tron-loss cross sections (σ_{-10}) decrease monotonically with increasing energy and in general increase with the atomic number, Z, of the target. This is consistent with the findings of Nikolaev[8] for $Z < 18$. The two electron-loss cross sections (σ_{-11}) also increase with the atomic number, Z, of the target but only vary slowly with energy.

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Electronic Transitions in Slow Collisions of Atoms and Molecules. I.*

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The semiclassical approximation is systematically applied to the study of electronic transitions in near-adiabatic collisions of atoms and molecules. The use of the eikonal approximation permits the coupled equations of scattering theory to be reduced to one-dimensional equations defined along classical trajectories. The theory for rearrangement collisions is developed into a form appropriate for use with the eikonal description of heavy-particle motion.

I. INTRODUCTION

In this paper we study the theory of electronic transitions in the collisions of slow atoms and molecules (for brevity, we shall refer to the particles as "atoms"). The conditions assumed will be such that the motion of the atomic centers of mass is essentially classical. Our goal is to systematically extract the possible approximations arising from this classical aspect of the problem.

Stationary-state scattering theory will be used. The state function will be expanded in terms of *adiabatic states* – often called "perturbed stationary states." We shall use the eikonal approximation for the coefficients in this expansion, which describe the motion of the atomic mass centers.[1]

Except when there are degeneracies, electronic transitions occur only for finite collision velocities (the adiabatic theorem). We shall use the term "near-adiabatic" to refer to transitions that occur at low velocities.

The formulation of the "perturbed stationary-state" method for cases in which rearrangement does not occur is well-known. We briefly review this in Sec. II, expressing it in a form suitable for our application. When rearrangement occurs, the problem is much more subtle. Discussions have been given in the context of time-dependent perturbation theory, for example, by Bates and McCarroll[2] and by Mittleman.[3] Thorson[4] has observed that the adiabatic (or Born-Oppenheimer) states of the perturbed stationary-state method do not lead to correct asymptotic incoming or outgoing states. He proposes an approximation scheme consistent with this formal requirement of scattering theory (a point previously ignored). In Sec. III and Appendix B we give a formulation for rearrangement collision that is consistent with formal scattering theory and with the eikonal approximation.

The use of the eikonal approximation to describe the mass-center motion is presented in Sec. IV. Matrix elements representing transitions between electronic states thus involve integrals of eikonal wave functions. In Sec. V we show how these three-dimensional integrals may be reduced to one-dimensional integrals along classical trajectories. Thus the coupled integral equations of stationary state scattering theory are reduced to equations in one dimension.

The first Born approximation to these equations appears to have considerable validity for the calculation of near-adiabatic transitions. For example, the well-known Landau-Zener expression for transitions between "crossing" levels has recently been shown,[1] by the methods described in this paper, to follow from the first Born approximation.

To develop the approximations made in our analysis we shall assume that several dimensionless parameters are small. First, we shall make use of the fact that

$$\eta_1 \equiv m/M \ll 1, \tag{1.1}$$

where m is the electron mass and M the mass of either colliding atom. To satisfy the conditions for near-adiabatic scattering, we shall require that

$$\eta_2 \equiv v/(e^2/\hbar) \ll 1, \tag{1.2}$$

where v is the relative velocity of the colliding atoms and $e^2/\hbar \simeq 2\times 10^8$ cm/sec is a characteristic bound-electron velocity.

For the validity of the semiclassical approximation, we shall further require that

$$\eta_3 \equiv \hbar/pa_0 \ll 1, \tag{1.3}$$

and $$\eta_4 = (1\ \mathrm{Ry})/\epsilon < 1. \tag{1.4}$$

Here a_0 is the Bohr radius, p the relative momentum of the colliding atoms, $\epsilon = p^2/2M$, and 1 Ry $= e^2/2a_0$.

II. EXCITATIONS IN THE ABSENCE OF REARRANGEMENT

In this section we review briefly the theory of near-adiabatic excitations of the type

$$A + B \to A^* + B, \tag{2.1}$$

etc., where one (or both) of the colliding atoms is excited. The respective center-of-mass (c.m.) coordinates of the atoms are $\vec{y}_1$, $\vec{y}_2$, while

$$\vec{R} \equiv \vec{y}_1 - \vec{y}_2 \tag{2.2}$$

is their relative coordinate. The respective atomic masses are M_1 and M_2, and atomic Hamiltonians are h_1 and h_2. The interaction potential between the atoms will be written as V_{12}. In the c.m. system of both atoms, the Hamiltonian is

$$H = K + h_1 + h_2 + V_{12}, \tag{2.3}$$

where $$K = -(1/2M)\nabla_R^2 \tag{2.4}$$

and $M^{-1} = M_1^{-1} + M_2^{-1}$.

Eigenfunctions and eigenenergies for the internal states $n = 0, 1, 2\ldots$ of the isolated atoms are g_n and W_n, where

$$(h_1 + h_2)g_n = W_n g_n. \tag{2.5}$$

The g_n depend on internal coordinates only and not on the interatomic separation $\vec{R}$. The *adiabatic* Hamiltonian is defined as

$$h_a \equiv h_1 + h_2 + V_{12}. \tag{2.6}$$

Eigenfunctions and eigenvalues of h_a are written as φ_α and $w_\alpha(\vec{R})$, $\alpha = 0, 1, \ldots$, depending parametrically on $\vec{R}$:

$$h_a \varphi_\alpha = w_\alpha(\vec{R})\varphi_\alpha. \tag{2.7}$$

The state labels α and n above may be taken to be a single set specified by the condition

$$\lim_{R\to\infty} \varphi_\alpha = g_\alpha, \qquad \lim_{R\to\infty} w_\alpha = W_\alpha. \tag{2.8}$$

Then we may write

$$w_\alpha(\vec{R}) \equiv W_\alpha + v_\alpha(\vec{R}), \tag{2.9}$$

defining the *adiabatic* interatomic potential $v_\alpha(\vec{R})$.

We suppose the scattering to proceed from an initial state

$$\chi_a = \varphi_0 \lambda_{\vec{p}}(\vec{R}), \tag{2.10}$$

where $$\lambda_{\vec{p}}(\vec{R}) \equiv (2\pi)^{-3/2} e^{i\vec{p}\cdot\vec{R}}. \tag{2.11}$$

The total energy is then

$$E = W_0 + \epsilon_p, \tag{2.12}$$

where $\epsilon_p = p^2/2M$.

The Schrödinger equation for the state function ψ_a^+ is then[5]

$$(E + i\eta - H)\psi_a^+ = i\eta\chi_a. \tag{2.13}$$

Here η is the usual small positive parameter that is allowed to approach zero at a proper place in the calculation.

To simplify Eq. (2.13) we introduce the expansion

$$\psi_a^+ = \sum_\beta \varphi_\beta \Psi_\beta(\vec{R}). \tag{2.14}$$

On substituting this into Eq. (2.13) we obtain the coupled equations

$$[E+i\eta-K-w_\alpha]\Psi_\alpha-\sum_\beta\Delta_{\alpha\beta}\Psi_\beta=i\eta\,\delta_{\alpha 0}\lambda_{\vec{p}}. \quad (2.15)$$

The "interaction" $\Delta_{\alpha\beta}$ here is

$$\Delta_{\alpha\beta}=(\varphi_\alpha,[K,\varphi_\beta])$$
$$=-(1/2M)[(\varphi_\alpha,\nabla_R^2\varphi_\beta)+2(\varphi_\alpha\nabla_R\varphi_\beta)\cdot\nabla_R], \quad (2.16)$$

where, in the scalar products, integrals are performed over all internal atomic coordinates. We see that $\Delta_{\alpha\beta}$ has the general form

$$\Delta_{\alpha\beta}=Q_{\alpha\beta}(\vec{R})+\vec{P}_{\alpha\beta}(\vec{R})\cdot\nabla_R .$$

It is therefore nonlocal, although $Q_{\alpha\beta}$ and $\vec{P}_{\alpha\beta}$ are just *functions* of $\vec{R}$ which vanish at $R=\infty$.

For near-adiabatic scattering, we expect to be able to treat Δ as a small perturbation. To see this we note that

$$\Delta=O(v\hbar/a_o).$$

Since we expect $v_\alpha=O(1\text{ Ry})$, we have

$$\frac{|\Delta|}{|v_\alpha|}=O\left(\frac{v}{e^2/\hbar}\right)=O(\eta_2)\ll 1$$

by condition (1.2).

To put Eq. (2.15) into the conventional Lippmann-Schwinger form, we introduce the *coherent states* $\Psi_{c\alpha a}^{+}(\vec{R})$, defined by

$$[E+i\eta-K-w_\alpha]\Psi_{c\alpha\vec{q}}^{+}=i\eta\lambda_{\vec{q}} . \quad (2.17)$$

With these we rewrite (2.15) as the set of coupled integral equations

$$\Psi_\alpha=\delta_{\alpha 0}\Psi_{c0\vec{p}}^{+}+[1/(E+i\eta-K-w_\alpha)]\sum_\beta\Delta_{\alpha\beta}\Psi_\beta . \quad (2.18)$$

The scattering matrix for a final state

$$\chi_b=\varphi_\alpha\lambda_{\vec{k}}(\vec{R})$$

is seen to be

$$\langle\alpha,\vec{k}\,|T|0\vec{p}\rangle=\delta_{\alpha 0}(\lambda_{\vec{k}},v_0\Psi_{c0\vec{p}}^{+})+\left(\Psi_{c\alpha\vec{k}}^{-},\sum_\beta\Delta_{\alpha\beta}\Psi_\beta\right). \quad (2.19)$$

For applications it is probably useful to consider the diagonal matrix elements $\Delta_{\alpha\alpha}$ as absorbed in the v_α. Then the v_α describes *elastic* scattering and the $\Delta_{\alpha\beta}$ *transitions* between states. We have seen that $|\Delta_{\alpha\alpha}|\ll|v_\alpha|$, so the diagonal elements $\Delta_{\alpha\alpha}$ can probably be simply negelected, in general.

The differential cross section for scattering to a final state g_α with relative momentum $\vec{k}$ is then[6]

$$d\sigma/d\Omega=(2\pi)^4(k/p)M^2|\langle\alpha\vec{k}\,|T|0\vec{p}\rangle|^2 . \quad (2.20)$$

III. NEAR-ADIABATIC REARRANGEMENT COLLISIONS

In this section we consider a typical rearrangement collision in which an electron is exchanged between two colliding atoms. We now suppose h_1 and h_2 to represent the respective Hamiltonians of the two "core" atoms – with the electron in question missing from both. The interactions of this electron with cores "1" and "2" will be called V_1 and V_2, respectively, and the interaction between the cores called V_{12}. If the respective masses and coordinates of the cores and extra electron are M_1, M_2, m, and $\vec{y}_1$, $\vec{y}_2$, $\vec{z}$, the Hamiltonian for the system is

$$H=T+h_1+h_2+V_1+V_2+V_{12} , \quad (3.1a)$$

$$T=-\frac{1}{2M_1}\Delta_{y_1}^2-\frac{1}{2M_2}\Delta_{y_2}^2-\frac{1}{2m}\Delta_z^2 . \quad (3.1b)$$

For simplicity we shall suppose that wave functions in only two of the possible channels[7] need be considered in our analysis. The first is the "incoming" channel "i" in which the (extra) electron is *bound* on core "1." The second is the "final" channel "f" in which the electron is bound on core "2."

Convenient independent variables in channel i are $\vec{r}_1$ and $\vec{R}_1$, defined by the equations

$$\vec{X}_1\equiv(M_1\vec{y}_1+m\vec{z})/(M_1+m) ,$$
$$\vec{r}_1\equiv\vec{z}-\vec{y}_1 ,$$
$$\vec{R}_1\equiv\vec{X}_1-\vec{y}_2 ,$$
$$\vec{C}\equiv(M_1\vec{y}_1+M_2\vec{y}_2+m\vec{z})/M_T , \quad (3.2)$$

where $M_T=M_1+M_2+m.$ (3.3)

We shall analyze the scattering in the c.m. coordinate system, so the c.m. coordinate $\vec{C}$ will not appear in our equations. Expressed in terms of the variables (3.2), the kinetic energy (3.1b) becomes

$$T=-(1/2M)\nabla_{R_1}^2-(1/2\mu)\nabla_{r_1}^2 , \quad (3.4)$$

where we have ignored the c.m. energy $-(1/2M_T)\times\nabla_C^2$ and

$$1/M = 1/(M_1+m) + 1/M_2 ,$$

$$1/\mu = 1/m + 1/M_1 . \qquad (3.5)$$

When we use $\vec{r}_1$ and $\vec{R}_1$ as independent variables, the Hamiltonian (3.1) takes the form

$$H = K + h_a , \qquad (3.6a)$$

$$K = -(1/2M)\nabla_{R_1}^2 , \qquad (3.6b)$$

$$h_a = -(1/2\mu)\nabla_{r_1}^2 + h_1 + h_2 + V_1 + V_2 + V_{12} . \qquad (3.6c)$$

The asymptotic states in channel i are eigenfunctions of the channel Hamiltonian

$$H_i = K + h_i , \qquad (3.7a)$$

where

$$h_i = -(1/2\mu)\nabla_{r_1}^2 + h_1 + h_2 + V_1 . \qquad (3.7b)$$

The internal-state eigenfunctions for the isolated atoms in channel i are g_b, g_d, ..., defined by

$$h_i g_b = W_b g_b , \text{ etc.} \qquad (3.8)$$

The g_b ...are functions of $\vec{r}_1$ and other internal coordinates ξ(space coordinates of other electrons and spin coordinates). For brevity, we shall write $g_b = g_b(\vec{r}_1)$, not explicitly indicating the other coordinates ξ. The channel eigenfunctions in i are then of the form

$$\chi_{b\vec{p}}^{(i)} = g_b(\vec{r}_1)\lambda_{\vec{p}}(\vec{R}_1) , \text{ etc.} \qquad (3.9)$$

For channel f, the appropriate set of coordinates is

$$\vec{x}_2 \equiv (M_2\vec{y}_2 + m\vec{z})/(M_2+m),$$

$$\vec{r}_2 \equiv \vec{z} - \vec{y}_2 ,$$

$$\vec{R}_2 \equiv \vec{y}_1 - \vec{x}_2 , \qquad (3.10)$$

with $\vec{C}$, of course, unchanged. Some useful relations between the two sets of coordinates are

$$\vec{r}_1 = -\vec{R}_2 + [M_2/(M_2+m)]\vec{r}_2 ,$$

$$\vec{R}_1 = \frac{M_1}{M_1+m}\vec{R}_2 + \frac{mM_T}{(M_1+m)(M_2+m)}\vec{r}_2 ,$$

$$\vec{r}_2 = \vec{R}_1 + [M_1/(M_1+m)]\vec{r}_1 ,$$

$$\vec{R}_2 = \frac{M_2}{M_2+m}\vec{R}_1 - \frac{mM_T}{(M_1+m)(M_2+m)}\vec{r}_1 . \qquad (3.11)$$

In terms of these coordinates, treating $\vec{r}_2$ and $\vec{R}_2$ as *independent* variables, the kinetic energy (3.1b) becomes

$$T = -(1/2M')\nabla_{R_2}^2 - (1/2\mu')\nabla_{r_2}^2 , \qquad (3.12)$$

where $1/M' = 1/M_1 + 1/(M_2+m)$, (3.13)

$$1/\mu' = 1/m + 1/M_2 .$$

For f, the channel Hamiltonian is now

$$H_f = K' + h_f' , \qquad (3.14a)$$

where $K' = -(1/2M')\nabla_{R_2}^2$,

$$h_f' = -(1/2\mu')\nabla_{r_2}^2 + h_1 + h_2 + V_2 . \qquad (3.14b)$$

Internal-state eigenfunctions for the isolated atoms in this channel are g_l', g_n', ..., defined by

$$h_f' g_l' = W_l' g_l' , \text{ etc.} \qquad (3.15)$$

These are functions of the variables ξ and $\vec{r}_2$ – and we write $g_l = g_l(\vec{r}_2)$, again not indicating explicitly the ξ dependence.

As in Eq. (2.7), we can define a set of *adiabatic* eigenfunctions ϕ_α by the equations

$$h_a \phi_\alpha = w_\alpha(\vec{R}_1)\phi_\alpha , \qquad (3.16)$$

where, of course, we now use Eq. (3.6c) to define h_a. We shall again suppress the explicit dependence on variables ξ to write $\phi_\alpha = \phi_\alpha(\vec{r}_1;\vec{R}_1)$, indicating the *parametric* dependence on $\vec{R}_1$.

We may evidently choose the α labels so that for certain of the states, namely, $\alpha = b, d, \ldots$,

$$\lim_{R_1\to\infty} \varphi_b(\vec{r}_1;\vec{R}_1) = g_b(\vec{r}_1) , \qquad (3.17a)$$

$$\lim_{R_1\to\infty} w_b(\vec{R}_1) = W_b , \text{ etc.} \qquad (3.17b)$$

We now proceed to develop the Schrödinger equation for the state function ψ_a^+, as was done in Sec. II. Using the notation of Eqs. (2.10)–(2.13), we introduce

$$\chi_a = \phi_0\lambda_{\vec{p}}(\vec{R}_1) , \qquad (3.18)$$

where $g_0\lambda_{\vec{p}}$ is the initial state in channel i. The Schrödinger equation is then

$$(E + i\eta - H)\psi_a^+ = i\eta\chi_a . \qquad (3.19)$$

Following the discussion which led to Eq. (2.15), we introduce the expansion

$$\psi_a^+ = \sum_\alpha \phi_\alpha(\vec{r}_1;\vec{R}_1)\Upsilon_\alpha(\vec{R}_1) . \qquad (3.20)$$

This permits us to write Eq. (3.19) as the set of coupled equations

$$[E+i\eta-K-w_\alpha]\Upsilon_\alpha-\sum_\beta\Delta_{\alpha\beta}\Upsilon_\beta = i\eta\delta_{\alpha 0}\lambda_{\vec{p}}\,, \quad (3.21)$$

where [compare Eq. (2.16)]

$$\Delta_{\alpha\beta}=(\varphi_\alpha,[K,\varphi_\beta]) = -(1/2M)[(\varphi_\alpha,\nabla_{R_1}^2\varphi_\beta) + 2(\varphi_\alpha,\nabla_{R_1}\varphi_\beta)\cdot\nabla_{R_1}]. \quad (3.22)$$

We emphasize that the scalar products here are of the form

$$\int_{\vec{R}_1} d\xi\, d^3r_1\,\phi_\alpha^*(\vec{r}_1;\vec{R}_1)\nabla_{R_1}^2\phi_\beta(\vec{r}_1;\vec{R}_1)\,, \quad (3.23)$$

etc., where the subscript $\vec{R}_1$ is placed under the integral sign to indicate that $\vec{R}_1$ is held constant when the integration is performed.

As $R_1\to\infty$ it is evident that some of the ϕ_α will correspond to states in channel f with the (extra) electron bound on core "2." We choose the α label so that for $\alpha = l, n, \ldots$, these correspond to states defined by (3.15). That is, reference to Eqs. (3.11) shows that

$$\lim_{R_1\to\infty}\varphi_l(\vec{r}_1;\vec{R}_1) = g_l\left(\vec{R}_1+[M_1/(M_1+m)]\vec{r}_1\right)=g_l(\vec{r}_2)\,. \quad (3.24)$$

From Eq. (3.6c) we see that g_l, g_n, $\cdots$, are eigenfunctions of the Hamiltonian

$$h_f=-(1/2\mu)\nabla_{r_1}^2+h_1+h_2+V_2\,; \quad (3.25)$$

that is,

$$h_f g_l = W_l g_l\,, \text{ etc.},$$

where $W_l=\lim_{R_1\to\infty} w_l$. (3.26)

Reference to Eq. (3.14b) shows that g_l or g_l' differ only to order η_1 [see Eq. (1.1)]; or,

$$\lim_{M_1,\,M_2\to\infty} g_l' = g_l.$$

To calculate the scattering to states in channel f we must identify in $\psi_a^\dagger$ the correct channel functions g_l'. The fact that $g_l'\cong g_l$ will simplify this problem.

In preparation for doing this, let us look at the asymptotic form of Eq. (3.21) as $R_1\to\infty$. The "potentials"

$$v_\alpha(\vec{R}_1)\equiv w_\alpha-\lim_{R_1\to\infty} w_\alpha$$

vanish at $R_1=\infty$ by construction, and it is convenient to suppose that

$$\lim_{R_1\to\infty}(R_1 v_\alpha)\to 0.$$

at least as fast as some negative power of R_1. The "interaction" $\Delta_{\alpha\beta}$ depends on $\vec{R}_1$ and ∇_{R_1} and does not in general vanish as $R_1\to\infty$. This is to be expected, since the asymptotic states $g_l,\ldots$ in channel f are *not* the correct states $g_l,\ldots$.

For matrix elements between states such as $b, d,\ldots$ in channel i we do have

$$\lim_{R_1\to\infty}\Delta_{bd}\equiv\Delta_{bd}^{\,0}=0\,, \quad (3.27a)$$

however. This can be seen from Eqs. (3.22) and (3.17a). In the limit that $R_1\to\infty$ the states ϕ_b, $\ldots$ are independent of R_1. Also, for matrix elements between states in channels i and f, we have

$$\lim_{R_1\to\infty}\Delta_{bl}\equiv\Delta_{bl}^{\,0}=0\,, \quad (3.27b)$$

etc. This is evident from Eqs. (3.17a) and (3.24), since for large interatomic separations there is no overlap of the bound-wave functions. On the other hand, for states in channel f we have

$$\lim_{R_1\to\infty}\Delta_{ln}\equiv\Delta_{ln}^{\,0} = -(1/2M)\left[(g_l,\nabla_{r_2}^2 g_n) + 2(g_l,\nabla_{r_2}g_n)\cdot\nabla_{R_1}\right]\neq 0. \quad (3.27c)$$

The above discussion suggests that we write

$$\Delta_{\alpha\beta}\equiv\Delta_{\alpha\beta}^{\,0}+J_{\alpha\beta}\,, \quad (3.28)$$

where now $J_{\alpha\beta}=0$ in the limit $R_1\to\infty$. We can thus define

$$v_{\alpha\beta}[\vec{R}_1,(1/i)\nabla_{\vec{R}_1}]\equiv v_\alpha(\vec{R}_1)\delta_{\alpha\beta} + J_{\alpha\beta}[\vec{R}_1,(1/i)\nabla_{\vec{R}_1}]. \quad (3.29)$$

Then, for a given state n in channel f, we can write Eq. (3.21) in the form

$$(E+i\eta-K-W_n)\Upsilon_n - \Sigma_l(g_n,[K,g_l])\Upsilon_l-\Sigma_\beta v_{n\beta}\Upsilon_\beta=0\,,$$

where the sum on β extends over both channels. Use of Eq. (3.26) lets us write this as

$$[E+i\eta]\Upsilon_n-\Sigma_l(g_n,(K+h_f)g_l)\Upsilon_l - \Sigma_\beta v_{n\beta}\Upsilon_\beta=0 \quad (3.30)$$

We now introduce the "wave function" Υ defined as

$$\Upsilon(\vec{r}_1, \vec{R}_1) = \sum_n g_n(\vec{r}_2)\Upsilon_n(\vec{R}_1), \tag{3.31}$$

where the sum runs over the states corresponding to channel f only. A projection operator Λ_f is defined by the same sum:

$$\Lambda_f = \sum_n g_n g_n^* . \tag{3.32}$$

It follows that

$$\Lambda_f \Upsilon = \Upsilon . \tag{3.33}$$

Also, as $R_1 \to \infty$, we have

$$\Upsilon = \Lambda_f \psi_a^+ , \tag{3.34}$$

which means that we can use Υ to obtain the scattered waves in channel f.

If we multiply Eq. (3.30) by g_n and sum over n, we obtain

$$\Lambda_f \left[(E + i\eta - K' - h_f') \Upsilon - \sum_{n,\beta} g_n v_{n\beta} \Upsilon_\beta \right] = 0 ,$$

since $K' + h_f' = K + h_f$. The above is equivalent to the equation

$$\left[E + i\eta - K' - h_f' \right] \Upsilon - \sum_{n,\beta} g_n v_{n\beta} \Upsilon_\beta = \sum_b g_b Q_b(\vec{R}_1) , \tag{3.35}$$

where the sum on b runs over the states in channel i and the Q_b are chosen to ensure that the condition (3.33) is satisfied.

We have not so far made approximations in our analysis. Equation (3.35) may be considerably simplified if we make use of the assumed smallness of η_1 and η_2 [conditions (1.1) and (1.2)],[8] keeping only the lowest-order nonvanishing terms in these quantities. Thus, we may take

$$g_n' = g_n , \tag{3.36}$$

valid to lowest order in η_1. Since $J_{\alpha\beta}$ is of $O(\eta_2)$, we may consider Υ to be of $O(\eta_2)$. This means that we may set

$$\Upsilon_n(\vec{R}_1) = \Upsilon_n(\vec{R}_2) , \tag{3.37}$$

the relative error being of $O(\eta_2)$. To see this, we note that the Υ_n contains oscillating exponentials which describe the relative motion of the two atoms.[9] The error in (3.37) is thus of the order of $p|\vec{R}_2 - \vec{R}_1| = \eta_1 p r_2$. Now for the bound electron state $r_2 \approx a_0$, so $\eta_1 p r_2 = O(\eta_2)$.

Equations (3.36) and (3.37) permit us to write

$$\Upsilon(\vec{r}_2, \vec{R}_2) = \sum_n g_n'(\vec{r}_2)\, \Upsilon_n'(\vec{r}_2) , \tag{3.38}$$

where we now consider $\vec{r}_2$ and $\vec{R}_2$ as the independent variables. To the same order of accuracy, we, of course, have

$$\Upsilon_n' = \Upsilon_n , \tag{3.39}$$

but shall keep the prime superscript to indicate the change to the variable set $(\vec{r}_2, \vec{R}_2)$ in Υ.

On substituting the expansion (3.38) into Eq. (3.35), we obtain a set of coupled equations to determine the Υ_n'. The quantities Q_v are seen to vanish, since the condition (3.33) is automatically satisfied (to the order of the calculation by the expansion (3.38). The resulting equations are

$$(E + i\eta - K' - W_l')\, \Upsilon_l'(\vec{R}_2) - \sum_n v_{ln}(\vec{R}_2)\Upsilon_n'(\vec{R}_2) - \sum_b v_{lb}(\vec{R}_2)\, \Upsilon_b(\vec{R}_2) = 0 . \tag{3.40}$$

In deriving this result we have replaced $\vec{R}_1$ by $\vec{R}_2$ in the $v_{l\beta}$ and Υ_b, and made use of Eq. (3.39). The corresponding components of Eq. (3.21) for channel i are

$$(E + i\eta - K - W_b)\, \Upsilon_b(\vec{R}_1) - \sum_d v_{bd}(\vec{R}_1)\Upsilon_d(\vec{R}_1) - \sum_n v_{bn}(\vec{R}_1)\Upsilon_n'(\vec{R}_1) = i\eta\, \delta_{bo} \lambda_{\vec{p}}(\vec{R}_1) . \tag{3.41}$$

Equations (3.40) and (3.41) may be written in more compact form if we simply write $\vec{R}$ for $\vec{R}_2$ in the first, $\vec{R}$ for $\vec{R}_1$ in the second, and introduce

$$\Psi_l(\vec{R}) \equiv \Upsilon_l'(\vec{R}) \quad \text{in channel } f,$$

$$\Psi_b(\vec{R}) \equiv \Upsilon_b(\vec{R}) \quad \text{in channel } i ,$$

$$K_c \equiv K' \ \text{in } f, \quad W_{cl} \equiv W_l' \ \text{in } f, \quad \equiv K \ \text{in } i, \quad W_{cb} \equiv W_b \ \text{in } i . \tag{3.42}$$

Then, using Eq. (3.29), we may write both sets of equations in the form

$$[E + i\eta - K_c - W_{c\alpha} - v_\alpha(\vec{R})]\Psi_\alpha(\vec{R}) - \sum_\beta J_{\alpha\beta}(\vec{R}, \nabla_R)\Psi_\beta(\vec{R}) = i\eta\, \delta_{\alpha 0} \lambda_{\vec{p}}(\vec{R}) , \tag{3.43}$$

where for convenience we may again include the diagonal element $J_{\alpha\alpha}$ into the v_α.

Coherent states $\Psi_{c\alpha\vec{k}}^{\pm}$ may be defined as in Eq. (2.17)

$$(E + i\eta - K_c - W_{c\alpha} - v_\alpha)\Psi_{c\alpha\vec{k}}^{\pm} = \pm i\eta \lambda_{\vec{k}} . \tag{3.44}$$

With these we may write (3.43) as coupled integral equations

$$\Psi_\alpha = \delta_{\alpha 0}\Psi_{c0\vec{p}}{}^{+} + (E+i\eta - K_c - W_{c\alpha} - v_\alpha)^{-1} \times \sum_\beta J_{\alpha\beta}\Psi_\beta \,. \qquad (3.45)$$

These are generalizations, to include rearrangement, of Eqs. (2.18). The scattering matrix is seen to be, in the notation of Eq. (2.19),

$$\langle \alpha\vec{k} \mid T \mid 0\vec{p}\rangle = \delta_{\alpha 0}(\lambda_{\vec{k}}, v_0\Psi_{c0\vec{p}}{}^{+}) + \sum_\beta (\Psi_{c\alpha\vec{k}}{}^{-}, J_{\alpha\beta}\Psi_\beta) \,. \qquad (3.46)$$

The differential scattering cross section is again given by Eq. (2.20).

If we had not assumed η_2 to be small, equations of the form of (3.43) would still be obtained, but with modified interactions $J_{\alpha\beta}$. These more general equations are developed in Appendix B.

IV. THE EIKONAL APPROXIMATION

It is our purpose to explore the use of the eikonal approximation to the coherent states (3.44) for obtaining solutions to Eqs. (3.45). In this section we shall review those aspects of this approximation which will be needed. For a general presentation of the theory in a form applicable to nonlocal potentials, Weinberg's presentation is recommended.[10,11]

Following Weinberg,[10] we consider an equation of the form

$$D(\vec{R}, -i\nabla)\,\Psi = 0. \qquad (4.1)$$

Here $\nabla = \partial/\partial\vec{R}$, D is a differential operator, and Ψ a wave function. For later applications Ψ will be one of the solutions $\Psi_{c\alpha\vec{k}}{}^{\pm}$ of Eq. (3.44) – but to simplify notation in this section, we shall not carry all relevant sub- and superscripts. The form of D corresponding to Eqs. (3.44) is

$$D = \nabla^2 + k^2 - 2Mv(\vec{R}), \qquad (4.2)$$

with $k^2 = 2M(E - W_{c\alpha})$. In the approximation in which η_2 is small $v(\vec{R})$ is *local* – that is, does not depend upon ∇. To avoid a superficial complication in notation, we shall assume in this section that $v(\vec{R})$ is local. The extension to nonlocal v's is essentially trivial.[10]

In the first eikonal approximation, Ψ is written in the form

$$\Psi(\vec{R}) = e^{iS(\vec{R})}/(2\pi)^{3/2}, \qquad (4.3)$$

where S is real, and

$$D(\vec{R}, -i\nabla)\,\Psi \simeq D(\vec{R}, \vec{\kappa})\,\Psi = 0.$$

Here $\vec{\kappa}(\vec{R}) \equiv \nabla S(\vec{R})$ (4.4)

and it follows that

$$D(\vec{R}, \vec{\kappa}) = 0\,, \qquad (4.5a)$$

or [using Eq. (4.2)]

$$\kappa^2 = k^2 - 2Mv(\vec{R})\,. \qquad (4.5b)$$

[For a nonlocal v, $v(\vec{R})$ would be replaced by $v(\vec{R}, \vec{\kappa})$ in Eq. (4.5b).]

To complete the solution, trajectories are defined as functions of a parameter τ by the equations

$$\frac{d\vec{R}}{d\tau} = \frac{\partial D}{\partial\vec{\kappa}}, \quad \frac{d\vec{\kappa}}{d\tau} = -\frac{\partial D}{\partial\vec{R}}\,. \qquad (4.6)$$

[Hereafter, when we refer to "trajectories", we shall mean certain solutions of Eqs. (4.6).] Finally, the eikonal $S(\vec{R})$ is defined by the path integral along a trajectory through $\vec{R}$ as

$$S(\vec{R}) \equiv \int^{\vec{R}} \vec{\kappa}(\vec{x}) \cdot d\vec{x}\,. \qquad (4.7)$$

To construct the solution $\Psi_p{}^{+}$ we refer to Fig. 1a, where the trajectory of the scattered particle is illustrated. In the "prior region," ahead of the scattering region, the particle has the initial momentum $\vec{p}$. To define $\Psi_{\vec{p}}{}^{+} = \exp(iS^{+})$, we choose the constant of integration in (4.7) so that

$$S^{+}(\vec{R}) = \vec{p}\cdot\vec{R}$$

in the "prior region." To define $\Psi_{\vec{k}}{}^{-} = \exp(iS^{-})$, we refer to Fig. 1b and choose the constant of integration, so that

$$S^{-}(\vec{R}) = \vec{k}\cdot\vec{R}$$

in the "post region" – that is, the asymptotic re-

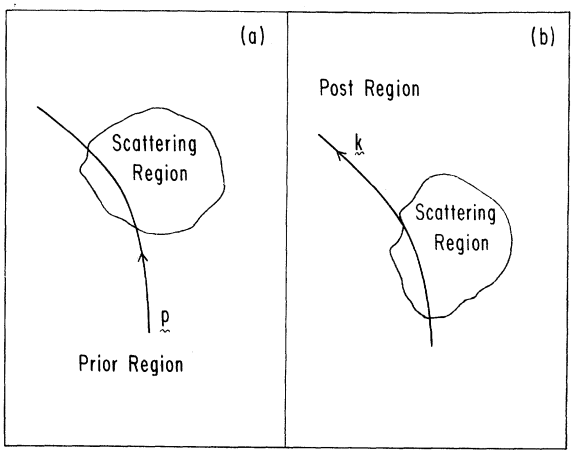

FIG. 1. Construction of $\Psi_p{}^{+}$ and $\Psi_k{}^{-}$.

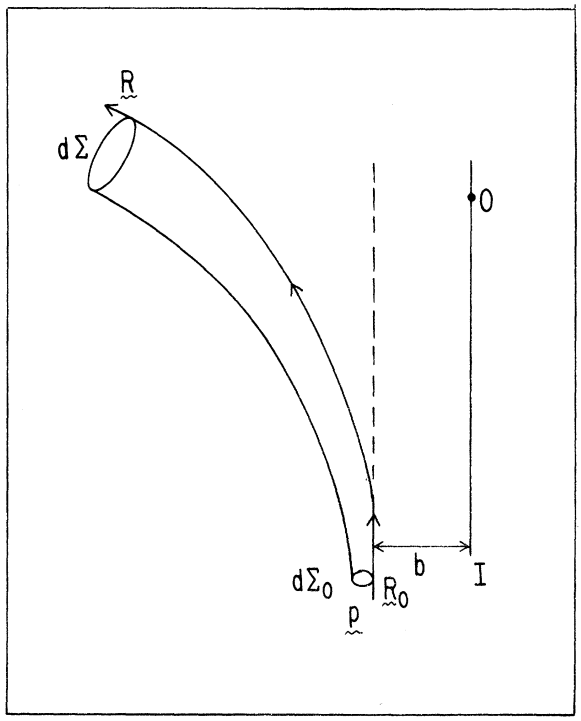

FIG. 2. Geometrical construction of the amplitude A of Eq. (4.9).

gion following the scattering.[12]

In the second eikonal approximation, we replace Eq. (4.3) by the expression

$$\Psi(\vec{R}) = (2\pi)^{-3/2} A(\vec{R})\, e^{iS(\vec{R})} , \tag{4.8}$$

where $|\nabla \ln A|$ is considered to be small compared with κ. We give now a geometrical definition of A (and later a more mathematical definition). Referring to Fig. 2, we choose a point $\vec{R}_0$ in the "prior region." The trajectory for a particle with momentum $\vec{p}$ passes through $\vec{R}_0$ with an impact parameter b, and later passes through a second point $\vec{R}$. [This refers to Ψ^+ – to construct Ψ^- we consider $\vec{p}$ to be the final momentum and $\vec{R}_0$ to lie in the "post region."] Let us imagine rotating $\vec{R}_0$ about the axis IO, parallel to $\vec{p}$ and passing through the force center, through the angle $d\phi$ and then increasing the impact parameter by an amount db. In this way a tube of trajectories is generated, having cross sectional area $d\Sigma_0 = d\phi\, b\, db$ and $d\Sigma(\vec{R})$ at points $\vec{R}_0$ and $\vec{R}$, respectively. The particle flux passing through this tube is

$$A^2(\kappa(\vec{R})/M) d\Sigma = (p/M) d\phi\, b\, db.$$

From this it is seen that

$$A(\vec{R}) = \left[\frac{p}{\kappa(\vec{R})} \left(\frac{d\Sigma}{d\phi\, b\, db} \right)^{-1} \right]^{1/2} . \tag{4.9}$$

The magnitude of the scattering amplitude $f(\theta)$ corresponding to a scattering angle θ is

$$|f| = \lim_{\vec{R}\to\infty} R A(\vec{R}) ,$$

for $\vec{R}$ in the "post region" on a given trajectory. In this asymptotic region $d\Sigma = d\phi R^2 \sin\theta\, d\theta$, so

$$|f| = (b db / \sin\theta\, d\theta)^{1/2} . \tag{4.10}$$

The scattering cross section is given by the usual classical formula

$$d\sigma/d\Omega = b db / \sin\theta\, d\theta . \tag{4.11}$$

In anticipation of our intended applications, it is instructive to repeat the calculation of the scattering amplitude (4.10) from the expression

$$T_{\vec{k}\vec{p}} = (\lambda_{\vec{k}}, v\, \psi_{\vec{p}}^{+}) = (2\pi)^{-3} \int d^3R\, v(\vec{R}) A(\vec{R}) e^{i[S(\vec{R}) - \vec{k}\cdot\vec{R}]} , \tag{4.12}$$

for the scattering matrix $T_{\vec{k}\vec{p}} = -[(2\pi)^2 M]^{-1} f$. The expression (4.12) represents, of course, just the first term in Eq. (3.46).

We evaluate the integral above in an approximation consistent with the eikonal approximation. As a first step we suppose that the family of trajectories [solutions to Eqs. (4.6)] have been constructed which correspond to an incident momentum $\vec{p}$. A given trajectory is picked and a point $\vec{R}_0$ at which k is tangent to this trajectory is located. [If there is no such point, another trajectory is chosen. If there are no such trajectories then $T_{\vec{k}\vec{p}}$ vanishes in the classical approximation.] A plane P with normal $\hat{k}$ is passed through $\vec{R}_0$. The surface S of constant eikonal, defined by $S(\vec{R}) = S(\vec{R}_0)$ is tangent to P at $\vec{R}_0$. This is illustrated in Fig. 3.

Let $\vec{l}$ be a vector from $\vec{R}_0$ to $\vec{R}$, a neighboring point in P. The distance h from $\vec{R}$ to the surface S is then

$$h = \tfrac{1}{2} \left(\frac{l_1^2}{R_1} + \frac{l_2^2}{R_2} \right) \left[1 + O\left(\frac{l^2}{R_2} \right) \right] . \tag{4.13}$$

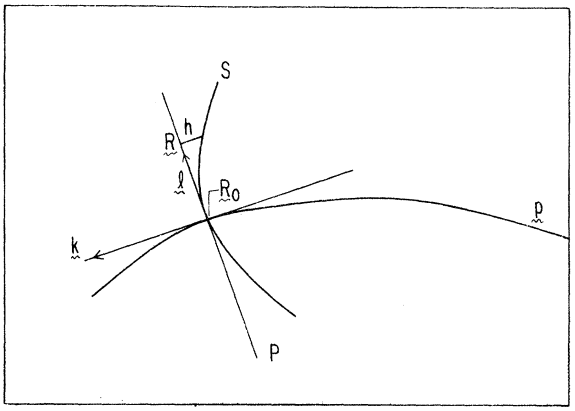

FIG. 3. Diagram of coordinates pertinent to the evaluation of Eq. (4.16).

Here $\mathcal{R}_1$ and $\mathcal{R}_2$ are the principal radii of curvature of S at $\vec{R}_0$, and l_1 and l_2 are the components of $\vec{l}$ referred to the principal axes of curvature. We have indicated the order of magnitude of the error in (4.13) by letting $\mathcal{R}$ represent an effective radius of curvature.

Now,

$$S(\vec{R}) = S(\vec{R}_0) + \kappa(\vec{R}_0)h + O\left(\frac{\partial\kappa}{\partial s}h^2\right) , \tag{4.14}$$

where s denotes path length along the trajectory. When

$$\eta(h) \equiv l^2/\mathcal{R}^2 \ll 1,$$

$$\eta(S) \equiv |\partial\kappa/\partial s|\, h^2 \ll 1, \tag{4.15}$$

the integral over $\vec{l}$ is elementary

$$L(\vec{R}_0) \equiv \int d^2l\ e^{i\kappa h} = \frac{2\pi}{\kappa(\vec{R}_0)}\,(|\mathcal{R}_1\mathcal{R}_2|)^{1/2}$$

$$\times \exp\left[i\frac{\pi}{4}\left(\frac{\mathcal{R}_1}{|\mathcal{R}_1|} + \frac{\mathcal{R}_2}{|\mathcal{R}_2|}\right)\right] \tag{4.16}$$

Thus

$$T_{\vec{k}\vec{p}} \cong (2\pi)^{-3} \int ds\ L(\vec{R}_0)v(\vec{R}_0) \times A(\vec{R}_0)e^{i\Phi(s)} \tag{4.17}$$

where $$\Phi(s) = S(\vec{R}_0) - \vec{k}\cdot\vec{R}_0 , \tag{4.18}$$

and the integral is along a path parallel to $\vec{k}$ and tangent to a sequence of trajectories. In obtaining (4.17), we have replaced $v(\vec{R})\,A(\vec{R})$ by $v(\vec{R}_0)\,A(\vec{R}_0)$. This is valid when

$$\eta(l) \equiv (l/a_0)^2 \ll 1. \tag{4.19}$$

The principal contribution to the integral (4.17) comes from points where the scattering is almost completed (entrance to the "post region") and $v(\vec{R}_0)$ is *small*, since otherwise $\Phi(s)$ oscillates rapidly. Then, since $k = p$,

$$\Phi(s) = \int ds\,(\kappa - p) = \int ds\,(\kappa^2 - p^2)/(\kappa + p) \simeq -(M/p)\int ds\, v(\vec{R}_0) . \tag{4.20}$$

In this near-asymptotic domain we have

$$L(\vec{R}_0) = 2\pi i R_0/\kappa(\vec{R}_0)$$

and $R_0A(R_0) = f$[Eq. (4.10)], both to within neglected phase factors. Thus, using (4.20) we can write (4.17) as

$$T_{\vec{k}\vec{p}} = -[if/(2\pi)^2M]\int d\Phi\, e^{i\Phi} = -[1/(2\pi)^2M]f + \text{oscillating terms.} \tag{4.21}$$

The "oscillating terms" do not contribute to a cross section averaged over an appropriate "small" solid angle. The phase factors neglected in deriving (4.21) can, of course, be expressed in terms of the asymptotic value of the eikonal, if desired. The derivation of Eq. (4.21) required the validity of conditions (4.15) and (4.19). To investigate these we make the following characteristic and order-of-magnitude estimates:

$$\theta \approx a_0/\mathcal{R} \approx v/\epsilon \approx 1\ \text{Ry}/\epsilon,$$

$$h \approx 1/p, \quad l^2 \approx \mathcal{R}^2/p.$$

Here θ is the scattering angle. With these we obtain [using the notation of expressions (1.1)–(1.4)]

$$\eta(h) \approx \eta_3\,\eta_4 \ll 1 ,$$

$$\eta(S) \approx \eta_3\,\eta_4 \ll 1 ,$$

$$\eta(l) \approx \eta_3/\eta_4 \ll 1. \tag{4.22}$$

The validity of the first two conditions follows directly from (1.3) and (1.4). The third condition here requires also (1.2). Since the angle of *diffraction* scattering is $\theta_d \approx \hbar/p\ a_0$, the third condition above is equivalent to the familiar one that $\theta_d \ll \theta$ if classical scattering theory is applicable.

In addition to the wave functions (3.44), we require also the eikonal approximation to the Green's functions

$$G_\alpha^{+} = (E + i\eta - K_c - W_{c\alpha} - v_\alpha)^{-1}. \tag{4.23}$$

On dropping the α index and using the notation of Eq. (4.2), we see that the Green's function (4.23) satisfies the equation[13]

$$[\nabla^2 + k^2 - 2Mv(\vec{R})]\langle\vec{R}|G^{+}|\vec{R}'\rangle = 2M\delta(\vec{R} - \vec{R}') . \tag{4.24}$$

Since this is the same as the equation satisfied by Ψ, except at $\vec{R} = \vec{R}'$, it is evident that G^{+} will have the form (4.8):

$$\langle\vec{R}|G^{+}|\vec{R}'\rangle = Ae^{iS(\vec{R},\vec{R}')} = \langle\vec{R}'|G^{+}|\vec{R}\rangle , \tag{4.25}$$

where

$$S(\vec{R},\ \vec{R}') = \int_{\vec{R}'}^{\vec{R}} \vec{\kappa}(\vec{x})\cdot d\vec{x} \tag{4.26}$$

and the path of integration runs over that trajectory which passes through $\vec{R}'$ and $\vec{R}$. To determine A we first observe that for $\vec{R} \simeq \vec{R}'$ G^{+} has the familiar form

$$G^{+} \simeq -(M/2\pi)/|\vec{R} - \vec{R}'| . \tag{4.27}$$

Now let us consider a bundle of trajectories passing through $\vec{R}'$ lying within the solid angle $\delta\Omega$ and enclos-

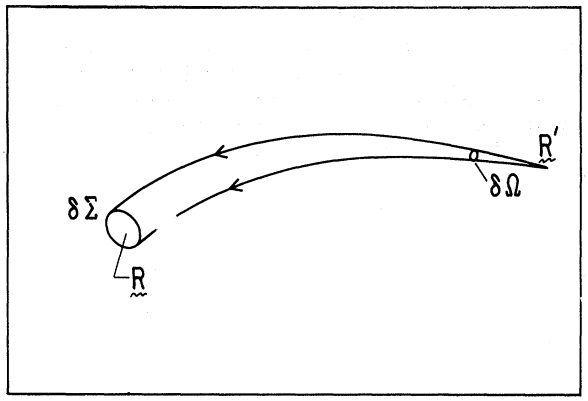

FIG. 4. Construction of the Green's function [Eqs. (4.25) and (4.28)].

ing the point $\vec{R}$. This is illustrated in Fig. (4). The cross sectional area of this bundle at $\vec{R}$ is $\delta\Sigma$. We can think of a flux of particles passing through the tube formed by this bundle; it is

$$A^2 \frac{\kappa(\vec{R})}{M}\delta\Sigma = \left(\frac{M}{2\pi}\right)^2 \frac{\kappa(\vec{R}')}{M}\delta\Omega ,$$

where we have used (4.27) near $\vec{R}'$. From this we obtain A as

$$A = -\frac{M}{2\pi}\left[\frac{\kappa(\vec{R}')}{\kappa(\vec{R})}\left(\frac{\partial\Sigma}{\partial\Omega}\right)^{-1}\right]^{1/2} \tag{4.28}$$

[The reader who desires practice in handling eikonal phases may wish to show that Eqs. (4.8) and (4.25) are consistent with the equation

$$\Psi_{\vec{k}}^{+}(\vec{R}) = \lambda_{\vec{k}}(\vec{R}) + \int d^3R' \ \langle \vec{R}|G^{+}|\vec{R}'\rangle \lambda_{\vec{k}}(\vec{R}') \ .]$$

Another form of Eq. (4.28) may be derived directly from the differential equation (4.24). Referring to Fig. (5), let us choose a point $\vec{R}$ on a surface S = constant. The trajectory through $\vec{R}$ has a tangent $\hat{e}_3$ which is, of course, normal to S at $\vec{R}$. Let $\hat{e}_1$ and $\hat{e}_2$ be two unit vectors lying in S and directed along the principal axes of curvature, so

$$\frac{\partial\hat{e}_3}{\partial x_1} = \frac{\hat{e}_1}{\mathcal{R}_1}, \quad \frac{\partial\hat{e}_3}{\partial x_2} = \frac{\hat{e}_2}{\mathcal{R}_2} , \tag{4.29}$$

where x_1, x_2, and x_3 are distances along the three axes.

Since $\nabla S = \hat{e}_3\kappa$, we obtain

$$\nabla^2 e^{iS} = \nabla\cdot(\hat{e}_3\,\partial/\partial x_3)\, e^{iS}$$

$$= e^{iS}\left[(1/\mathcal{R}_1 + 1/\mathcal{R}_2)\, i\kappa - \kappa^2 + i\,\partial\kappa/\partial x_3\right] , \tag{4.30}$$

using (4.29). Thus, insertion of the expression (4.25) into (4.24) gives

$$(\Delta^2 + k^2 - v)G = e^{iS}\{[k^2 - 2M\mathcal{U}(\vec{R}) + (1/\mathcal{R}_1 + 1/\mathcal{R}_2)\, i\kappa - \kappa^2 + i\,\partial\kappa/\partial x_3]A + 2i\kappa\,\partial A/\partial x_3 + \nabla^2 A\} = 0, \tag{4.31}$$

except at $\vec{R} = \vec{R}'$. The first-order equation is, of course,

$$\kappa^2 = \kappa^2 - 2M\mathcal{U}(\vec{R}) \ . \tag{4.32}$$

The second-order equation is obtained by neglecting $\nabla^2 A$ in (4.31), which is smaller than the other terms by a factor of order η_3 [Eq. (1.3)]. The resulting equation is

$$\frac{\partial \ln A}{\partial x_3} + \frac{\partial \ln \kappa^{1/2}}{\partial x_3} = -\frac{1}{2}\left(\frac{1}{\mathcal{R}_1} + \frac{1}{\mathcal{R}_2}\right) , \tag{4.33}$$

or

$$A = \frac{C}{[\kappa(\vec{R})]^{1/2}} \exp\left[-\frac{1}{2}\int^{\vec{R}}\left(\frac{1}{\mathcal{R}_1} + \frac{1}{\mathcal{R}_2}\right) dx_3\right], \tag{4.34}$$

where C is a constant. With an appropriate choice of constants this expression applies to either (4.9) or (4.28).

For the wave function (4.8), the above expression is evidently

$$A = \left(\frac{k}{\kappa(\vec{R})}\right)^{1/2} \exp\left[-\frac{1}{2}\left(\frac{1}{\mathcal{R}_1} + \frac{1}{\mathcal{R}_2}\right)\int_{-\infty}^{\vec{R}} dx_3\right]. \tag{4.35}$$

Since $\mathcal{R}_1 = \mathcal{R}_2 = \infty$ in the "prior region" of Fig. 1a, this expression gives $A = 1$ for the incoming wave. For the Green's function we take the origin of x_3 to be at $\vec{R}'$ and note that when $\vec{R} \simeq \vec{R}$, $\mathcal{R}_1 \simeq \mathcal{R}_2 \simeq |\vec{R} - \vec{R}'|$. A convenient lower limit for the integral is then some very small distance δ from $\vec{R}'$ and the choice

$$C = -(M/2\pi)[\kappa(\vec{R}')]^{1/2}/\delta \ . \tag{4.36}$$

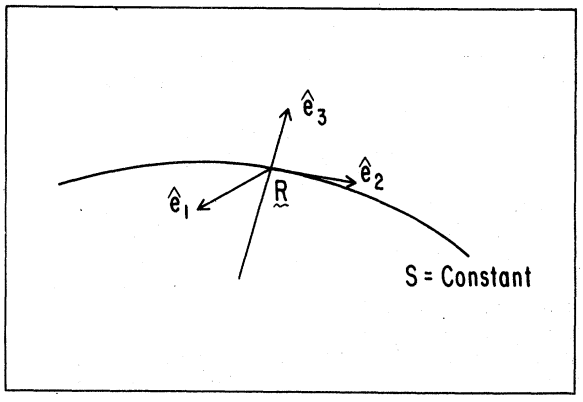

FIG. 5. Illustration of the unit vectors used in Eqs. (4.29) and (4.30).

V. EVALUATION OF MATRIX ELEMENTS

The process of obtaining solutions to Eq. (3.45) and also of evaluating the second term of Eq. (3.46) leads us to calculate matrix elements of the form

$$M=\int \Psi_{c\alpha\vec{k}}^{-}(\vec{R})J_{\alpha\beta}(\vec{R},\ -i\nabla) \times \Psi_{c\beta\vec{p}}^{+}(\vec{R})\,d^3R\ , \quad (5.1a)$$

$$M'=\int \langle \vec{R}|G_{\alpha}\dagger|\vec{R}\rangle J_{\alpha\beta}(\vec{R},\ -i\nabla) \times \Psi_{c\beta\vec{p}}^{+}(\vec{R})d^3R, \quad (5.1b)$$

etc. In this section we shall show that the assumed smallness of the η parameters [Eqs. (1.1)–(1.5)] lets us simplify these matrix elements. The argument is essentially that used in evaluating the integral (4.12).

First, we have

$$J_{\alpha\beta}(R,\ -i\nabla)\Psi_{c\beta\vec{p}}^{+}(\vec{R}) =J_{\alpha\beta}(\vec{R},\vec{\kappa}_p(\vec{R}))\Psi_{c\beta\vec{p}}^{+}\ , \quad (5.2)$$

if we neglect terms of relative order η_3. Here $\vec{\kappa}_p(\vec{R})$ is the momentum obtained from the eikonal S_p^{+} of $\Psi_{c\beta\vec{p}}^{+}$,

$$\vec{\kappa}_p(\vec{R})=\nabla S_p^{+}(\vec{R})\,. \quad (5.3)$$

Then, using Eq. (4.8) etc., we have to consider integrals of the form

$$M=(2\pi)^{-3}\int d^3R\,A_p(\vec{R})A_k(\vec{R})J(\vec{R}) \times \exp i[S_p^{+}(\vec{R})-S_k^{-}(\vec{R})] \quad (5.4)$$

etc., where

$$J(\vec{R})\equiv J(\vec{R},\vec{\kappa}_p(\vec{R}))$$

and we have dropped the α, β indices. We shall discuss only (5.4) explicitly, since the evaluation of (5.1b), etc., is similar.

For each point $\vec{R}$ in the integrand of (5.4) we must consider two trajectories which pass through this point. One has the incident momentum $\vec{p}$ and the other the final momentum $\vec{k}$ (and now we do not, in general, have $k=p$, because of the change of atomic states). As was done in the evaluation of (4.12), let us suppose $\vec{R}$ is in the neighborhood of a point $\vec{R}_0$ at which the two trajectories of the $\vec{R}_0$ pair are tangent. Next, we construct a plane P passing through $\vec{R}_0$ and normal to the trajectories at this point. We then let $\vec{R}=\vec{l}+\vec{R}_0$, where l is a vector in P, and write

$$d^3R=d^2l\,ds,$$

where ds is an element of path along the two trajectories passing through $\vec{R}_0$. This is illustrated in Fig. 6. The two constant eikonal surfaces, $S_p^{+}=S_p^{+}(\vec{R}_0)$ and $S_k^{-}=S_k^{-}(\vec{R}_0)$, pass through $\vec{R}_0$ and are tangent to the plane P at this point.

For small l we can then write

$$S_p^{+}(\vec{R})-S_k^{-}(\vec{R})\simeq\Phi(s) + \sum_{i<j=1}^{2}\alpha_{ij}(\vec{R}_0)l_i l_j, \quad (5.5)$$

where

$$\Phi(s)\equiv S_p^{+}(\vec{R}_0)-S_k^{-}(\vec{R}_0) \quad (5.6)$$

and l_1 and l_2 are Cartesian components of $\vec{l}$. When the parameters (4.15) and (4.19) are small, we may neglect higher-order terms in (5.5), and replace $\vec{R}$ by $\vec{R}_0$ in A_p, A_k, and J in the integrand of (5.4). The integral over $\vec{l}$ is elementary and we are left with just the one-dimensional path integral over s.

We may illustrate this in detail for the special case that the potentials $v_\alpha(\vec{R})$ are spherically symmetric. Then (except for possible singular interactions) the two trajectories at $\vec{R}_0$ both lie in the scattering plane of the vectors $\vec{k}$ and $\vec{p}$. The principal axes for both eikonal surfaces then lie in and perpendicular to the scattering plane. On choosing these to be the coordinate axes in Eq. (5.5), we have $\alpha_{12}=0$ and

$$\alpha_{11}=\tfrac{1}{2}[\kappa_p/\mathcal{R}_1(p)-\kappa_k/\mathcal{R}_1(k)]\,,$$

$$\alpha_{22}=\tfrac{1}{2}[\kappa_p/\mathcal{R}_2(p)-\kappa_k/\mathcal{R}_2(k)]\ . \quad (5.7)$$

Here $\vec{\kappa}_p=\nabla S_p^{+}$, etc., and $\mathcal{R}_j(p)$ $(j=1, 2)$ is a principal radius of curvature of S_p^{+} at $\vec{R}_0$, etc.

The approximate expression (5.5) then lets us write

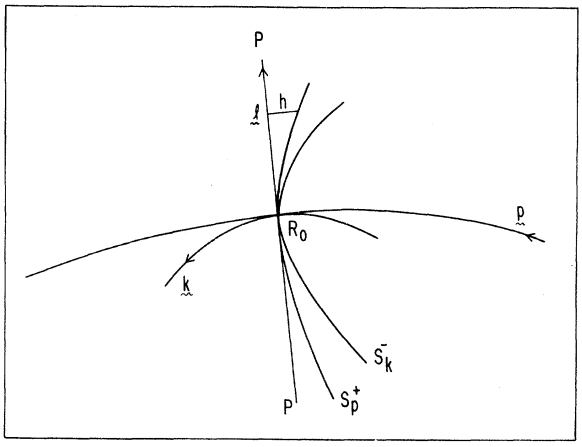

FIG. 6. Illustration of the eikonal surfaces and trajectories for the integral [Eq. (5.8)].

$$\int d^2l \exp i[S_p{}^+(\vec{R}) - S_k{}^-(\vec{R})]$$

$$\cong e^{i\Phi(s)}(\pm 2\pi i)/(|\alpha_{11}||\alpha_{22}|)^{1/2}; \quad (5.8)$$

where $(\pm) = (\text{sign of } \alpha_{11}) \times (\text{sign of } \alpha_{22})$. If we can neglect quantities of the order of the small parameter $\eta(h)$, $\eta(S)$, and $\eta(l)$ [conditions (4.15) and (4.19)], we then have

$$M = \frac{\pm i}{(2\pi)^2} \int ds \left(\frac{A_p(\vec{R}_0) A_k(\vec{R}_0) J(\vec{R}_0)}{|\alpha_{11}\alpha_{22}|^{1/2}} \right) e^{i\Phi(s)}. \quad (5.9)$$

It was pointed out in Ref. 1 that under some circumstances a saddle point or stationary phase approximation may provide an explicit expression for (5.9). An example discussed was the curve-crossing model which gives the Landau-Zener expression for near-adiabatic transitions.

Having shown how to reduce the evaluation of matrix elements such as (5.1) to path integrals along trajectories, we have completed our task of formally exploiting the classical limit for heavy-particle motion in calculating electronic transitions. To carry the analysis further, one must in general obtain the particle trajectories in order to actually evaluate the path integrals. Also, of course, the residual real quantum-mechanical aspects of the phenomena are to be found in the evaluation of (3.45) and the interactions $J_{\alpha\beta}$ and $\mathcal{V}_\alpha$. In paper II of this series we shall illustrate the methods developed here with some specific applications.

APPENDIX A: ADIABATIC INCOMING STATES

We now demonstrate the equivalence of Eq. (2.13) and the conventional scattering equation

$$(E + i\eta - H)\bar{\psi}_a{}^+ = i\eta\bar{\chi}_a, \quad (A.1)$$

where $\bar{\chi}_a \equiv g_0 \lambda_{\vec{p}}(\vec{R})$. (A.2)

If we subtract (A.1) from (2.13), there results the equation

$$(E + i\eta - H)\delta\psi = i\eta\delta\chi, \quad (A.3)$$

where $\delta\psi \equiv \psi_a{}^+ - \bar{\psi}_a{}^+$,

$$\delta x \equiv \chi_a - \bar{\chi}_a = \lambda_p(\varphi_0 - g_0).$$

Since $\varphi_0 \to g_0$ when $R \to \infty$, it is reasonable to suppose that $(\delta_\chi, \delta_\chi)$ is *finite*. The "solution" of Eq. (A.3) is

$$\delta\psi = i\eta G\delta\chi, \quad (A.4)$$

where $G = 1/(E + i\eta - H)$.

Now,

$$(\delta\psi, \delta\psi) = (i\eta)(-i\eta)(\delta\chi, G^\dagger G\delta\chi)$$

$$= -\frac{i\eta}{2}\left(\delta\chi, \left(\frac{1}{E - H - i\eta} - \frac{1}{E - H + i\eta}\right)\delta\chi\right)$$

$$= \eta\pi(\delta\chi, \delta(E - H)\delta\chi). \quad (A.5)$$

If we let ψ_λ and E_λ represent a complete set of eigenfunctions and eigenvalues of H, we may write (A5) in the form

$$(\delta\psi, \delta\psi) = \eta\pi \sum_\lambda \delta(E - E_\lambda)|(\delta\chi, \psi_\lambda)|^2,$$

where $\sum_\lambda = \int dE_\lambda \int d\rho_\lambda$,

and $d\rho_\lambda$ is the density of states per unit energy interval.

If $E_{\lambda_0} = E$, we have

$$(\delta\psi, \delta\psi) = \eta\pi \int d\rho_{\lambda_0} |(\delta\chi, \psi_{\lambda_0})|^2. \quad (A.6)$$

However,

$$\int dE_\lambda \int d\rho_\lambda |(\delta\chi, \psi_\lambda)|^2 = (\delta\chi, \delta\chi) < \infty,$$

by hypothesis. The integral

$$\int d\rho_{\lambda_0} |(\delta\chi, \psi_{\lambda_0})|^2$$

must therefore be finite, except for possible isolated singular values of E. (In any energy interval we can avoid such possible singularities.) It follows then from Eq. (A.6) that

$$\lim_{\eta \to O(+)} (\delta\psi, \delta\psi) = 0,$$

or $\delta\psi$ converges strongly to zero.

APPENDIX B. SCATTERING WHEN η_2 IS NOT SMALL

Since we are considering only bound electron states in channels i and f and since η_1 is a small quantity in any case, we again have Eqs. (3.36) and (3.38) as valid approximations. This means that the $\mathcal{Q}_b$ in Eq. (3.35) again vanish.

Now, according to Eqs. (3.11), we have in the eikonal approximation[14]

$$\Upsilon_n'(\vec{R}_2) = e^{-i(m/M)\vec{\kappa}_n(\vec{R}_2)\cdot\vec{r}_2} \times \Upsilon_n'\{[(M_1 + m)/M_1]\vec{R}_1\}, \quad (B.1)$$

where $\vec{\kappa}_n(\vec{R}_2)$ is the local momentum at $\vec{R}_2$. From Eqs. (3.31) and (3.38) we have

$$\Upsilon_n(\vec{R}_1) = \sum_l \alpha_{nl} \Upsilon_l'\{[(M_1 + m)/M_1]\vec{R}_1\}, \quad (B.2)$$

where $\alpha_{nl} \equiv \int_{\vec{R}_1} d\mathcal{S} d^3r_2 \, g_n{}^*(\vec{r}_2) g_l(\vec{r}_2) \times e^{-i(m/M)\vec{\kappa}_l\cdot\vec{r}_2}$ (B.3)

and the notation of Eq. (3.23) has been used.

On inserting the expansion (3.38) into Eq. (3.35), we obtain

$$(E+i\eta-K'-W_l')\Upsilon_l'(\vec{R}_2) - \sum_{n,\beta}\int_{\vec{R}_2} d\mathcal{E}\, d^3r_2\, g_l^*(\vec{r}_2) g_n(\vec{r}_2) \times v_{n\beta}(\vec{R}_2)\Upsilon_\beta(\vec{R}_1)=0, \quad \text{(B.4)}$$

where we have set $v_{n\beta}(\vec{R}_1)=v_{n\beta}(\vec{R}_2)$, valid to lowest order in η_1. Using a relation analogous to (B.1), we obtain

$$(E+i\eta-K'-W_l')\Upsilon_l'(\vec{R}_2) - \sum_{n,\beta}\alpha_{ln}(\beta)v_{n\beta}(\vec{R}_2) \times \Upsilon_\beta\{[M_1/(M_1+m)]\vec{R}_2\}=0, \quad \text{(B.5)}$$

where $\alpha_{ln}(\beta)\equiv\int_{\vec{R}_2} d\mathcal{E}\, d^3r_2\, g_l(\vec{r}_2)g_n(\vec{r}_2) \times e^{i(m/M)\vec{\kappa}_\beta(\vec{R}_2)\cdot\vec{r}_2}$. (B.6)

Because of (B.2), we have

$$[E+i\eta-K'-W_l']\Upsilon_l'(\vec{R}_2) - \sum_n \mathcal{J}_{ln}(\vec{R}_2)\Upsilon_n'(\vec{R}_2) - \sum_b \mathcal{J}_{lb}(\vec{R}_2)\Upsilon_b\{[M_1/(M_1+m)]\vec{R}_2\}=0, \quad \text{(B.5')}$$

where $\mathcal{J}_{ln}(\vec{R}_2)\equiv\sum_{q,t}\alpha_{lq}(t)v_{qt}(\vec{R}_2)\alpha_{tn}$,

$$\mathcal{J}_{lb}(\vec{R}_2)\equiv\sum_q\alpha_{lq}(b)v_{qb}(\vec{R}_2) \quad \text{(B.6')}$$

and the sums run over the states in channel f. The corresponding form of Eqs. (3.41) are

$$(E+i\eta-K-W_b)\Upsilon_b(\vec{R}_1)-\sum_d\mathcal{J}_{bd}(\vec{R}_1)\Upsilon_d(\vec{R}_1) - \sum_n\mathcal{J}_{bn}(\vec{R}_1)\Upsilon_n'\{[(M_1+m)/M_1]\vec{R}_1\} = i\eta\delta_{b0}\lambda_{\vec{p}}(\vec{R}_1), \quad \text{(B.7)}$$

where $\mathcal{J}_{bn}(\vec{R}_1)=\sum_l v_{bl}(\vec{R}_1)\alpha_{ln}$,

$$\mathcal{J}_{bd}=v_{bd}. \quad \text{(B.8)}$$

On introducing a *scattering potential* $\bar{v}_\alpha(=\mathcal{J}_{nn}$ for α in f and $=\mathcal{J}_{bb}$ for α in i), we see that Eqs. (B.5) and (B.7) have the same structure as Eq. (3.43).

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[1]A preliminary discussion of some applications of the eikonal approximation to electronic transitions in atomic collision has been given by K. M. Watson, in Properties of Matter under Unusual Conditions, edited by Hans Mark (John Wiley & Sons, Inc., New York, 1968).

[2]D. R. Bates and R. McCarroll, Proc. Roy. Soc. (London) A245, 175 (1958).

[3]M. H. Mittleman, Phys. Rev. 122, 499 (1961).

[4]W. R. Thorson, J. Chem. Phys. 42, 3878 (1965).

[5]The usual form for Eq. (2.13) would replace the expression (2.10) by $\chi_a=g_0\,\lambda_{\vec{p}}$. We show in Appendix A that both forms of χ_a yield the same wave function ψ_a^+.

[6]We shall generally follow the notation of M. L. Goldberger and K. M. Watson, Collision Theory (John Wiley & Sons, New York, 1964).

[7]The formal theory of multichannel scattering is described in Ref. 6, Chaps. 4 and 5.

[8]In Appendix B we give the modified form of the scattering equations when η_2 is unrestricted.

[9]The explicit form for the Υ_n's will be seen in the next two sections, where the eikonal approximation is applied to the calculation of these.

[10]S. Weinberg, Phys. Rev. 126, 1899 (1962).

[11]See also, H. M. Van Horn and E. E. Salpeter, Phys. Rev. 157, 751 (1967).

[12]A more detailed discussion of the $\psi^\pm$ boundary conditions in the eikonal approximation was given in Ref. 1.

[13]See, for example, Chap. 6 of Ref. 6.

[14]Equation (B.1) follows from the eikonal relation $S(\vec{R}+\vec{r})=S(\vec{R})+\vec{\kappa}(\vec{R})\cdot\vec{r}$ valid for small r.