the final time, can turn out to be complex at the end of the trajectory, but this actually causes no problem. From the "formal theory of scattering"²⁴ it is clear that the relation

$$S = \lim_{(t_2 - t_1) \rightarrow \infty} e^{iH_0 t_2 / \hbar} e^{-iH(t_2 - t_1) / \hbar} e^{-iH_0 t_1 / \hbar}$$

is valid for complex $(t_2 - t_1)$, and the limit actually requires $\text{Re}(t_2 - t_1) \rightarrow +\infty$ with $\text{Im}(t_2 - t_1)$ finite and non-negative.

For more than one nuclear degree of freedom, however, although it is possible to choose t_0' so that $q_1(t_0')$ is real, the other coordinates are not necessarily real at t_0' . To make sense of this dilemma it is necessary to re-think just which variables one must require to be real and which ones are not observable and therefore may be complex. If $q_1(t)$ and $p_1(t)$ are the usual translation coordinate and momentum (i.e., $q_1 \equiv R$, $p_1 \equiv P_R$) and $\{q_i, p_i\}$, $i = 2, \dots, N$, are the action-angle variables for the internal nuclear degrees of freedom (i.e., p_i , $i = 2 \dots N$ are the nuclear quantum numbers), then it should be clear that the only physical requirements are that q_1 and $\{p_i\}$, $i = 2 \dots N$ be real in the asymptotic regions $t_1 \rightarrow -\infty$, $t_2 \rightarrow +\infty$; since $E = H_0 = p_1^2 / 2\mu + \epsilon(p_2, \dots, p_N)$ in the asymptotic regions, where $\epsilon(p_2, \dots, p_N)$ is the internal (rotational and vibrational) energy (which is real since $\{p_i\}$ $i = 2, \dots, N$, are real), it follows that the translational momentum is also real in the asymptotic regions. Thus the translational coordinate and momentum are both real in the asymptotic regions, but for the internal nuclear degrees of freedom only the action variables (i.e., quantum numbers) are required to be real; the phase angles $\{q_i\}$, $i = 2, \dots, N$, may have complex values. During the time of interaction, of course, any (and all) of the variables may take on complex values, for scattering boundary conditions refer only to the initial and final asymptotic regions.

Let us see how the boundary conditions work out for this case of N nuclear degrees of freedom. The quantum numbers $\{p_i\}$, $i = 2, \dots, N$, are initially set equal to some integers, q_1 has a large (real) value, and p_1 is determined by total energy conservation (and is thus real); the initial phase angles $\{q_i\}$ $i = 2, \dots, N$ are unspecified at this point and may be complex. One integrates Hamiltonian equations, allowing for branchings at complex times for which two potential surfaces intersect, and in the final asymptotic region for each branch of the trajectory one demands the following:

$$\text{Im } p_i = 0 \tag{4.23a}$$

$$\text{Re } p_i = \text{specified integers,} \tag{4.23b}$$

$i = 2, \dots, N$, and

$$q_1 = \text{real} \tag{4.24}$$

The $2N-2$ equations in Equation (4.23) are satisfied by proper choice of the $2N-2$ initial variables ($\text{Re } q_i, \text{Im } q_i$), $i = 2, \dots, N$, and the final requirement, Equation (4.24), is achieved by the choice of $\text{Im } t_2$. Thus there are precisely the number of variables at our disposal to fulfill Equations (4.23) and (4.24), but it is necessary to utilize the fact that the initial phase angles $\{q_i\}$, $i = 2, \dots, N$, and the final time t_2 can be complex.

In earlier "classical S-matrix" work involving only one potential

surface it was necessary to allow the phase angles $\{q_i\}$, $i = 2, \dots, N$, to be complex in order to describe classically forbidden transitions.⁴ The discussion in the previous paragraph thus emphasizes the fact that an electronic transition is an intrinsically classically forbidden process. The form found previously for the transition probability associated with a classically forbidden process was $\exp[-2 \text{Im } \phi/\hbar]$, ϕ being the classical action along the appropriate trajectory; this is identical to the form obtained above in Equations (3.33) and (4.17). With the additional flexibility introduced by allowing the time to be complex¹¹, therefore, it is seen that the entire problem of electronic transitions emerges as a special type of classically forbidden process. The proper definition of a classically forbidden process thus appears to be one that can take place only for classical trajectories which require some (or all) of the coordinates and momenta, and/or the time, to be complex for some part of the trajectory; the result of this is that the classical action ϕ acquires an imaginary part along such a trajectory, and the classical S-matrix has the damping factor $\exp(-\text{Im } \phi/\hbar)$ which is the signature of classically forbidden processes.

C. Localization.

The problem of determining initial conditions for new branches of the trajectory was solved in the previous section by integrating the equations of motion directly to the complex time t_* at which the original surface actually intersects the surface on which the new branch originates. The price paid in achieving the general solution for this problem of "switching conditions", however, is that all the coordinates and momenta, and the time also, must be allowed to be complex. Thus it appears that

the classical action ϕ could have imaginary contributions all along the trajectory. This would be highly unsatisfactory, however, for then it would not be possible to speak meaningfully about separate crossing encounters, and one would not be able to identify the probabilities $P_{21} = \exp(-2 \text{Im } \phi/\hbar)$ and $P_{11} = 1 - P_{21}$ that are associated with an individual crossing encounter.

In order to be able to construct the probability factors P_{21} and P_{11} , therefore, it is imperative that one be able to localize the region of time during which the classical action acquires imaginary contributions. If this is not possible, then one would not be able to deal with the electronic transitions as isolated "binary" events, and this present type of semiclassical theory would probably not be useful. The procedure outlined below is formally capable of achieving localization in general; if the electronic transition is physically very de-localized, however, one would expect practical difficulties in carrying it out. The basic idea is to exploit the fact that the coordinates and momenta at time t , $\{q_i(t), p_i(t)\}$, $i = 1, \dots, N$, depend only on their initial values at time t_1 and the time difference $(t - t_1)$; i.e., $\{q_i(t), p_i(t)\}$, $i = 1, \dots, N$, are independent of the path in the complex t -plane from t_1 to t along which the time is incremented in integrating Hamilton's equations of motion. (This follows because the Hamiltonian is time independent.)

More specifically, consider a particular trajectory beginning at t_1 on potential surface 1; as discussed in Section IVb, the initial phase angles $\{q_i\}$, $i = 2, \dots, N$, may be complex. The phase of the S-matrix in the action-angle variable representation, however, is

$$\phi = - \int dt \sum_{i=1}^N q_i(t) \dot{p}_i(t) \quad , \quad (4.25)$$

so that even if the phase angles are complex in the initial asymptotic region, the fact that the quantum numbers $\{p_i\}$, $i = 2, \dots, N$, are constant prevents ϕ from accumulating any complex part. As the interaction region is reached the quantum numbers change with time, and ϕ becomes non-zero; for a short time increment Δt , the phase gains an increment $\Delta\phi$,

$$\Delta\phi = -\Delta t \sum_{i=1}^N q_i(t) \dot{p}_i(t) \quad . \quad (4.26)$$

To prevent ϕ from becoming complex, therefore, one does not integrate precisely along the real time axis, but allows Δt to be complex and chooses its direction in the complex t -plane so that the increment $\Delta\phi$ in Equation (4.26) is real; i.e., the choice is

$$\Delta t = |\Delta t| \exp \left\{ i n \pi - i \arg \left[\sum_{i=1}^N q_i(t) \dot{p}_i(t) \right] \right\} \quad , \quad (4.27)$$

where $|\Delta t|$ is the magnitude of the time increment and n is some integer such that $\text{Re}(\Delta t) > 0$. This manner of incrementing the time variable continues (with ϕ thus remaining purely real) until, as discussed before, a time t_0 is passed for which $|W_1(t) - W_i(t)|$ is observed to go through a minimum, signaling that there is a t_* close by for which $W_1(t_*) = W_i(t_*)$. At this point one integrates to this time t_* (the criterion in Equation (4.27) now abandoned) and at t_* starts a new branch of the trajectory on surface i . From t_* each branch of the trajectory is integrated in the direction of the complex t -plane that decreases the imaginary increment to ϕ ;

for a given branch the condition $\text{Im}(\Delta\phi) = 0$ determines the time t_0' from which one increments the time once more according to Equation (4.27). In this manner the imaginary contribution to ϕ is localized to the time interval (t_0, t_0') , so that one can indeed speak of the electronic transition as localized, and the local transition probability $P_{21} = \exp(-2 \text{Im} \phi/\hbar)$ is thus well-defined for each isolated crossing encounter.

Finally, it is interesting to note that this localization of the imaginary contribution to the classical action would actually not be necessary if there were just one crossing encounter: the probability P_{21} would still be $\exp(-2 \text{Im} \phi/\hbar)$ even if the imaginary contribution were spread out over a long time interval (i.e., the value of ϕ is independent of the path in the t -plane so long as the path goes through t_*), and the probability $(1 - P_{21})$ would likewise be unambiguously identified. If there is more than one crossing encounter, however, it is absolutely essential that the imaginary contribution to ϕ associated with each separate encounter be localized; i.e., it is only this that allows one to calculate the local probability factors, P_{21} and $(1 - P_{21})$, associated with the various individual crossings and non-crossings.

V. Discussion and Summary.

The previous sections have explored the possibility of constructing a general theory of electronic transitions in low energy atomic and molecular collisions that involve more than just one (i.e., the translational) nuclear degree of freedom. The basic physical idea is that of Stueckelberg's solution for the case of one nuclear degree of freedom, namely that the motion of the nuclei is governed by classical dynamics on the electronically

adiabatic potential energy surfaces, with the possibility of transitions between the surfaces localized in space and time. The quantum principle of superposition is incorporated for both electronic and nuclear degrees of freedom by using the classical dynamics to construct the classical limit of transition amplitudes (i.e., S-matrix elements) in the same manner as has been done previously for systems with many nuclear degrees of freedom and only one adiabatic electronic state. Since the electronic transition involves only two electronic states at each crossing encounter, there is no limit in principle to the number of electronic states that can be included in the description.

Section III has developed an approximate scheme that should be applicable if the adiabatic potential energy surfaces have a well-defined "surface of avoided intersection" of dimension $f-1$, or if the adiabatic states are of different symmetry and have a real surface of intersection of dimension $f-1$; in the latter case some "residual interaction" (e.g., spin-orbit coupling, or the non-adiabatic coupling itself) would have to be taken into account. These results were seen to have several features in common with the "surface hopping model" employed by Tully and Preston⁸ in their classical trajectory study of $H^+ + D_2$. Since the transition occurs when the surface of avoided intersection is crossed, localization of the electronic transitions is achieved automatically in this approximate theory. The switching conditions of Section IIIc also have a simple physical interpretation and are seen to conserve total energy and total angular momentum.

The "exact" version of this semiclassical theory has been presented in Section IV, "exact" meaning that there are no inherent dynamical

approximations in this formulation other than that of electronic adiabaticity itself. The switching conditions are particularly simple in this approach, for the transitions take place at complex times on the "complex surface of intersection" (an $f-1$ dimensional surface) for which the adiabatic potential surfaces are degenerate. To make the procedure internally consistent it was found necessary to allow all coordinates and momenta, and the time, to take on complex values; this causes no problems in principle, however, there being precisely the number of boundary conditions available to insure that physically observable variables are real quantities. The transition probability P_{21} emerges naturally in terms of the imaginary part of the classical action (which signals the classically forbidden character of the transition), and localization of the electronic transition was achieved by choosing the path of integration in the complex t -plane so that the classical action acquired imaginary increments only for finite time intervals.

Finally, although we have not discussed the possibility of reactive collisions explicitly, it should be clear from previous work⁴ dealing with only one electronic state how the results are generalized to account for this. In fact Equation (2.11) applies as written if one allows the indices 1 and 2 to represent specific electronic states of specific nuclear arrangements. The electronic aspect of the problem is completely unaltered by the fact that the nuclear trajectory may end in one of several nuclear arrangements.

APPENDIX I

Here we wish to show that the functions $f_{\pm}(t)$ defined in Equation (4.8) have the limiting forms of Equation (4.12) for t far from t_0 . If one expands $k(t)$ [defined in Equation (4.6)] in powers of \hbar ,

$$k(t) \approx \frac{\Delta W}{2\hbar} + \frac{i}{2} \left[-\frac{\dot{\Delta W}}{\Delta W} + \frac{\dot{B}}{B} \right] + O(\hbar) \quad , \quad (I.1)$$

where $\Delta W = \Delta W(t)$, $B = B(t)$, then it is easy to show that

$$\pm i \int_{t_0}^t dt' k(t') = \pm \frac{i}{2\hbar} \int_{t_0}^t dt' \Delta W(t') \pm \ln \left(\frac{\Delta W}{B} \frac{B_0}{\Delta W_0} \right)^{\frac{1}{2}} \quad (I.2)$$

where $B_0 = B(t_0)$, $\Delta W_0 = \Delta W(t_0)$. With Equation (I.2), Equation (4.8)

becomes:

$$f_{\pm}(t) = \left(\frac{\hbar B_0}{\Delta W_0} \right)^{\frac{1}{2}} B(t)^{-\frac{1}{2}} \exp \left\{ \frac{i}{2\hbar} \int_{t_0}^t dt' \Delta W(t') \right\} \quad (I.3a)$$

$$f_{-}(t) = \left(\frac{\Delta W_0}{\hbar B_0} \right)^{\frac{1}{2}} \frac{\hbar B(t)^{\frac{1}{2}}}{\Delta W(t)} \exp \left\{ \frac{-i}{2\hbar} \int_{t_0}^t dt' \Delta W(t') \right\} \quad (I.3b)$$

This would be identical to Equation (4.12) if the dimensionless constant $\hbar B_0 / \Delta W_0$ were equal to unity; there is no obvious way, however, to see that this must be so. (In fact it is not true.)

The failure in the above straight-forward procedure stems from the neglect of the term $B(t)^2$ in the expression for $k(t)^2$ [Equation (4.6)]; i.e., it is clear that there can be no transitions if $B(t) \equiv 0$, and it is for this reason that inconsistencies appear if it is neglected at too

early a stage in the development. Thus the expansion in Equation (I.1) is replaced by

$$k(t) = \left[\left(\frac{\Delta W}{2\hbar} \right)^2 + B^2 \right]^{\frac{1}{2}} + \frac{1}{2} \left[\left(\frac{\Delta W}{2\hbar} \right)^2 + B^2 \right]^{-\frac{1}{2}} \frac{i}{2\hbar} \left(-\Delta \dot{W} + \Delta W \frac{\dot{B}}{B} \right),$$

which can also be written as

$$k(t) = \left[\left(\frac{\Delta W}{2\hbar} \right)^2 + B^2 \right]^{\frac{1}{2}} - i \left[\left(\frac{\Delta W}{2\hbar B} \right)^2 + 1 \right]^{-\frac{1}{2}} \frac{d}{dt} \left(\frac{\Delta W}{2\hbar B} \right), \quad (\text{I.4})$$

so that Equation (I.2) is replaced by

$$\begin{aligned} \pm i \int_{t_0}^t dt' k(t') &= \pm i \int_{t_0}^t dt' \left[\left(\frac{\Delta W}{2\hbar} \right)^2 + B^2 \right]^{\frac{1}{2}} \\ &+ \ln \left\{ \frac{\left(\frac{\Delta W}{2\hbar B} \pm \left[\left(\frac{\Delta W}{2\hbar B} \right)^2 + 1 \right]^{\frac{1}{2}} \right)^{\frac{1}{2}}}{\left(\frac{\Delta W_0}{2\hbar B_0} \pm \left[\left(\frac{\Delta W_0}{2\hbar B_0} \right)^2 + 1 \right]^{\frac{1}{2}} \right)^{\frac{1}{2}}} \right\}. \end{aligned} \quad (\text{I.5})$$

Since

$$\frac{\Delta W}{2\hbar B} \pm \left[\left(\frac{\Delta W}{2\hbar B} \right)^2 + 1 \right]^{\frac{1}{2}} \approx \pm \left(\frac{\Delta W}{\hbar B} \right)^{\pm 1} \quad (\text{I.6})$$

as $\hbar B/\Delta W \rightarrow 0$, it is easy to see that Equation (I.5) reduces to Equation (I.2) if $\hbar B/\Delta W$ and $\hbar B_0/\Delta W_0$ are assumed small.

The non-adiabatic coupling $B(t)$ is indeed expected to be negligibly small for t not close to t_0 , so that Equation (I.6) applies for t not near t_0 . At t_0 , however, which is a local minimum of $\Delta W(t)$, the non-

adiabatic coupling is strong, so that instead of Equation (I.6) one had the opposite limit

$$\frac{\Delta W_0}{2\hbar B_0} \pm \left[\left(\frac{\Delta W_0}{2\hbar B_0} \right)^2 + 1 \right]^{\frac{1}{2}} = \pm 1 \quad (\text{I.7})$$

as $\Delta W_0/\hbar B_0 \rightarrow 0$. Equation (I.5) thus becomes (with Equations (I.6) and (I.7))

$$\pm i \int_{t_0}^t dt' k(t') = \pm i \int_{t_0}^t dt' \left[\left(\frac{\Delta W}{2\hbar} \right)^2 + B^2 \right]^{\frac{1}{2}} \pm \ln \left(\frac{\Delta W}{\hbar B} \right)^{\frac{1}{2}} \quad (\text{I.8})$$

In the integrand of the first term on the RHS of Equation (I.8) the term B^2 can now be neglected in comparison to $\Delta W/2\hbar$ since it is non-zero only near t_0 , and the desired result [Equation (4.12)] then follows directly from Equation (I.8).

In conclusion we note that the discussion in this Appendix applies equally well to the case that the potential surfaces W_1 and W_2 are of different symmetry and actually intersect at t_0 , $\Delta W_0 = 0$; Equations (I.6)-(I.8) apply as written. The non-adiabatic coupling at t_0 is of course required in this case and must be included in the barrier penetration integral; Equation (4.20) is thus replaced by

$$2\delta = -i \int dt \left[\left(\frac{\Delta W}{2\hbar} \right)^2 + B^2 \right]^{\frac{1}{2}} \quad (\text{I.9})$$

If $B(t)$ is roughly constant and $\Delta W(t)$ is linear near t_0 , for example, Equation (I.9) gives a Landau-Zener-like expression

$$2\delta = 2\pi n B_0^2 / \Delta \dot{W}_0$$

(I.10)

APPENDIX II

Here we wish to show that the normalization factor in Equation (4.22a) for the $1 \rightarrow 1$ electronic transition can be obtained from the known $1 \rightarrow 2$ transition amplitude by invoking unitarity of the full S-matrix. The result is the same as that in Equations (4.22) and thus confirms the derivation in Section IVa.

Consider the case that there is just one crossing encounter; since the electronic transition is localized (see Section IVc), the results for one crossing can be applied repeatedly to deal with several independent crossing encounters. If q and n denote collectively the angle and action variables for the internal nuclear degrees of freedom (i.e., n denotes the quantum numbers for rotation and vibration), then the $1 \rightarrow 2$ electronic transition amplitude is given directly in terms of the appropriate classical action function:

$$S_{2n_2, 1n_1} = \left(\frac{\partial^2 \phi_{21}(n_2, n_1)}{\partial n_2 \partial n_1} / 2\pi\hbar \right)^{\frac{1}{2}} \exp [i\phi_{21}(n_2, n_1)/\hbar], \quad (\text{II.1})$$

where $\phi_{21}(n_2, n_1)$ is the classical action computed along the trajectory that begins on potential surface 1 with nuclear quantum numbers n_1 , crosses to surface 2 at the time t_* that the potentials intersect, and ends on potential surface 2 with quantum numbers n_2 ; ϕ_{21} is complex.

The $1 \rightarrow 1$ transition amplitude is

$$S_{1n_2, 1n_1} = A(n_2, n_1) \left(\frac{\partial^2 \phi_{11}(n_2, n_1)}{\partial n_2 \partial n_1} / 2\pi\hbar \right)^{\frac{1}{2}} \exp [i\phi_{11}(n_2, n_1)/\hbar], \quad (\text{II.2})$$

where $\phi_{11}(n_2, n_1)$ is the classical action for the trajectory that remains on potential surface 1 and has initial and final quantum numbers n_1 and n_2 ; ϕ_{11} is real. The usual Jacobian factor has been included in Equation (II.2), and $A(n_2, n_1)$ is the additional factor which is to be determined.

The statement of unitarity for the S-matrix is

$$\sum_{\alpha''} \int dn_2 S_{\alpha'' n_2, \alpha' n_1} S_{\alpha'' n_2, \alpha n_1}^* = \delta_{\alpha', \alpha} \delta(n_1' - n_1) \quad , \quad (\text{II.3})$$

where the discrete electronic index α takes on values 1 and 2, and the nuclear quantum numbers are assumed continuous for purposes of normalization. If $\alpha' \neq \alpha$, then it is easy to see that the integral over n_2 gives no contribution, for there is no point of stationary phase. Thus one only needs to consider the case $\alpha = \alpha' = 1$, and n_1 and n_1' infinitesimally close to one another.

For this case Equation (II.3) is

$$\delta(n_1' - n_1) = \int dn_2 S_{1n_2, 1n_1'} S_{1n_2, 1n_1}^* + \int dn_2 S_{2n_2, 1n_1'} S_{2n_2, 1n_1}^* \quad (\text{II.4})$$

and with Equations (II.1) and (II.2), this becomes

$$\begin{aligned} 2\pi\hbar \delta(n_1' - n_1) = & \int dn_2 |A(n_2, n_1)|^2 \left| \frac{\partial^2 \phi_{11}(n_2, n_1)}{\partial n_2 \partial n_1} \right| \\ & \times \exp \left\{ \frac{i}{\hbar} \left[\phi_{11}(n_2, n_1') - \phi_{11}(n_2, n_1) \right] \right\} \\ & + \int dn_2 \left| \frac{\partial^2 \phi_{21}(n_2, n_1)}{\partial n_2 \partial n_1} \right| \exp \left\{ \frac{i}{\hbar} \left[\phi_{21}(n_2, n_1') \right. \right. \\ & \left. \left. - \phi_{21}^*(n_2, n_1) \right] \right\} \quad , \quad (\text{II.5}) \end{aligned}$$

where n_1' has been set equal to n_1 everywhere except in the phases. Expanding $\phi(n_2, n_1')$ about n_1 ,

$$\phi(n_2, n_1') = \phi(n_2, n_1) + \frac{\partial \phi(n_2, n_1)}{\partial n_1} (n_1' - n_1)$$

gives

$$\begin{aligned} 2\pi\hbar\delta(n_1' - n_1) &= \int dn_2 |A(n_2, n_1)|^2 \left| \frac{\partial^2 \phi_{11}(n_2, n_1)}{\partial n_2 \partial n_1} \right| \\ &\times \exp \left[\frac{i}{\hbar} \frac{\partial \phi_{11}(n_2, n_1)}{\partial n_1} (n_1' - n_1) \right] \\ &+ \int dn_2 \left| \frac{\partial^2 \phi_{21}(n_2, n_1)}{\partial n_2 \partial n_1} \right| \\ &\times \exp \left[-2 \operatorname{Im} \phi_{21}(n_2, n_1) / \hbar + \frac{i}{\hbar} \frac{\partial \phi_{21}(n_2, n_1)}{\partial n_1} (n_1' - n_1) \right]. \quad (\text{II.6}) \end{aligned}$$

The action functions $\phi(n_2, n_1)$ are generators of canonical transformations of the F_4 -type²⁵ and thus obey the derivative relation

$$\frac{\partial \phi(n_2, n_1)}{\partial n_1} = q_1, \quad (\text{II.7})$$

where q_1 is the initial angle variable determined by n_2 and n_1 . Thus

$$\frac{\partial^2 \phi(n_2, n_1)}{\partial n_2 \partial n_1} = \left(\frac{\partial q_1}{\partial n_2} \right)_{n_1}, \quad (\text{II.8})$$

so that (for fixed n_1) the Jacobians that appear in the integrands of

Equation (II.6) are precisely the factors necessary to change the integration variable from n_2 to q_1 ; with this change of integration variables Equation (II.6) becomes

$$\begin{aligned}
 2\pi\hbar\delta(n_1'-n_1) = & \int_0^{2\pi} dq_1 |A[n_2^{(1)}(q_1, n_1), n_1]|^2 \exp\left[\frac{i}{\hbar}q_1(n_1'-n_1)\right] \\
 & + \int_C dq_1 \exp\left\{-\frac{2}{\hbar} \text{Im}\phi_{21}[n_2^{(2)}(q_1, n_1), n_1]\right\} \\
 & \times \exp\left[\frac{i}{\hbar}q_1(n_1'-n_1)\right] \quad , \quad (II.9)
 \end{aligned}$$

where $n_2^{(1)}(q_1, n_1)$ and $n_2^{(2)}(q_1, n_1)$ are the final nuclear quantum numbers, as a function of the initial values q_1 and n_1 , that end on potential surfaces 1 and 2, respectively. In the first term of Equation (II.9) q_1 is real, but in the second term the q_1 integral is a line integral along the curve C in the complex q_1 -plane that is defined (for fixed n_1) by

$$\text{Im } n_2^{(2)}(q_1, n_1) = 0 \quad . \quad (II.10)$$

If the integrand of the second term is sufficiently well-behaved (i.e., analytic), however, the integration path can be distorted to lie along the real q_1 axis from 0 to 2π . Fourier transforming Equation (II.9) then gives

$$1 = |A[n_2^{(1)}(q_1, n_1), n_1]|^2 + \exp\left\{-\frac{2}{\hbar} \text{Im}\phi_{21}[n_2^{(2)}(q_1, n_1), n_1]\right\} \quad ,$$

so that the desired result is obtained:

$$A(n_2, n_1) = \left(1 - e^{-2\delta}\right)^{\frac{1}{2}} \quad (\text{II.11})$$

where

$$\delta = \frac{1}{\hbar} \text{Im } \phi_{21} \left[n_2^{(2)}(q_1, n_1), n_1 \right],$$

with q_1 equal to that value for which

$$n_2^{(1)}(q_1, n_1) = n_2.$$

APPENDIX III

It is interesting to show how one can find (formally at least) the time t_* at which the potential surfaces $W_1(\underline{q})$ and $W_2(\underline{q})$ intersect; one utilizes the formal solution of the Liouville equation²⁶. If $f(\underline{q}, \underline{p})$ is any function of the coordinates and momenta, its total time derivative is given by the chain rule

$$\frac{d}{dt} f[\underline{q}(t), \underline{p}(t)] = \sum_i \frac{\partial f}{\partial q_i} \dot{q}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \equiv \dot{\underline{q}} \cdot \frac{\partial f}{\partial \underline{q}} + \dot{\underline{p}} \cdot \frac{\partial f}{\partial \underline{p}}, \quad (\text{III.1})$$

and with introduction of Hamilton's equations

$$\dot{\underline{q}} = \frac{\partial H(\underline{q}, \underline{p})}{\partial \underline{p}}, \quad \dot{\underline{p}} = -\frac{\partial H(\underline{q}, \underline{p})}{\partial \underline{q}},$$

this becomes

$$\frac{d}{dt} f[\underline{q}(t), \underline{p}(t)] = -iL f, \quad (\text{III.2})$$

where L is the Liouville operator

$$L = i \left(\frac{\partial H}{\partial \underline{p}} \cdot \frac{\partial}{\partial \underline{q}} - \frac{\partial H}{\partial \underline{q}} \cdot \frac{\partial}{\partial \underline{p}} \right). \quad (\text{III.3})$$

The formal solution to Equation (III.2) is

$$f[\underline{q}(t_2), \underline{p}(t_2)] = \exp[-i(t_2-t)L] f(\underline{q}, \underline{p}), \quad (\text{III.4})$$

or if the exponential operator is expanded in its power series this is

$$f[q(t_2), p(t_2)] = \sum_{n=0}^{\infty} \frac{(t_2-t)^n}{n!} \left(\frac{\partial H}{\partial p} \cdot \frac{\partial}{\partial q} - \frac{\partial H}{\partial q} \cdot \frac{\partial}{\partial p} \right)^n \times f(q, p) \quad (\text{III.5})$$

where q and p are the coordinates and momenta at time t .

For our case the function $f(q, p)$ is $\Delta W(q) \equiv W_2(q) - W_1(q)$, H is the Hamiltonian for motion on potential surface 1, and we wish to find the time t_* at which ΔW is zero. The equation for t_* , therefore, is

$$0 = \sum_{n=0}^{\infty} \frac{(t_*-t)^n}{n!} \left(\frac{\partial H}{\partial p} \cdot \frac{\partial}{\partial q} - \frac{\partial H}{\partial q} \cdot \frac{\partial}{\partial p} \right)^n \Delta W(q), \quad (\text{III.6})$$

where

$$H = \frac{1}{2} p \cdot M^{-1} \cdot p + W_1(q),$$

and q and p are the coordinates and momenta at time t . The value of t_* defined by Equation (III.6) is independent of the particular choice for t ; i.e., if one changes t , then the values of $q(t)$ and $p(t)$ also change so that t_* is unchanged. If Equation (III.6) is to be used to calculate t_* , however, one wishes to choose t as close to t_* as possible so that the power series in (t_*-t) is rapidly convergent. If t is chosen as t_0 , the minimum of $\Delta W(t)$ for real t , and terms through $(t_*-t)^2$ retained in Equation (III.6), then the quadratic approximation of Equations (3.29) and (3.30) is obtained for t_* .

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