ATOMIC COLLISIONS
OF LOW RELATIVE VELOCITY

Thesis by

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ABSTRACT

Approximate solutions for the excitation of an atom by a colliding charged particle, developed as perturbations of the state of the system at infinite or asymptotic separation of atom and particle and also as perturbations of the state of the system at vanishing velocity of relative motion, are extended, in the impact parameter form (suitable to collision of heavy particles), to include the interaction of states that are degenerate at asymptotic separation, and to obtain thereby a condition for the Born approximation that depends on the phase relations of degenerate states in the collision and excludes the low velocity region to the Born approximation, except for the excitation of S states. This is a correction of previous theories, which conclude that the Born solution is a general approximation at low velocities for weak interactions.

A low velocity perturbation solution is established in terms of the stationary states of the system and developed to show that, at sufficiently low velocity of relative motion, the atomic states are coupled to the moving particle in the range of interaction. Differences in coupling energy affect the coherence of asymptotically-degenerate states in the collision and influence the orientations of final excited states.

1. Introduction.

At low velocities of collision, the electronic state of an atom is considerably altered by the presence of the colliding charged system or particle and becomes the very slowly changing state associated with a nearly stationary incident charge as the velocity approaches zero. These stationary states are appropriate bases for a perturbation theory of the collision and excitation of atoms for low relative velocity.

Two supplementary theories of collision have been developed in terms of stationary states: one by Mott[1] in the approximate impact parameter form where the relative state of motion is assumed to be constant; and the other by Mott and Massey[2] in the form of scattered wave motions. Both developments conclude that, for weak interaction, the approximate or perturbation solutions at low velocities become the familiar Born approximation of the high velocity region. Applications of the theories to specific collisions have been made by Frame[3] in the Mott impact parameter form, which is appropriate to the collision of heavy particles, and by Massey and Smith[4] in the complete scattering form.

Neither the theories nor applications develop the properties of the stationary states on which they are based, and in consequence, are not complete and contain errors. The conclusion that the Born approximation appears for weak interaction is, in general, incorrect.

The purpose of the thesis is to make a more exhaustive analysis of the low velocity collision, to establish the important coupling property of stationary states at low velocities, and to show that, except for S state excitations, the Born approximation is limited by a velocity effect and does not appear for weak interactions at low velocities.

For this study, the collision is taken to occur between an atom and a charged particle with a spherically symmetric field.

The Hamiltonian of the equation of motion may be separated into three parts representing the energy of relative motion, the energy of the atomic state, and the energy of interaction. Eigenfuntions of the first Hamiltonian operator are plane waves, and of the second operator are asymptotic states of the atom at asymptotic or infinite separation of atom and particle. Eigenfunctions of the second and third operators are stationary atomic states which appear at vanishing velocity of the relative motion of atom and particle. Both asymptotic state and stationary state functions form complete sets for the electronic variables of the atom, and the collision may be described in terms of each set.

In the development of the theory, the collision is first described in the impact parameter form in which the state of relative motion is assumed constant and the equation of motion reduces to an equation for the electronic state of the atom under the influence of a moving charge. In this form, a perturbation solution is developed in terms of asymptotic states in order to establish a velocity-dependent condition of validity and to obtain approximate forms of solution (elaborations of the Born expression) comparable to the stationary state forms. The equation of motion is then developed in terms of stationary states to obtain approximate solutions for low velocities and, in addition, for weak interactions for comparison with the asymptotic state forms.

A perturbation solution is next developed for the complete equation of motion in terms of stationary states with associated wave functions of relative action.

In the following arrangement of the theory, the general forms of the equation of motion together with the approximate solutions for the excitation of S states are well-known expressions. The special place of the S state excitation and the developments which concern the excitation of non-S states at low velocities may be considered the contribution of the thesis.

2. The equation of motion

The solution of the collision and excitation problem is the solution of the quantum mechanical equation

$$(H_r + H_a + V)\,\Psi = i\hbar \frac{\partial}{\partial t}\,\Psi \qquad (1)$$

where the terms of the Hamiltonian are grouped to form parts representing the atomic state $H_a(\vec{r}_a)$, the state of relative motion of atom and incident particle $H_r(\vec{r})$ in a center of mass system, and their interaction $V(\vec{r},\vec{r}_a)$, and where the wave function $\Psi(\vec{r},\vec{r}_a,t)$ for the system of particles satisfies the boundary condition of associating a plane-wave relative motion with the initial ground state of the atom at asymptotic separation of atom and particle, where $V(\vec{r},\vec{r}_a) \to 0$.

3. The approximate equations of motion in the impact parameter form

Writing the solution of (1) in the form

$$\Psi = f(\vec{r},\vec{r}_a) e^{ik_0 z} e^{-i\frac{E}{\hbar}t} \tag{2}$$

where the plane wave $e^{ik_0 z}$ is the initial state of relative motion and E is the total energy, the equation (1) takes the form

$$\left(-\frac{\hbar^2}{2M}\nabla_r^2 + H_a + V\right) f = \left(E_0 + i\hbar v_0 \frac{\partial}{\partial z}\right) f(\vec{r},\vec{r}_a) \tag{3}$$

where $E_0 = E - \frac{\hbar k_0^2}{2M}$ is the energy of the initial ground state. If the reduced mass M is taken to be arbitrarily large such that the term $\frac{\hbar^2}{2M}\nabla_r^2 f$ is relatively negligible, an assumption that does not violate the boundary conditions, the equation (3) may be written in the approximate form

$$(H_a + V)\left(f e^{-i\frac{E}{\hbar v}z}\right) = i\hbar v_0 \frac{\partial}{\partial z}\left(f e^{-i\frac{E}{\hbar v}z}\right)$$

or, writing

$$\Psi(\vec{r},\vec{r}_a) = f(\vec{r},\vec{r}_a)\, e^{-i\frac{E_0}{\hbar v_0}z} \tag{4}$$

in the form

$$\left[H_a(\vec{r}_a) + V(\vec{r},\vec{r}_a)\right]\Psi = i\hbar v_0 \frac{\partial}{\partial z}\Psi(\vec{r},\vec{r}_a) \tag{5}$$

This is an equation for the electronic state of the system in which it is assumed that energy changes from the initial value E_0 are balanced by negligibly small changes in the state of relative motion. Since $V(\vec{r},\vec{r}_a)$ contains no derivatives in the relative coordinate $\vec{r}$, the solution of (5) may be constructed as a sequence of states for a constant value of x and y , beginning with an initial state at $z=-\infty$.

Since $V=0$ at $z=-\infty$, the initial atomic state is isolated, and, with no distinction between x and y values, the constant parameter becomes $r_0 = \sqrt{x^2+y^2} = \sqrt{r^2-z^2}$. Hence, the state of the system is independently established on each straight line defined by an impact parameter r_0.

Writing $z = v_0 t$ and transforming the equation (5) to the form

$$(H_a + V)\Psi = i\hbar \frac{\partial}{\partial t}\Psi(\vec{r},\vec{r}_a) \quad \text{WITH} \quad r=\sqrt{r_0^2+z^2} \tag{6}$$

the equation of motion can be interpreted as a description of the electronic state under the influence of a classical charged particle moving with constant velocity on a straight line separated from the atom center by the impact parameter distance r_0. The impact parameter equation (6) is an appropriate equation of motion for the electronic interaction with very heavy particles, although it is also a suitable approximation wherever the effect of the term $\frac{\hbar^2}{2M}\nabla_r^2 f$ is relatively negligible. The derivation of (6) is equivalent to the derivation by Mott.[5]

The solution of equation (6) is the probability amplitude of the electronic state and must, therefore, satisfy the relation

$$\int \Psi^* \Psi(\vec{r},\vec{r}_a)\, d\tau_a = 1 \tag{7}$$

for each value of $\vec{r}$, where the integration is over the space of all electrons, represented here by the single notation $\vec{r}_a$.

For the values $t=\pm\infty$ on a given path r_0, (6) becomes

$$H_a(\vec{r}_a)\Psi_{\pm\infty} = i\hbar\frac{\partial}{\partial t}\Psi_{\pm\infty}(r_0,\vec{r}_a)$$

with a solution that may be written as a linear combination of the individual solutions $\psi_n(\vec{r}_a)\, e^{-i\frac{E_n t}{\hbar}}$ where the functions $\psi_n(\vec{r}_a)$, defined by

$$H_a(\vec{r}_a)\,\psi_n = E_n \psi_n(\vec{r}_a) \qquad \text{and} \qquad \int \psi_n^* \, \psi_m \, d\tau_a = \delta_{nm} \tag{8}$$

and the polar orientation of the set, are the asymptotic states of the isolated atom, which have a spatial degeneracy associated with the arbitrary direction of the angular momentum components.

4. The asymptotic state representation of the solution and the asymptotic state or Born approximation in the impact parameter form.

(a) the equation of motion in terms of asymptotic states

If the solution of the equation of motion (6) for a given impact parameter is expressed in terms of the complete set of asymptotic states ψ_n in the form

$$\Psi = \sum_n a_n(r_0,t)\,\psi_n(\vec{r}_a)\,e^{i\frac{E_n}{\hbar}t} \tag{9}$$

then the sum is a solution with constant coefficients at asymptotic separation and a solution otherwise for coefficients satisfying the set of equations

$$\dot{a}_n(r_0,t) = \frac{1}{i\hbar}\sum_m V_{nm}(\vec{r})\,a_m(t)\,e^{i\omega_{nm}t} \tag{10}$$

obtained by substituting (9) in (6) and using (8), where $V_{nm}(\vec{r}) = \int \psi_n^* V(\vec{r},\vec{r}_a)\,\psi_m(\vec{r}_a)\,d\tau_a$ and $\omega_{nm} = \frac{E_n - E_m}{\hbar}$, and the additional relation

$$\sum_n |a_n(r_0,t)|^2 = 1 \tag{11}$$

obtained from (7). The solution of the problem is the solution of this infinite set of linear equations for the boundary condition that the initial atomic state is the ground state $\psi_0(\vec{r}_a)$ or $|a_0(r_0,\infty)| = 1$.

Because of the spatial degeneracy of the functions ψ_n, the forms of the terms in (9) depend on the orientation of the asymptotic atomic states, but since this is arbitrary, the form of Ψ should be independent of the orientation. That is, distinguishing the members of a degenerate group by superscripts such that $H_a\psi_n^{(i)} = E_n\psi_n^{(i)}$

the form of $a_n^{(i)}(t)$ and of $\psi_n^{(i)}(\vec{r}_a)$ will depend on the relative directions of the polar orientation and the particle path, but the expression

$$\left(a_n^{(1)}\psi_n^{(1)} + a_n^{(2)}\psi_n^{(2)} + \cdots \right) e^{-i\frac{E_n}{\hbar}t} \tag{12}$$

should be invariant, for the degenerate states $(\psi_n^{(i)})_a$ of one orientation are unitary transformations of the degenerate states $(\psi_n^{(j)})_b$ of a second orientation, such that

$$(\psi_n^{(i)})_a = a_{i1}(\psi_n^{(1)})_b + a_{i2}(\psi_n^{(2)})_b + \cdots \tag{13}$$

and (12) may be written

$$\left(a_n^{(1)}(\psi_n^{(1)})_a + a_n^{(2)}(\psi_n^{(2)})_a + \cdots \right) e^{-i\frac{E_n}{\hbar}t} = \left(b_n^{(1)}(\psi_n^{(1)})_b + b_n^{(2)}(\psi_n^{(2)})_b + \cdots \right) e^{-i\frac{E_n}{\hbar}t}$$

so that any chosen set of states may be reduced to another. Consequently, an exact solution of (10) is independent of the orientation of states, but an approximate solution may not be, and for this reason the condition of invariance is a measure of its validity.

(b) an approximate solution for the perturbation of an initial state

If the interaction $V(\vec{r},\vec{r}_a)$ has the effect of a perturbation of an initial, spherically symmetric, ground state such that $|a_0(t)| \simeq 1$ and according to (11), $\sum_{n\neq 0}|a_n(t)|^2 \ll 1$ or $|a_n(t)| \ll 1 \quad (n \neq 0)$, then the solution may be obtained by means of successive approximations. In the first approximation to (10), the equation for the coefficient $a_0(t)$ becomes

$$\dot{a}_0 + \frac{i}{\hbar} V_{00}(r)\, a_0 = 0 \tag{14}$$

with the solution $$a_0 = e^{-\frac{i}{\hbar}\int_0^t V_{00}(r)\,dt} \tag{15}$$

where $t=0$ marks a convenient phase.

For an excited S state, the approximate equation is

$$\dot{a}_s + \frac{i}{\hbar} V_{ss}(r)\, a_s = \frac{1}{i\hbar} V_{s0}(r)\, e^{i\omega_{s0}t} a_0 \tag{16}$$

which, substituting from (15), becomes

$$\frac{\partial}{\partial t}\left(a_s e^{\frac{i}{\hbar}\int_0^t V_{ss}(r)\,dt} \right) = \frac{1}{i\hbar} V_{s0}(r)\, e^{i\omega_{s0}t + \frac{i}{\hbar}\int_0^t (V_{ss}-V_{00})\,dt}$$

with the solution $$a_s(t) = e^{-\frac{i}{\hbar}\int_0^t V_{ss}(r)\,dt} \frac{1}{i\hbar v}\int_{-\infty}^{vt} V_{s0}(r)\, e^{i\frac{\omega_{s0}}{v}z + \frac{i}{\hbar v}\int_0^z (V_{ss}-V_{00})\,dz} \tag{17}$$

This is sufficiently small if the velocity is sufficiently large or the interaction sufficiently weak.

For excited states forming degenerate groups, the first approximation may be written

$$\begin{aligned}
\dot{a}_n^{(1)} &+ \frac{i}{\hbar} V_{nn}^{(1)}(\vec{r})\, a_n^{(1)} + \frac{i}{\hbar} V_{nn}^{(12)}(\vec{r})\, a_n^{(2)} + \cdots &&= \frac{1}{i\hbar} V_{n0}^{(1)}(\vec{r})\, a_0\, e^{i\omega_{n0}t} \\
\dot{a}_n^{(2)} &+ \frac{i}{\hbar} V_{nn}^{(21)}(\vec{r})\, a_n^{(1)} + \frac{i}{\hbar} V_{nn}^{(2)}(\vec{r})\, a_n^{(2)} + \cdots &&= \frac{1}{i\hbar} V_{n0}^{(2)}(\vec{r})\, a_0\, e^{i\omega_{n0}t} \\
\dot{a}_n^{(3)} &+ \cdots \\
&\vdots
\end{aligned} \tag{18}$$

where the terms of the same energy state are grouped on the left. If the effect of the non-diagonal terms is relatively negligible, then the solution of (18) becomes

$$a_n^{(i)}(t) = e^{-\frac{i}{\hbar}\int_0^t V_{nn}^{(i)}(\vec{r})\,dt} \frac{1}{i\hbar v}\int_{-\infty}^{vt} V_{nn}^{(i)}(\vec{r})\, e^{i\frac{\omega_{n0}}{v}z + \frac{i}{\hbar v}\int_0^z \left(V_{nn}^{(i)} - V_{00}\right)dz} \tag{19}$$

If these first order approximations are designated as $a_{n(0)}$, then the second order additions

$$\frac{1}{i\hbar v}\int_{-\infty}^{vt} V_{nm}^{(i)}(\vec{r})\, e^{i\frac{\omega_{nm}}{v}z}\, a_{n(0)}^{(j)}(z)\, dz$$

will be assuredly negligible if

$$\left| \frac{1}{\hbar v}\int_{-\infty}^{z} V_{nm}^{(i)}(\vec{r})\, e^{i\frac{\omega_{nm}}{v}z}\, dz \right| << 1 \tag{20}$$

which is of the form $|a_{n(m)}(t)| \ll 1$. For the neglected degenerate transitions of (18) the condition becomes

$$\left| \frac{1}{\hbar v} \int_{-\infty}^{z} V_{nn}^{(ij)}(\vec{r})\, dz \right| \ll 1 \qquad (21)$$

If the elements $V_{nn}^{(ij)}(\vec{r})$, defined in terms of some arbitrarily oriented set $(\psi_n^{(i)})_a$, are transformed to the set $(\psi_n^{(i)})_1$, oriented to the atom-particle axis, then, since the symmetric interaction $V(\vec{r},\vec{r}_a)$ of a central field particle cannot connect different particle-oriented azimuthal states,

$$(V_{nn}^{(ij)})_a = a_{i1} a_{j1} (V_{nn}^{(1)}(r))_1 + \cdots \quad \cdots + a_{i\ell} a_{j\ell} (V_{nn}^{(\ell)}(r))_1 + \cdots \qquad (22)$$

where the coefficients $a_{k\ell}$ are functions of the angle between the polar orientation $(\,)_a$ and $\vec{r}$. Since

$$a_{i1} a_{j1} + \cdots \quad \cdots + a_{i\ell} a_{j\ell} + \cdots = 0 \quad \text{and} \quad a_{i1}^2 + \cdots \quad \cdots + a_{i\ell}^2 + \cdots = 1 \qquad (23)$$

the magnitude of (22) over the possible range of angles is bounded by the differences

$$(V_{nn}^{(k)}(r))_1 - (V_{nn}^{(\ell)}(r))_1$$

so (21) is ensured if

$$\left| \frac{1}{\hbar v} \int_{-\infty}^{z} [(V_{nn}^{(k)})_1 - (V_{nn}^{(\ell)})_1]\, dz \right| \ll 1 \qquad (24)$$

The forms of the elements $V_{no}^{(i)}$ and $V_{nn}^{(i)}$ in the solution (19) will depend on the orientation of $(\psi_n^{(i)})_a$ and hence the invariance of (12) is assured only where

$$e^{\frac{i}{\hbar v} \int_0^z [(V_{nn}^{(i)})_a - (V_{nn}^{(j)})_a]\, dz} \simeq 1 \qquad (25)$$

since, then, the linear group (12) may be formed within the integral of (19) where, according to (13) and (23),

$$(V_{no}^{(1)})_a (\psi_n^{(1)})_a + \cdots \quad \cdots + (V_{no}^{(\ell)})_a (\psi_n^{(\ell)})_a + \cdots = (V_{no}^{(1)})_b (\psi_n^{(1)})_b + \cdots \quad \cdots + (V_{no}^{(\ell)})_b (\psi_n^{(\ell)})_b + \cdots$$

The difference $(V_{nn}^{(i)})_a - (V_{nn}^{(j)})_a$ may also be transformed to show that, according to (23), it is bounded by the angle-independent difference $(V_{nn}^{(k)})_1 - (V_{nn}^{(\ell)})_1$, so the phase condition (25) may be put in the form

$$\left| \frac{1}{\hbar v} \int_0^z \left| (V_{nn}^{(i)})_1 - (V_{nn}^{(j)})_1 \right| dz \right| << 1 \qquad (26)$$

which is practically equivalent to (24) and hence is a condition on the effect of the degeneracy of excited states. If this condition is satisfied, then the choice of the lower bound to the phase integral of (19) is arbitrary since it has an appreciable effect only on the magnitude of a constant phase for the degenerate set. Writing $V_{nn}^{(i)}$ for the angle-independent elements $(V_{nn}^{(i)})_1$, the condition of approximation may be written

$$\left| \frac{1}{\hbar v} \int_0^z \left(V_{nn}^{(i)}(r) - V_{nn}^{(j)}(r) \right) dz \right| << 1 \qquad (27)$$

as part of, and in addition to, the condition $|a_{n(m)}(t)| << 1$. These are conditions for the sufficiency of the first order approximation and are related to the perturbation condition $\sum_{n \neq 0} |a_n(t)|^2 << 1$.

The condition (27) is ensured for paths that are sufficiently distant and velocities that are sufficiently large. The elements $V_{nn}^{(i)}$ are the electrostatic potentials between atom and particle, and so the difference $V_{nn}^{(i)} - V_{nn}^{(j)}$ is the difference in potential for the atom in the states $(\psi_n^{(i)})_1$ and $(\psi_n^{(j)})_1$, in which large contributions such as from the nucleus are cancelled. These same nuclear cancellations occur in the difference $V_{nn}^{(i)} - V_{00}$.

The condition $|a_n(t)| \ll 1$ for the first order coefficient has the same velocity dependence as (27) for sufficiently high velocities, but differs in the low velocity region because of the effect of the phase variation. Integrating (19) by parts, the coefficients may be written in the form

$$a_n^{(i)}(t) = -\frac{V_{no}^{(i)}(r)}{E_n - E_o + V_{nn}^{(i)} - V_{oo}}\, e^{i\frac{\omega_{no}}{v}z - \frac{i}{\hbar v}\int_0^z V_{oo}(r)dz} + e^{-\frac{i}{\hbar v}\int_0^z V_{nn}^{(i)}dz} \int^{vt} \frac{\partial}{\partial z} V_{no}^{(i)}\, \frac{e^{i\frac{\omega_{no}}{v}z + \frac{i}{\hbar v}\int_0^z (V_{nn}^{(i)} - V_{oo})dz}}{E_n - E_o + V_{nn}^{(i)} - V_{oo}}\, dz \tag{28}$$

In the region of $t=0$ and at sufficiently low velocity, the second term becomes negligible compared to the first, because of the large variation in the phase factor in the range of interaction and since $\frac{\partial V_{no}^{(i)}}{\partial z}$ is not singular, and the magnitude of the first term is independent of the velocity. Because of the large variation of $e^{i\frac{\omega_{no}}{v}z - \frac{i}{\hbar v}\int_0^z V_{oo}(r)dz}$ in the range of $V_{no}^{(i)}(r)$ at sufficiently low velocity and the corresponding negligibility of the second term, the conditions (21) and (25) leading to (27) are stronger than necessary for the existence of the intermediate first order term of (28). However, the final value of (28) depends on the second term and this, in turn, depends on (25) and (27).

(c) an illustration of the approximate solution

As an illustration of the approximate solution, consider the P state excitation of an effectively single electron, central field atom for which

$$\begin{aligned} (\psi_p^{(1)})_a &= f_p(r_1)\cos\theta_a \\ (\psi_p^{(2)})_a &= f_p(r_1)\sin\theta_a\cos\varphi_a \\ (\psi_p^{(3)})_a &= f_p(r_1)\sin\theta_a\sin\varphi_a \end{aligned} \tag{29}$$

where the subscript marks some polar reference. Only two established directions exist, that of z and that of $\vec{r}$. Denoting the former reference by the subscript o and the latter by 1 , so that $(\psi_p^{(1)})_0 = f_p(r_1)\cos\theta_0$, etc., and $(\psi_p^{(1)})_1 = f_p(r_1)\cos\theta_1$, etc., (29) may be written

$$\begin{aligned}
(\psi_p^{(1)})_a &= \cos\lambda(\psi_p^{(1)})_0 + \sin\lambda\cos\mu(\psi_p^{(2)})_0 + \sin\lambda\sin\mu(\psi_p^{(3)})_0 \\
(\psi_p^{(2)})_a &= -\sin\lambda(\psi_p^{(1)})_0 + \cos\lambda\cos\mu(\psi_p^{(2)})_0 + \cos\lambda\sin\mu(\psi_p^{(3)})_0 \\
(\psi_p^{(3)})_a &= \qquad - \sin\mu(\psi_p^{(2)})_0 + \cos\mu(\psi_p^{(3)})_0
\end{aligned} \tag{30}$$

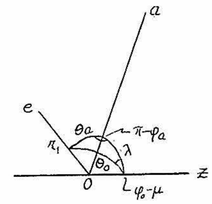


fig. 1a

where the angles λ and μ relate $O\text{-}a$ and z . In turn,

$$\begin{aligned}
(\psi_p^{(1)})_0 &= \cos\varpi(\psi_p^{(1)})_1 \qquad - \sin\varpi(\psi_p^{(2)})_1 \\
(\psi_p^{(2)})_0 &= \sin\varpi\cos\varphi(\psi_p^{(1)})_1 + \cos\varpi\cos\varphi(\psi_p^{(2)})_1 - \sin\varphi(\psi_p^{(3)})_1 \\
(\psi_p^{(3)})_0 &= \sin\varpi\sin\varphi(\psi_p^{(1)})_1 + \cos\varpi\sin\varphi(\psi_p^{(2)})_1 + \cos\varphi(\psi_p^{(3)})_1
\end{aligned} \tag{31}$$

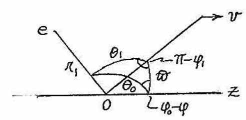


fig. 1b

where the angles ϖ and φ relate $\vec{r}$ and z . Since, for a central field particle, $V(\vec{r}, \vec{r}_a)$ is an axially symmetric function of r_1 , and $(\psi_p)_1$ is defined by (29),

$$(V_{po}^{(1)})_1 = V_{po}^{(1)}(r) \qquad and \qquad (V_{po}^{(2)})_1 = (V_{po}^{(3)})_1 = 0 \tag{32}$$

so from (30), (31), and (32),

$$\begin{aligned}
(V_{po}^{(1)}(r))_a &= (\cos\lambda\cos\varpi + \sin\lambda\sin\varpi\cos(\mu-\varphi))\, V_{po}^{(1)}(r) \\
(V_{po}^{(2)}(r))_a &= (-\sin\lambda\cos\varpi - \cos\lambda\sin\varpi\cos(\mu-\varphi))\, V_{po}^{(1)}(r) \\
(V_{po}^{(3)}(r))_a &= (\qquad - \sin\varpi\sin(\mu-\varphi))\, V_{po}^{(1)}(r)
\end{aligned} \tag{33}$$

In these expressions (33) only ϖ and $V_{po}^{(1)}(r)$ are functions of time. Hence, if

$$e^{\frac{i}{\hbar v}\int_0^z [(V_{pp}^{(i)})_a - (V_{pp}^{(j)})_a]\, dz} \simeq 1$$

the coefficients (19) become

$$a_p^{(1)}(t) = e^{-\frac{i}{\hbar v}\int_0^{vt} \bar{V}_{pp}\,dz} \frac{1}{i\hbar v}\left[\cos\lambda \int_{-\infty}^{vt} V_{po}^{(1)}(r)\cos\varpi \, e^{i\frac{\omega_{po}}{v}z + \frac{i}{\hbar v}\int_0^z (\bar{V}_{pp}-V_{oo})dz} dz + \right.$$
$$\left. + \sin\lambda\cos(\mu-\varphi)\int_{-\infty}^{vt} V_{po}^{(1)}(r)\sin\varpi \, e^{i\frac{\omega_{po}}{v}z + \frac{i}{\hbar v}\int_0^z (\bar{V}_{pp}-V_{oo})dz} dz \right]$$

and so forth, yielding the group

$$a_p^{(1)}(t)(\psi_p^{(1)})_a + a_p^{(2)}(t)(\psi_p^{(2)})_a + a_p^{(3)}(t)(\psi_p^{(3)})_a = e^{-\frac{i}{\hbar v}\int_0^{vt}\bar{V}_{pp}\,dz} \frac{1}{i\hbar v}\left\{ \int_{-\infty}^{vt} V_{po}^{(1)}(r)\cos\varpi \, e^{i\frac{\omega_{po}}{v}z + \frac{i}{\hbar v}\int_0^z (\bar{V}_{pp}-V_{oo})dz} dz \cdot (\psi_p^{(1)})_o \right.$$
$$\left. + \int_{-\infty}^{vt} V_{po}^{(1)}(r)\sin\varpi \, e^{i\frac{\omega_{po}}{v}z + \frac{i}{\hbar v}\int_0^z (\bar{V}_{pp}-V_{oo})dz} dz \cdot \left[(\psi_p^{(2)})_o \cos\varphi + (\psi_p^{(3)})_o \sin\varphi\right] \right\}$$

whcih is independent of λ and μ if the form $\bar{V}_{pp}$ taken for $(V_{pp}^{(i)})_a$ is independent of λ and μ. This condition is satisfied, according to (29), (30), and (31), by the average

$$(V_{pp}^{(i)})_a \simeq \bar{V}_{pp} = \frac{1}{3}\left[(V_{pp}^{(1)})_a + (V_{pp}^{(2)})_a + (V_{pp}^{(3)})_a\right] = \frac{1}{3}\left[V_{pp}^{(1)} + V_{pp}^{(2)} + V_{pp}^{(3)}\right]$$

With this possible invariance established and taking z as the most convenient polar coordinate for the atomic functions, the P state differences $(V_{pp}^{(i)})_o - (V_{pp}^{(j)})_o$, according to (29) and (31), take the forms

$$(V_{pp}^{(1)})_o - (V_{pp}^{(2)})_o = (\cos^2\varpi - \sin^2\varpi\cos^2\varphi)\left(V_{pp}^{(1)} - V_{pp}^{(2)}\right)$$
$$(V_{pp}^{(2)})_o - (V_{pp}^{(3)})_o = \sin^2\varpi\,(\cos^2\varphi - \sin^2\varphi)\left(V_{pp}^{(1)} - V_{pp}^{(2)}\right)$$
$$(V_{pp}^{(3)})_o - (V_{pp}^{(1)})_o = (\sin^2\varpi\sin^2\varphi - \cos^2\varpi)\left(V_{pp}^{(1)} - V_{pp}^{(2)}\right)$$

and

$$(V_{pp}^{(12)})_o = \cos\varpi\sin\varpi\cos\varphi\left(V_{pp}^{(1)} - V_{pp}^{(2)}\right)$$
$$(V_{pp}^{(23)})_o = \sin^2\varpi\sin\varphi\cos\varphi\left(V_{pp}^{(1)} - V_{pp}^{(2)}\right)$$
$$(V_{pp}^{(31)})_o = \cos\varpi\sin\varpi\sin\varphi\left(V_{pp}^{(1)} - V_{pp}^{(2)}\right)$$

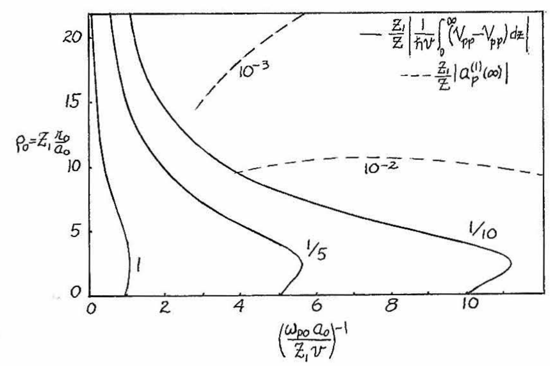
where the last three expressions are the neglected terms of (18). Hence, the condition of validity for this development is equivalent to the condition

$$\left|\frac{1}{\hbar v}\int_0^z \left(V_{pp}^{(1)}(r) - V_{pp}^{(2)}(r)\right) dz\right| << 1 \tag{34}$$

on the upper bound. The coefficients, with the arbitrary φ taken to be zero, become

$$\begin{matrix} a_p^{(1)}(t) \\ a_p^{(2)}(t) \end{matrix} = e^{-\frac{i}{\hbar}\int_0^t \bar{V}_{pp}\,dt} \frac{1}{i\hbar v} \int_{-\infty}^{vt} V_{po}^{(1)}(r) \begin{pmatrix} \cos\varpi \\ \sin\varpi \end{pmatrix} e^{i\frac{\omega_{po}}{v}z + \frac{i}{\hbar v}\int_0^z (\bar{V}_{pp} - V_{oo})\,dz} dz \tag{35}$$

For the hydrogenlike 2^1P state with nuclear charge $Z_1 e$ and coulomb particle of charge Ze, the difference $V_{pp}^{(1)} - V_{pp}^{(2)} = ZZ_1 \frac{e^2}{a_0} \frac{18}{\rho^3}\left[1 - e^{-\rho}\left(1 + \rho + \frac{1}{2}\rho^2 + \frac{1}{6}\rho^3 + \frac{1}{24}\rho^4 + \frac{1}{144}\rho^5\right)\right]$ which may be approximated by $ZZ_1 \frac{e^2}{a_0} \frac{9}{32}\left(\frac{\rho}{4}\right)^2\left[1 + \left(\frac{\rho}{4}\right)^2\right]^{-5/2}$ where $\rho = Z_1 \frac{r}{a_0}$, yielding as a maximum value of (34), $\frac{Z}{Z_1}\left(\frac{\omega_{po} a_0}{Z_1 v}\right) \frac{1 + 3(\rho_0/4)^2}{\left[1 + (\rho_0/4)^2\right]^2}$. Curves of constant value $\times \frac{Z_1}{Z}$ are shown in figure 2. Included are curves of constant $a_p^{(1)}(r_0, \infty)$ for the approximate form $V_{po}^{(1)} \simeq ZZ_1 \frac{e^2}{a_0} \frac{3}{4} \frac{\rho}{(4 + \rho^2)^{3/2}}$. The expression $\frac{\omega_{po} a_0}{Z_1 v}$ is of the order of the ratio of the internal electron to the external particle velocity.



(d) intermediate behavior of the approximate solution at low velocity

With the approximate coefficients in the form (28), the atomic state (9) becomes, absorbing the index (i) in n,

$$\Psi = \left\{ \psi_0 + \sum_{n \neq 0} \frac{V_{no}(\vec{r})}{(E_0 - E_n)\left(1 + \frac{V_{nn} - V_{oo}}{E_n - E_0}\right)} \psi_n \right\} e^{-\frac{i}{\hbar}\int_0^t (E_0 + V_{oo})\,dt} + \sum_{n \neq 0} \left\{ \int_{-\infty}^{vt} \frac{\partial V_{no}}{\partial z} \frac{e^{\frac{i}{\hbar v}\int_0^z (E_n - E_0 + V_{nn} - V_{oo})\,dz}}{(E_0 - E_n)\left(1 + \frac{V_{nn} - V_{oo}}{E_n - E_0}\right)} dz \right\} \psi_n e^{-\frac{i}{\hbar v}\int_0^t (E_n + V_{nn})\,dz} \tag{36}$$

For a sufficiently low velocity, the second sum becomes relatively negligible in the neighborhood of $t=0$, and on a path sufficiently distant to admit the approximation (28) at low velocities, $1+\frac{V_{nn}-V_{00}}{E_n-E_0}\simeq 1$. Hence, in this region, subject to the perturbation condition

$$\sum_{n\neq 0}\left|\frac{V_{n0}}{E_0-E_n}\right|^2 << 1 \tag{37}$$

the intermediate state of (36) is dominated by the behavior of

$$\Psi \simeq \left\{\psi_0+\sum_{n\neq 0}\frac{V_{n0}(r)}{E_0-E_n}\psi_n\right\} e^{-\frac{i}{\hbar}\int_0^t (E_0+V_{00}(r))\,dt} \tag{38}$$

which has the form of the first order perturbation approximation for the ground state of the atom in the presence of the stationary charged particle at the separation r , except that $e^{-\frac{i}{\hbar}\int_0^t V_{00}(r)dt}$ appears in place of $e^{-\frac{i}{\hbar}V_{00}(r)t}$. The expression (38) represents an atomic state coupled to the slowly moving particle, and because of the integral form of the exponent, both members of the equation of motion (6) yield the average

$$\int \Psi^*(H_a+V)\Psi\, d\tau_a = i\hbar\int\Psi^*\frac{\partial}{\partial t}\Psi\, d\tau_a \simeq E_0+V_{00}(r)$$

to the first order in V . At vanishing velocity where r is no longer a function of time, $e^{-\frac{i}{\hbar}\int_0^t V_{00}(r)dt}$ may be written $e^{-\frac{i}{\hbar}V_{00}(r)t}$ and (38) becomes identical with the usual stationary approximation.

5. The stationary state representation of the solution and the stationary state approximation in the impact parameter form.

In order to obtain an approximate solution in the region of low velocities, where the asymptotic state approximation fails, the description $\psi(\vec{r},\vec{r}_a,t)$ of the electronic state of the system will be expressed in terms of the complete set of functions representing the atomic states that come into existence when the motion of the incident charge becomes vanishingly small.

(a) a description of stationary states

In the extreme circumstance of vanishing velocity, the equation of motion (1), with $H_r = 0$ becomes

$$\left[H_a(\vec{r}_a) + V(\vec{r},\vec{r}_a)\right]\Psi_s = i\hbar\frac{\partial}{\partial t}\Psi_s(\vec{r},\vec{r}_a,t) \tag{39}$$

with solutions

$$\chi_n(\vec{r},\vec{r}_a)\,e^{-i\frac{\mathcal{E}_n(r)}{\hbar}t} \quad \text{OR} \quad \chi_n(\vec{r},\vec{r}_a)\,e^{-\frac{i}{\hbar}\int^t \mathcal{E}_n(r)\,dt} \tag{40}$$

where the stationary states χ_n eigenfunctions of the equation

$$\left[H_a(\vec{r}_a) + V(\vec{r},\vec{r}_a)\right]\chi_n = \mathcal{E}_n(r)\,\chi_n(\vec{r},\vec{r}_a) \tag{41}$$

are the wave functions of the atomic electron in the presence of the charged particle at r . In contrast to the asymptotic states, the stationary states are not spatially degenerate, being polarized by the central field of the charged particle.

Because of the symmetry of $V(\vec{r},\vec{r}_a)$ about the atom particle axis, the possible dependence of $\chi_n(\vec{r},\vec{r}_a)$ on the azimuthal angle φ_1 about the axis takes the complex form $e^{\pm i\sigma\varphi_1}$ or the real form $\begin{pmatrix}\sin\sigma\varphi_1\\ \cos\sigma\varphi_1\end{pmatrix}$, and since this is independent of $V(\vec{r},\vec{r}_a)$, the φ_1-state persists over the range of separations. The particle-oriented states χ_n form a complete set for each value of r, such that

$$\int \chi_n^* \chi_m \, d\tau_a = \delta_{nm} \tag{42}$$

Since the operators of (41) are real, the functions χ_n can be established in real form.

At asymptotic or infinite separation, (39) becomes

$$H_a \Psi_{s\infty} = i\hbar \frac{\partial}{\partial t} \Psi_{s\infty}$$

and the individual solutions

$$\chi_n(\vec{r},\vec{r}_a)\, e^{-i\frac{\mathcal{E}_n}{\hbar}t} \underset{r\to\infty}{\longrightarrow} \psi_n(\vec{r}_a)\, e^{-i\frac{E_n}{\hbar}t}$$

so that each stationary state is identified by its asymptotic state. In order for χ_n to be unique, capture of the electron must be precluded, either by restricting the nearness of approach or by restricting the descriptions to systems in which the possible binding of electron to particle is weaker than the atomic bond.

At sufficiently distant separations r, $\chi_n(\vec{r},\vec{r}_a)$ and $\mathcal{E}_n(r)$ may be expressed as perturbations of their asymptotic state in the forms

$$\begin{aligned} \chi_n(\vec{r},\vec{r}_a) &= \psi_n(\vec{r}_a) + \sum_{m\neq n} \frac{V_{mn}(\vec{r})}{E_n - E_m}\psi_m(\vec{r}_a) + \cdots \\ \mathcal{E}_n(r) &= E_n + V_{nn}(r) + \cdots \end{aligned} \tag{43}$$

where ψ_n is the state asymptotically approached by χ_n, having the same polar orientation, if it is not spherically symmetric. According to (42) and (8), the representation (43) is valid where

$$\sum_{m\neq n}\left|\frac{V_{mn}}{E_n-E_m}\right|^2 \ll 1 \tag{44}$$

(b) the equations of motion in terms of stationary states

The impact parameter equation of motion (6) has the same form as (39) but with the auxiliary relation $r=\sqrt{r_0^2+(vt)^2}$, for which H_a+V, χ_n, and $\mathcal{E}_n$ become functions of time, such that, at each value of t, χ_n is the eigenfunction of the operator H_a+V with the eigenvalue $\mathcal{E}_n(r)$ and represents a state coupled to the moving particle. Of the two forms (40), which are equivalent for the system at rest, the second is the more appropriate for the system in motion. In this form, a ground state $\chi_0(\vec{r},\vec{r}_a)\, e^{-\frac{i}{\hbar}\int^t \mathcal{E}_0(r)dt}$ of asymptotic spherical symmetry becomes, at sufficiently large separations for the approximation (43),

$$\left(\psi_0 + \sum_{n\neq 0}\frac{V_{n0}}{E_0-E_n}\,\psi_n + \cdots\right) e^{-\frac{i}{\hbar}\int^t (E_0+V_{00}(r)+\cdots\,)dt} \tag{45}$$

which is to be compared with the same approximation (38) obtained at low velocities in the asymptotic state development.

In terms of stationary states, the general representation of the atomic state on a given path becomes

$$\Psi = \sum_n c_n(t)\,\chi_n(\vec{r},\vec{r}_a)\; e^{-\frac{i}{\hbar}\int_0^t \mathcal{E}_n(r)\,dt} \tag{46}$$

where $r=\sqrt{r_0^2+(vt)^2}$ and where $t=0$ marks a convenient phase. With constant coefficients, this representation becomes a solution as the velocity approaches zero. Substituting (46) in (6), the equation of motion becomes

$$\sum_n \frac{\partial}{\partial t}\left(c_n(t)\,\chi_n(\vec{r},\vec{r}_a)\right) e^{-\frac{i}{\hbar}\int_0^t \mathcal{E}_n(r)\,dt} = 0 \tag{47}$$

or with (41) and (42), the set

$$\dot{c}_n(t) = -\sum_m c_m(t)\left(\int \chi_n^* \frac{\partial}{\partial t}\chi_m\, d\tau_a\right) e^{\frac{i}{\hbar}\int_0^t(\mathcal{E}_n-\mathcal{E}_m)\,dt} \tag{48}$$

(c) an approximate form of the equations for the perturbation of a ground state

If the operator $i\hbar\frac{\partial}{\partial t}$ has the effect of perturbing an initial state χ_0 of asymptotic spherical symmetry such that $|c_0(t)|\simeq 1$ and accordingly $\sum_{n\neq 0}|c_n(t)|^2 \ll 1$, then a first approximation may take the form

$$c_n(t) = -\int_{-\infty}^{t}\left(\left(\int \chi_n^*\frac{\partial}{\partial t}\chi_0\, d\tau_a\right) e^{\frac{i}{\hbar}\int_0^t(\mathcal{E}_n-\mathcal{E}_0)\,dt}\right)dt$$

or

$$c_n(t) = -\int_{-\infty}^{vt}\left(\left(\int \chi_n^*\frac{\partial}{\partial z}\chi_0\, d\tau_a\right) e^{\frac{i}{\hbar v}\int_0^z(\mathcal{E}_n-\mathcal{E}_0)\,dz}\right)dz \tag{49}$$

With the integral written in terms of z, the velocity appears explicitly only as a factor $\frac{1}{v}$ in the exponent. Accordingly, the values of the approximate coefficients become arbitrarily small for velocities that are sufficiently small, if the integrands $\int \chi_n^*\frac{\partial}{\partial z}\chi_0\, d\tau_a$ are not singular on the path. In general, negligibility of succeeding orders of approximation, although dependent on the effect of the operator $\frac{\partial}{\partial z}$, is assured by a sufficiently large variation of the phase factors $e^{\frac{i}{\hbar v}\int_0^z (\mathcal{E}_n - \mathcal{E}_m) dz}$ in the range of interaction. Since this variation is least for the terms of (48) that connect asymptotically-degenerate states, a more reliable first order approximation at sufficiently low velocity may be obtained in the form of the limited set

$$\dot{c}_n^{(i)}(t) = -c_o(t)\left(\int \chi_n^{(i)*} \frac{\partial}{\partial t} \chi_o \, d\tau_a\right) e^{\frac{i}{\hbar}\int_0^t (\mathcal{E}_n^{(i)} - \mathcal{E}_o) dt} - \sum_j c_n^{(j)}(t) \left(\int \chi_n^{(i)*} \frac{\partial}{\partial t} \chi_n^{(j)} d\tau_a\right) e^{\frac{i}{\hbar}\int_0^t (\mathcal{E}_n^{(i)} - \mathcal{E}_n^{(j)}) dt} \qquad (50)$$

for the states χ_o and the asymptotically-degenerate states $\chi_n^{(i)}$. Since χ_o is real in this formulation, $\int \chi_o^2 d\tau_a = 1$ and hence the approximate equation for c_o becomes

$$\dot{c}_o(t) = -\left(\int \chi_o \frac{\partial}{\partial t} \chi_o \, d\tau_a\right) c_o(t) \equiv 0$$

and

$$c_o(t) \simeq 1 \qquad (51)$$

(d) an approximate form for stationary states of weak interaction

Further study of the solution requires more explicit expressions for χ_n , which are complex and difficult to obtain. However, the perturbation representation is accurate on sufficiently distant paths, for which the ground state takes the form

$$\chi_o(\vec{r}, \vec{r}_a) = \psi_o(\vec{r}_a) + \sum_{m \neq o} \frac{(V_{mo}^{(i)}(\vec{r}))_o}{E_o - E_m} (\psi_m^{(i)}(\vec{r}_a))_o + \cdots \qquad (52)$$

and the excited states, the forms

$$\chi_n^{(i)}(\vec{r},\vec{r}_a) = b_n^{(i1)}(\psi_n^{(1)})_0 + b_n^{(i2)}(\psi_n^{(2)})_0 + \cdots \qquad + \sum_{\substack{m\neq n \\ j}} \frac{(V_{mn}^{(ji)}(\vec{r}))_0}{E_n - E_m}(\psi_m^{(j)})_0 + \cdots \tag{53}$$

where possibly degenerate asymptotic states are grouped in the first order, and where the subscript $_0$ denotes the incident direction as the polar orientation of ψ_m .

Since the symmetric $V(\vec{r},\vec{r}_a)$ cannot connect different φ_1-states, (53) may also be written

$$\chi_n^{(i)}(\vec{r},\vec{r}_a) = (\psi_n^{(i)})_1 + \sum_{m\neq n} \frac{V_{mn}^{(i)}(r)}{E_n - E_m}(\psi_m^{(i)})_1 + \cdots \tag{54}$$

in terms of the particle-oriented states $(\psi_n)_1$.

The representations (52) and (53) are valid for the condition

$$\sum_{m\neq n} \left| \frac{V_{mn}^{(i)}}{E_n - E_m} \right|^2 << 1 \tag{55}$$

(e) the approximate solution for S state excitation with weak interaction

For an excited S state, the pertinent term of (52) or

$$\chi_0(\vec{r},\vec{r}_a) = \psi_0 + \cdots \qquad \cdots + \frac{V_{S0}(r)}{E_0 - E_S}(\psi_S)_0 + \cdots$$

is spherically symmetric in r . The excited state to the first order is

$$\chi_S(\vec{r},\vec{r}_a) = \psi_S + \cdots$$

marking an energy difference of

$$\mathcal{E}_S(r) - \mathcal{E}_0(r) = E_S - E_0 + V_{SS}(r) - V_{00}(r) + \cdots$$

and the approximate solution (50) becomes

$$C_s(t) = \frac{1}{E_s - E_0} \int_{-\infty}^{vt} \frac{\partial V_{s0}(r)}{\partial z} \, e^{\frac{i}{\hbar v}\int_0^z (E_s - E_0 + V_{ss} - V_{00})\,dz} \, dz$$

$$= \frac{V_{s0}(r)}{E_s - E_0} \, e^{\frac{i}{\hbar v}\int_0^z (E_s - E_0 + V_{ss} - V_{00})\,dz} + \frac{1}{i\hbar v} \int_{-\infty}^{vt} V_{s0}(r) \left[1 + \frac{V_{ss} - V_{00}}{E_s - E_0} \right] e^{\frac{i}{\hbar v}\int_0^z (E_s - E_0 + V_{ss} - V_{00})\,dz} \, dz \qquad (56)$$

yielding a final value $c_s(\infty)$ similar to $a_s(\infty)$ of the asymptotic state approximation (17) but an intermediate form considerably different, for it diminishes with the velocity. The condition $|c_s(t)| \ll 1$ is ensured for velocities and interaction gradients that are sufficiently small, although, according to (55), the condition is also satisfied at sufficiently high velocities if the representations (52) and (53) are admissible.

(f) the approximate solution for P state excitations with weak interaction

Turning to the simple construction of an effectively single electron atom for the more complex P state excitation, the pertinent terms of the ground state take the forms

$$\chi_0(\vec{r}, \vec{r}_1) = \psi_0 + \cdots \quad \cdots + \frac{V_{p0}^{(1)}(r)}{E_0 - E_p} \left[\cos\varpi \, (\psi_p^{(1)})_0 + \sin\varpi \cos\varphi \, (\psi_p^{(2)})_0 + \sin\varpi \sin\varphi \, (\psi_p^{(3)})_0 \right] + \cdots \qquad (57)$$

The unperturbed excited states are degenerate and hence must be grouped linearly to form the perturbed states

$$\begin{aligned}
\chi_p^{(1)}(\vec{r}, \vec{r}_1) &= \cos\varpi \, (\psi_p^{(1)})_0 + \sin\varpi \cos\varphi \, (\psi_p^{(2)})_0 + \sin\varpi \sin\varphi \, (\psi_p^{(3)})_0 + \sum \frac{(V_{mp}^{(1)})_0}{E_p - E_m} (\psi_m^{(1)})_0 + \cdots \\
\chi_p^{(2)}(\vec{r}, \vec{r}_1) &= -\sin\varpi \, (\psi_p^{(1)})_0 + \cos\varpi \cos\varphi \, (\psi_p^{(2)})_0 + \cos\varpi \sin\varphi \, (\psi_p^{(3)})_0 + \cdots \qquad (58) \\
\chi_p^{(3)}(\vec{r}, \vec{r}_1) &= \qquad - \sin\varphi \, (\psi_p^{(2)})_0 + \cos\varphi \, (\psi_p^{(3)})_0 + \cdots
\end{aligned}$$

where ϑ is the angle between $\vec{r}$ and the fixed coordinate z, and φ is the azimuthal angle of $\vec{r}$ about z. Since, for $\vartheta=0$, $\varphi=0$,

$$\begin{aligned}
\chi_o(\vec{r},\vec{r}_1) &= \psi_o + \cdots \qquad \cdots + \frac{V_{po}^{(1)}(r)}{E_o-E_p}(\psi_p^{(1)})_1 + \cdots \\
\chi_p^{(1)}(\vec{r},\vec{r}_1) &= (\psi_p^{(1)})_1 + \sum \frac{V_{mp}^{(1)}}{E_p-E_m}(\psi_m^{(1)})_1 + \cdots \\
\chi_p^{(2)}(\vec{r},\vec{r}_1) &= (\psi_p^{(2)})_1 + \cdots \\
\chi_p^{(3)}(\vec{r},\vec{r}_1) &= (\psi_p^{(2)})_1 + \cdots
\end{aligned} \tag{59}$$

the orientation of the asymptotic states to the atom-particle axis is established by the perturbation development of χ_p. With the introduction of the relation $r=\sqrt{r_o^2+(vt)^2}$, the states are attributed a timelike behavior marked by an alignment to the moving particle.

Thus, the approximate equations of motion for the group of P states, upon substitution of (57) and (58) in (50), become

$$\begin{aligned}
\dot{c}_p^{(1)}(t) &= \frac{\partial V_{po}^{(1)}/\partial r}{E_p-E_o}\,\dot{r}\, e^{\frac{i}{\hbar}\int_o^t (E_p-E_o+V_{pp}^{(1)}-V_{oo})\,dt} + c_p^{(2)}(t)\,\dot{\vartheta}\, e^{\frac{i}{\hbar}\int_o^t (V_{pp}^{(1)}-V_{pp}^{(2)})\,dt} \\
\dot{c}_p^{(2)}(t) &= \frac{V_{po}^{(1)}}{E_p-E_o}\,\dot{\vartheta}\, e^{\frac{i}{\hbar}\int_o^t (E_p-E_o+V_{pp}^{(2)}-V_{oo})\,dt} - c_p^{(1)}(t)\,\dot{\vartheta}\, e^{-\frac{i}{\hbar}\int_o^t (V_{pp}^{(1)}-V_{pp}^{(2)})\,dt} \\
\dot{c}_p^{(3)}(t) &= 0
\end{aligned} \tag{60}$$

In these equations the operator $\frac{\partial}{\partial t}$ connects the particle-oriented states $(\psi_p^{(1)})_1$ and $(\psi_p^{(2)})_1$ independently of the interaction $V(\vec{r},\vec{r}_a)$. Because of the difference in phase factors, an exact solution of the equations is not easily obtained.

(g) the P state excitation--states in phase

For sufficiently distant paths at a given velocity

$$e^{\frac{i}{\hbar v}\int_o^z \left(V_{pp}^{(1)}(r) - V_{pp}^{(2)}(r)\right) dz} \simeq 1 \tag{61}$$

With this approximation, which is equivalent to assuming the excited states $\chi_p^{(1)}$ and $\chi_p^{(2)}$ to be in phase, the equations of motion reduce to

$$\begin{aligned}
\dot{c}_p^{(1)}(t) &= \frac{\partial V_{po}^{(1)}/\partial r}{E_p-E_o}\,\dot{r}\, e^{\frac{i}{\hbar}\int_0^t (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dt} + c_p^{(2)}(t)\,\dot{\varpi} \\
\dot{c}_p^{(2)}(t) &= \frac{V_{po}^{(1)}}{E_p-E_o}\,\dot{\varpi}\, e^{\frac{i}{\hbar}\int_0^t (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dt} - c_p^{(1)}(t)\,\dot{\varpi}
\end{aligned} \tag{62}$$

With the substitution

$$\begin{aligned}
c_p^{(1)} &= \bar{c}_p^{(1)}\cos\varpi + \bar{c}_p^{(2)}\sin\varpi \\
c_p^{(2)} &= -\bar{c}_p^{(1)}\sin\varpi + \bar{c}_p^{(2)}\cos\varpi
\end{aligned} \tag{63}$$

the equations (62) become

$$\begin{aligned}
\dot{\bar{c}}_p^{(1)}(t) &= \frac{1}{E_p-E_o}\frac{\partial}{\partial t}\left(V_{po}^{(1)}(r)\cos\varpi\right) e^{\frac{i}{\hbar}\int_0^t (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dt} \\
\dot{\bar{c}}_p^{(2)}(t) &= \frac{1}{E_p-E_o}\frac{\partial}{\partial t}\left(V_{po}^{(1)}(r)\sin\varpi\right) e^{\frac{i}{\hbar}\int_0^t (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dt}
\end{aligned} \tag{64}$$

with solutions

$$\begin{matrix}\bar{c}_p^{(1)}(t) \\ \bar{c}_p^{(2)}(t)\end{matrix} = \frac{1}{E_p-E_o}\int_{-\infty}^{vt} \frac{\partial}{\partial z}\left(V_{po}^{(1)}(r) \begin{matrix}\cos\varpi \\ \sin\varpi\end{matrix}\right) e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dz}\, dz \tag{65}$$

$$= \frac{V_{po}^{(1)}}{E_p-E_o}\begin{pmatrix}\cos\varpi \\ \sin\varpi\end{pmatrix} e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dz} + \frac{1}{i\hbar v}\int_{-\infty}^{vt} V_{po}^{(1)}(r)\begin{pmatrix}\cos\varpi \\ \sin\varpi\end{pmatrix}\left[1+\frac{\bar{V}_{pp}-V_{oo}}{E_p-E_o}\right] e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dz}\, dz$$

and, from (63), the final values

$$\begin{matrix}c_p^{(1)}(\infty) \\ c_p^{(2)}(\infty)\end{matrix} = \begin{matrix}\bar{c}_p^{(1)}(\infty) \\ \bar{c}_p^{(2)}(\infty)\end{matrix} = \frac{1}{i\hbar v}\int_{-\infty}^{\infty} V_{po}^{(1)}(r)\begin{pmatrix}\cos\varpi \\ \sin\varpi\end{pmatrix}\left[1+\frac{\bar{V}_{pp}-V_{oo}}{E_p-E_o}\right] e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dz}\, dz \tag{66}$$

which, like the S state solution (56), are similar to the final values of the asymptotic state approximation. Intermediately,

$$\begin{matrix}c_p^{(1)}(t) \\ c_p^{(2)}(t)\end{matrix} = \frac{1}{E_p-E_o}\left\{\begin{pmatrix}\cos\varpi \\ -\sin\varpi\end{pmatrix}\int_{-\infty}^{vt}\frac{\partial}{\partial z}\left(V_{po}^{(1)}\cos\varpi\right) e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dz}\, dz + \begin{pmatrix}\sin\varpi \\ \cos\varpi\end{pmatrix}\int_{-\infty}^{vt}\frac{\partial}{\partial z}\left(V_{po}^{(1)}\sin\varpi\right) e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+\bar{V}_{pp}-V_{oo})\,dz}\, dz\right\} \tag{67}$$

(h) the approximate solution in general form for weak interaction and asymptotically-degenerate states in phase

The reduction accomplished in (56) and (65) on the basis of coherent, first order excited states may be put in general form, for the equation of motion (47)

$$\sum_{n,i} \frac{\partial}{\partial t}\left(c_n^{(i)} \chi_n^{(i)}\right) e^{-\frac{i}{\hbar}\int_0^t \mathcal{E}_n^{(i)} dt} = 0 \tag{68}$$

with $\chi_n^{(i)} \simeq (\psi_n^{(i)})_1 = \sum_j b_n^{(ij)} (\psi_n^{(j)})_0$ and $e^{-\frac{i}{\hbar}\int_0^t \mathcal{E}_n^{(i)} dt} \simeq e^{-\frac{i}{\hbar}\int_0^t (E_n + \bar{V}_{nn}) dt}$ (69)

may be written $\frac{\partial}{\partial t}(c_0 \chi_0)\, e^{-\frac{i}{\hbar}\int_0^t \mathcal{E}_0 dt} + \sum_{\substack{n\neq 0\\ i}} \frac{\partial}{\partial t}\left(c_n^{(i)} \sum_j b_n^{(ij)}\right)(\psi_n^{(j)})_0\, e^{-\frac{i}{\hbar}\int_0^t (E_n + \bar{V}_{nn}) dt} = 0$

or, exchanging sums and writing $\bar{c}_n^{(j)} = \sum_i c_n^{(i)} b_n^{(ij)}$

$$\sum_{\substack{n\neq 0\\ j}} \dot{\bar{c}}_n^{(j)} (\psi_n^{(j)})_0\, e^{-\frac{i}{\hbar}\int_0^t (E_n + \bar{V}_{nn}) dt} = -\frac{\partial}{\partial t}(c_0 \chi_0)\, e^{-\frac{i}{\hbar}\int_0^t \mathcal{E}_0 dt}$$

Multiplying by $(\psi_n^{(i)*})_0$ and integrating, the solution is

$$\bar{c}_n^{(i)}(t) = -\int_{-\infty}^{t} \left(\int (\psi_n^{(i)*})_0 \frac{\partial}{\partial t}(c_0 \chi_0)\, d\tau_a \right) e^{\frac{i}{\hbar}\int_0^t (E_n - E_0 + \bar{V}_{nn} - V_{00}) dt}\, dt$$

or, with $c_0 \simeq 1$ and the representation (52),

$$\bar{c}_n^{(i)}(t) = \frac{1}{E_n - E_0} \int_{-\infty}^{vt} \frac{\partial}{\partial z}\left(V_{no}^{(i)}(\vec{r})\right)_0 e^{\frac{i}{\hbar v}\int_0^z (E_n - E_0 + \bar{V}_{nn} - V_{00}) dz}\, dz$$

$$= \frac{\left(V_{no}^{(i)}(\vec{r})\right)_0}{E_n - E_0} e^{\frac{i}{\hbar v}\int_0^z (E_n - E_0 + \bar{V}_{nn} - V_{00}) dz} + \frac{1}{i\hbar v}\int_{-\infty}^{vt} \left(V_{no}^{(i)}(\vec{r})\right)_0 \left[1 + \frac{\bar{V}_{nn} - V_{00}}{E_n - E_0}\right] e^{\frac{i}{\hbar v}\int_0^z (E_n - E_0 + \bar{V}_{nn} - V_{00}) dz}\, dz \tag{70}$$

For this approximation, the state of the system (46) takes the form

$$\Psi \simeq \chi_0\, e^{-\frac{i}{\hbar}\int_0^t \mathcal{E}_0 dt} + \sum_{\substack{n\neq 0\\ i}} c_n^{(i)}(t)\, (\psi_n^{(i)})_1\, e^{-\frac{i}{\hbar}\int_0^t (E_n + \bar{V}_{nn}) dt}$$

or, introducing (69),

$$\Psi \simeq \chi_0\, e^{-\frac{i}{\hbar}\int_0^t \mathcal{E}_0 dt} + \sum_{\substack{n\neq 0\\ j}} \bar{c}_n^{(j)}(t)\, (\psi_n^{(j)})_0\, e^{-\frac{i}{\hbar}\int_0^t (E_n + \bar{V}_{nn}) dt}$$

Then, from (52) and (70),

$$\Psi \simeq \left[\psi_0 + \sum_n \frac{(V_{no}^{(i)})_0}{E_0 - E_n} (\psi_n^{(i)})_0 + \cdots \right] e^{-\frac{i}{\hbar}\int_0^t (E_0 + V_{00})\,dt} - \sum_n \frac{(V_{no}^{(i)})_0}{E_0 - E_n} (\psi_n^{(i)})_0\, e^{-\frac{i}{\hbar}\int_0^t (E_0 + V_{00})\,dt} +$$

$$+ \sum_n \left\{ e^{-\frac{i}{\hbar}\int_0^t \bar{V}_{nn}\,dt} \frac{1}{i\hbar v} \int_{-\infty}^{vt} (V_{no}^{(i)})_0 \left[1 + \frac{\bar{V}_{nn} - V_{00}}{E_n - E_0} \right] e^{-\frac{i}{\hbar v}\int_0^z (E_n - E_0 + \bar{V}_{nn} - V_{00})\,dz} dz \right\} (\psi_n^{(i)})_0 e^{-\frac{i}{\hbar}E_n t}$$

or

$$\Psi \simeq \psi_0\, e^{-\frac{i}{\hbar}\int_0^t (E_0 + V_{00})\,dt} + \sum_n \left\{ e^{-\frac{i}{\hbar}\int_0^t \bar{V}_{nn}\,dt} \frac{1}{i\hbar v} \int_{-\infty}^{vt} (V_{no}^{(i)})_0 \left[1 + \frac{\bar{V}_{nn} - V_{00}}{E_n - E_0} \right] e^{\frac{i}{\hbar v}\int_0^z (E_n - E_0 + \bar{V}_{nn} - V_{00})\,dz} dz \right\} (\psi_n^{(i)})_0 e^{\frac{-i}{\hbar}E_n t} \tag{71}$$

which, except for the integrand factor $1 + \frac{\bar{V}_{nn} - V_{00}}{E_n - E_0}$ is identical with the asymptotic state approximation (9) and (19), and since the form (52) is admissible only for the sufficiently distant paths of condition (55), the factor $1 + \frac{\bar{V}_{nn} - V_{00}}{E_n - E_0}$ should be near one.

Thus, on sufficiently distant paths, the asymptotic state approximation has been reproduced and for the same condition, namely, in order to write (69),

$$\left| \frac{1}{\hbar v} \int_0^z \left(V_{nn}^{(i)}(R) - V_{nn}^{(j)}(R) \right) dz \right| << 1 \tag{72}$$

The two approximations differ in that the stationary state development (71), in addition to (72) is restricted by the velocity-independent condition (55), which appears for the asymptotic state form (28) only at sufficiently low velocity. The two conditions (55) and (72) have the effect of nearly eliminating, in the first order, the difference between a stationary excited state and an asymptotic excited state.

With the inclusion in the first order approximation, as in (60), of the terms that connect degenerate states, the higher order approximations depend on higher orders of the interaction elements V_{mn} , so that where the interaction is sufficiently weak for a given velocity, the first order approximation is adequate, and hence the solution (71) is not restricted to low velocities.

(i) the P state excitation--states not in phase

Writing $$\mathbb{V}(t) = \frac{V^{(1)}_{po}}{E_p - E_o}$$

$$\Delta(t) = \frac{1}{\hbar v}\int_0^{vt}(E_p - E_o + V^{(1)}_{pp} - V_{oo})\,dz \qquad \text{and} \qquad \delta(t) = \frac{1}{\hbar v}\int_0^{vt}(V^{(1)}_{pp} - V^{(2)}_{pp})\,dz \tag{73}$$

the equations of motion (60) may be put in the abbreviated form

$$\begin{aligned} \dot{c}^{(1)}_p &= \dot{\mathbb{V}} e^{i\Delta} + c^{(2)}_p \dot{\varpi} e^{i\delta} \\ \dot{c}^{(2)}_p &= \mathbb{V}\dot{\varpi} e^{i\Delta - i\delta} - c^{(1)}_p \dot{\varpi} e^{-i\delta} \end{aligned} \tag{74}$$

If $\delta(t)$ is negligible, then the equations (74) may be written

$$\begin{aligned} \dot{c}^{(1)}_p &= \dot{\mathbb{V}} e^{i\Delta} + c^{(2)}_p \dot{\varpi} \\ \dot{c}^{(2)}_p &= \mathbb{V}\dot{\varpi} e^{i\Delta} - c^{(1)}_p \dot{\varpi} \end{aligned} \tag{75}$$

and the solution (67) can be obtained by successive approximations, beginning with the forms

$$\begin{aligned} c^{(1)}_p &\simeq \int_{-\infty}^{t} \dot{\mathbb{V}} e^{i\Delta} dt \\ c^{(2)}_p &\simeq \int_{-\infty}^{t} \mathbb{V}\dot{\varpi} e^{i\Delta} dt \end{aligned} \tag{76}$$

and successively reduced in a series of integrations by parts, to yield the form

$$\begin{matrix} c^{(1)}_p \\ c^{(2)}_p \end{matrix} = \begin{pmatrix} \cos\varpi \\ -\sin\varpi \end{pmatrix} \int_{-\infty}^{t} \frac{\partial}{\partial t}(\mathbb{V}\cos\varpi) e^{i\Delta} dt + \begin{pmatrix} \sin\varpi \\ \cos\varpi \end{pmatrix} \int_{-\infty}^{t} \frac{\partial}{\partial t}(\mathbb{V}\sin\varpi) e^{i\Delta} dt \tag{77}$$

Because the reduction to (77) is independent of the nature of $\mathbb{V}$ and Δ , the modification of (76) is not a second order effect. If the interaction is considered negligible, the equations (75) reduce to $\dot{c}^{(1)}_p = c^{(2)}_p \dot{\varpi}$ and $c^{(2)}_p = -c^{(1)}_p \dot{\varpi}$ with solutions

$c_p^{(1)} = A\cos\varpi + B\sin\varpi$ and $c_p^{(2)} = -A\sin\varpi + B\cos\varpi$, so that, here, the variation in the coefficients is the variation of the projection of some constant vector on the rotating atom-particle axis and its normal in the plane of ϖ .

If the phase relation δ is not negligible, a coherent reduction is not possible, and if the velocity is sufficiently low that, according to (73), the variation of $e^{i\delta}$ is large in the range of interaction V , the first order approximation

$$c_p^{(1)} = \int_{-\infty}^{t} \dot{V} e^{i\Delta} dt$$
$$c_p^{(2)} = \int_{-\infty}^{t} V \dot{\varpi} e^{i\Delta - i\delta} dt \tag{78}$$

is sufficient. For, the higher order modifications of (78), obtained by successive substitution in (74), are composed of integrals of successively higher orders of multiplicity, and these, expressed in terms of $z = vt$, contain the velocity only as a factor $\frac{1}{v}$ in the exponents of $e^{i\Delta}$ and $e^{i\delta}$; so that, at sufficiently low velocity, the higher order modifications are proportional to higher orders of velocity v . Thus, to the second order,

$$c_p^{(1)}(z) = \int_{-\infty}^{z} V' e^{i\Delta} dz + \int_{-\infty}^{z} \varpi' e^{i\delta} \left(\int_{\infty}^{z} V \varpi' e^{i\Delta - i\delta} dz \right) dz$$

where primes denote $\partial/\partial z$ and where Δ and δ are proportional to $\frac{1}{v}$. The negligibility of the second and higher order terms can be attributed to the incoherence introduced by $e^{i\delta}$ since if $\delta \simeq 0$, the approximations can be reduced independently of the velocity to the form (77), which is a consequence of the coherence of $c_p^{(1)}$ and $c_p^{(2)}$. With a large variation in $e^{i\delta}$, the terms of (74) in $c_p^{(i)}$ are small compared to the term in c_0 and incoherent compared to the term in $\dot{c}_p^{(j)}$.

At sufficiently low velocities the intermediate values of the coefficients are dominated by the similar forms

$$\begin{aligned} c_p^{(1)} &= \dot{V}\frac{e^{i\Delta}}{i\dot{\Delta}} + \cdots \\ c_p^{(2)} &= V\dot{\varpi}\frac{e^{i\Delta}}{i\dot{\Delta}} + \cdots \end{aligned} \quad \text{for (77), and} \quad \begin{aligned} c_p^{(1)} &= \dot{V}\frac{e^{i\Delta}}{i\dot{\Delta}} + \cdots \\ c_p^{(2)} &= V\dot{\varpi}\frac{e^{i(\Delta-\delta)}}{i(\dot{\Delta}-\dot{\delta})} + \cdots \end{aligned} \quad \text{for (78).}$$

However, the final values become

$$\begin{matrix} c_p^{(1)}(\infty) \\ c_p^{(2)}(\infty) \end{matrix} = \int_{-\infty}^{\infty} V\begin{pmatrix}\cos\varpi \\ \sin\varpi\end{pmatrix}(i\dot{\Delta})e^{i\Delta}dt \quad \text{for (77), and} \quad \begin{aligned} c_p^{(1)}(\infty) &= \int_{-\infty}^{\infty} V(i\dot{\Delta})e^{i\Delta}dt \\ c_p^{(2)}(\infty) &= -\int_{-\infty}^{\infty}\frac{vV}{r}\sin\varpi\, e^{i(\Delta-\delta)}dt \end{aligned} \quad \text{for (78).}$$

The solution (74) may also be reduced by absorbing the phase factor of (74) in the coefficient $c_p^{(2)}$ and transforming the equations according to (63), but the successive approximations for this form do not produce higher orders of the velocity at low velocity, and the expansion is more appropriate in the high velocity range.

According to (78), the approximate solutions at sufficiently low velocity take the forms

$$\begin{aligned} c_p^{(1)}(t) &= \int_{-\infty}^{t}\frac{\partial V_{po}^{(1)}(r)/\partial r}{E_p-E_o}\dot{r}\, e^{\frac{i}{\hbar}\int_0^t (E_p-E_o+V_{pp}^{(1)}-V_{oo})dt}dt = \int_{-\infty}^{vt}\frac{\partial V_{po}^{(1)}/\partial z}{E_p-E_o}\, e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+V_{pp}^{(1)}-V_{oo})dz}dz \\ &= \frac{V_{po}^{(1)}(r)}{E_p-E_o}\, e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+V_{pp}^{(1)}-V_{oo})dz} + \frac{1}{i\hbar v}\int_{-\infty}^{vt} V_{po}^{(1)}(r)\left[1+\frac{V_{pp}^{(1)}-V_{oo}}{E_p-E_o}\right] e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+V_{pp}^{(1)}-V_{oo})dz}dz \qquad (79) \\ c_p^{(2)}(t) &= \int_{-\infty}^{t}\frac{V_{po}^{(1)}(r)}{E_p-E_o}\dot{\varpi}\, e^{\frac{i}{\hbar}\int_0^t (E_p-E_o+V_{pp}^{(2)}-V_{oo})dt}dt = -\int_{-\infty}^{vt}\frac{V_{po}^{(1)}(r)}{E_p-E_o}\,\frac{\sin\varpi}{r}\, e^{\frac{i}{\hbar v}\int_0^z (E_p-E_o+V_{pp}^{(2)}-V_{oo})dz}dz \end{aligned}$$

These approximations represent independent excitations of particle-oriented states with one depending on the radial and the other on the angular components of the particle motion.

The measure of validity of (79) is not as clear as the condition (61) for (67), but, since the variation of $e^{\frac{i}{\hbar v}\int_0^\infty (V_{pp}^{(1)}-V_{pp}^{(2)})dz}$ occurs within the range of interaction, it is certain that where

$$\left| \frac{1}{\hbar v}\int_0^\infty \left(V_{pp}^{(1)} - V_{pp}^{(2)}\right) dz \right| >> 1 \tag{80}$$

the solution (67), leading to asymptotic state or Born approximation is no longer valid. The more extreme the inequality (80), the more admissible becomes the approximate solution (79).

For the 2^1P excitation of a hydrogenlike atom by a coulomb particle, the phase difference $\left|\frac{1}{\hbar v}\int_0^\infty (V_{pp}^{(1)}-V_{pp}^{(2)})dz\right|$ is shown in figures 2 and 3. For the same system, the magnitude of $c_p^{(2)}(t)$ in the neighborhood of $t=0$, for example, may be taken to be very roughly of the order $\frac{V_{po}(r_0)}{E_p-E_0}\frac{a_0}{r_0}\frac{v}{\omega_{po}a_0}$ with $V_{po}(r_0) \simeq \frac{3}{4}\frac{ZZ_1}{a_0}\frac{1}{\rho_0^2}\left[1 - e^{-\frac{3}{2}\rho_0}\left(1+\frac{3}{2}\rho_0+\frac{9}{8}\rho_0^2+\frac{27}{64}\rho_0^3\right)\right]$.

According to the distribution of values the coefficient diminishes with diminishing range as the phase difference increases with increasing range. On moderately distant paths in this system, the phase difference cannot be neglected for values of $\frac{\omega_{po}a_0}{Z_1 v}$ greater than 3, for $\frac{Z}{Z_1} \simeq 1$, or where the velocity of the particle is of the order of the average electron velocity.

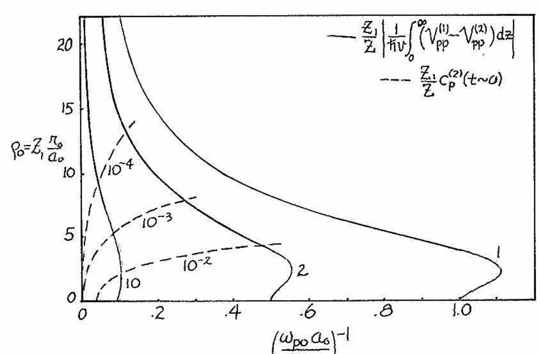


fig. 3

(j) the effect of a low velocity on phase relations in a weak interaction

The importance of the foregoing solution for a weak interaction lies in the effect of the velocity on the coherence of asymptotically-degenerate states. These states are coupled to the particle and differences in coupling energy appear even for weak interactions, so that, at low velocities, the states no longer form a coherent group during the collision. Thus, an interaction energy that is small compared to the energies of the relative motion and of the atomic state is not a sufficient condition for the asymptotic state or Born approximation which requires a coherence of the group of atomic states that has the property of an arbitrary orientation. For a weak interaction and sufficiently low velocity, the coefficients (79) and states $\chi_p^{(i)} \simeq (\psi_p^{(i)})_1$ represent the correct addition to the ground state (38) or (45).

(k) the approximate solution at low velocity in general form

The phase effect that appeared at low velocity in the P state excitation with weak interaction is a part of a general property of the stationary state description. For, if the variation of the phase factors of each of the terms of the equation of motion (48) is sufficiently large within the range of interaction, the approximate solution becomes

$$C_n^{(i)}(t) = -\int_{-\infty}^{vt} \left(\int \chi_n^{(i)*} \frac{\partial}{\partial z} \chi_0 \, d\tau_a \right) e^{\frac{i}{\hbar v} \int_0^z (\mathcal{E}_n^{(i)} - \mathcal{E}_0) \, dz} \, dz \qquad (81)$$

The possibility of solution is ensured by a sufficiently low velocity, for terms connecting degenerate states do not appear in the equation of motion, since the operator has the form

$$\frac{\partial}{\partial t} = \dot{r}\frac{\partial}{\partial r} + \dot{\varpi}\frac{\partial}{\partial \varpi} = \dot{r}\frac{\partial}{\partial r} + \dot{\varpi}\left(-\cos\varphi_1\frac{\partial}{\partial\theta_1} + \frac{\cos\theta_1}{\sin\theta_1}\sin\varphi_1\frac{\partial}{\partial\varphi_1}\right) \qquad (82)$$

and the degenerate states differ only in the functions $\sin\sigma\varphi_1$, and $\cos\sigma\varphi_1$. Since the energy differences of the non-degenerate states that are asymptotically degenerate depend solely on the energy of coupling, the variation of $e^{\frac{i}{\hbar v}\int_0^z(\mathcal{E}_n^{(i)}-\mathcal{E}_n^{(j)})dz}$ for these states is the critical measure of a sufficiently low velocity; and since the variation is confined to the range of interaction,

$$\left|\frac{1}{\hbar v}\int_z^\infty\left(\mathcal{E}_n^{(i)}-\mathcal{E}_n^{(j)}\right)dz\right| >> 1 \qquad (83)$$

for some value of z and for non-degenerate states, is a necessary condition of the approximation.

According to (82), the approximation (81) may be separated into the two parts

$$\begin{aligned} c_n^{(i)}(t) &= -\int_{-\infty}^{vt}\left(\int \chi_n^{(i)}\frac{\partial}{\partial r}\chi_0\,d\tau_a\right)\dot{r}\,e^{\frac{i}{\hbar v}\int_0^z(\mathcal{E}_n^{(i)}-\mathcal{E}_0)dz}\,dz \\ c_n^{(j)}(t) &= -\int_{-\infty}^{vt}\left(\int \chi_n^{(j)}\frac{\partial}{\partial\varpi}\chi_0\,d\tau_a\right)\dot{\varpi}\,e^{\frac{i}{\hbar v}\int_0^z(\mathcal{E}_n^{(j)}-\mathcal{E}_0)dz}\,dz \end{aligned} \qquad (84)$$

with one depending on the radial and the other on the angular component of the particle motion. With the state χ_0 independent of φ_1, the radial motion excites non-φ_1 states and the angular motion, $\cos\varphi_1$ states.

The states χ_n and χ_0 are coupled to the moving particle, but where $\left|\frac{1}{\hbar v}\int_z^\infty(\mathcal{E}_n^{(i)}-\mathcal{E}_n^{(j)})dz\right| \lesssim 1$, $\chi_n^{(i)}$ and $\chi_n^{(j)}$ are not independent, and their connection must be included in the approximate equations of motion.

(1) the distribution of solutions

The two approximations (19) and (81) are the extreme solutions of the impact parameter-and-velocity range, which may be roughly divided into three regions according to the limits of the approximations, based, for the Born approximation on the in-phase quality of degenerate asymptotic states, and for the stationary state approximation on the incoherence of non-degenerate stationary states. These regions may be indicated schematically as in figure 4. For the region between the two approximations, a simple solution does not exist, although for impact parameter greater than some lower bound, an approximate equation of motion can be developed for the entire velocity range, such as (60) for the P state excitation.

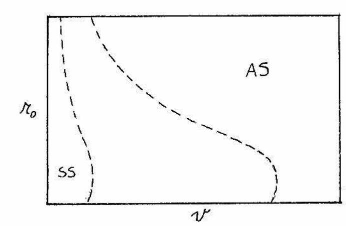


fig 4

Where, in the asymptotic state region, the atomic states have an arbitrary orientation, in the stationary state region, they are polarized and strongly coupled to the moving charge.

The total probability of excitation or total cross section is the sum of final probabilities for a uniform distribution of possible paths, or

$$I_n = \int_0^\infty \left| (\text{COEFFICIENT})_n \text{ at } t=\infty \right|^2 2\pi r_0 \, dr_0 \qquad (85)$$

which is also the number of particles associated with the excited state n for a unit incident flux. In both approximations, the final coefficient is the coefficient of $(\psi_n)_0$, the asymptotic state of polar orientation in the incident direction, since the orientation is arbitrary for the high velocity approximation and since the stationary state $\chi_n \to (\psi_n)_0$ as $t \to \infty$. At low velocities, the major contribution to the total excitation comes from near paths, and hence the stationary state approximation is valid for the effective range of impact parameters.

6. The stationary state representation of the low velocity collision.

Without approximation, the stationary states χ_n are associated with states of relative motion which describe the collision and scattering of particles as an energy-conserved phenomenon.

(a) the equation of motion in terms of stationary states

Writing
$$\Psi(\vec{r},\vec{r}_a,t) = \Phi(\vec{r},\vec{r}_a)\, e^{-i\frac{E}{\hbar}t} \tag{86}$$

the equation of motion (1) becomes the time-independent equation
$$\left(-\frac{\hbar^2}{2M}\nabla_r^2 + H_a + V\right)\Phi = E\,\Phi(\vec{r},\vec{r}_a) \tag{87}$$

for the constant, total energy E .

Representing the solution in terms of the complete set of stationary states,
$$\Phi(r,r_a) = \sum F_m(\vec{r})\, \chi_m(\vec{r},\vec{r}_a) \tag{88}$$

where χ_n is defined by

$$(H_a+V)\chi_n = \mathcal{E}_n(r)\,\chi_n(\vec{r},\vec{r}_a) \qquad \text{and} \qquad \int \chi_n^* \chi_m \, d\tau_a = \delta_{nm} \tag{89}$$

and has the particle-oriented asymptotic state $(\psi_n)_1$. The expressions $F_n(\vec{r})$ are wave functions of the relative motion of the system for the atom in the state χ_n , and are defined by the boundary conditions

$$F_0(\vec{r}) \sim e^{ik_0 z} + \frac{e^{ik_0 r}}{r} f_0(\theta,\varphi) \tag{90}$$

for the ground state, and
$$F_n(\vec{r}) \sim \frac{e^{ik_n r}}{r} f_n(\theta,\varphi) \tag{91}$$

for excited states, where θ and φ are polar and azimuthal angles of the atom-particle axis relative to the incident direction $+z$, and become scattering angles for asymptotic separations r.

Integrating over the electronic spaces, the expression

$$\int \Phi^* \Phi(\vec{r}, \vec{r}_a)\, d\tau_a = F_0^* F_0 + \cdots \qquad \cdots + F_n^* F_n + \cdots \tag{92}$$

becomes the probability distribution of the relative state. Probability of excitation and scattering in the direction is the relative flux of particles

$$\frac{k_n}{k_0} \left| f_n(\theta, \varphi) \right|^2$$

and probability of excitation becomes

$$\frac{k_n}{k_0} \int \left| f_n(\theta, \varphi) \right|^2 \sin\theta\, d\theta\, d\varphi \tag{93}$$

Substituting (88) in (87) and using (89), the equation (87) becomes the set

$$-\frac{\hbar^2}{2M} \nabla_r^2 F_n + \left[\mathcal{E}_n(r) - E \right] F_n = \sum_m \frac{\hbar^2}{2M} \int \chi_n^* \left(2 \nabla_r F_m \cdot \nabla \chi_m + F_m \nabla_r^2 \chi_m \right) d\tau_a$$

or grouping all states n on the left

$$\begin{aligned} -\frac{\hbar^2}{2M} \nabla_r^2 F_n + \left[\mathcal{E}_n(r) - E - \frac{\hbar^2}{2M} \int \chi_n^* \nabla_r^2 \chi_n\, d\tau_a - \frac{\hbar^2}{2M} \int \chi_n^* \nabla_r \chi_n\, d\tau_a \cdot \nabla_r \right] F_n = \\ = \sum_m \frac{\hbar^2}{2M} \int \chi_n^* \left(2 \nabla_r F_m \cdot \nabla_r \chi_m + F_m \nabla_r^2 \chi_m \right) d\tau_a \end{aligned} \tag{94}$$

(b) angular momentum operators

Consider the transformation[6] of the operators ∇_r and ∇_r^2 from the fixed system xyz, with z the direction of initial relative momentum, to the system $\mathfrak{x}\mathfrak{y}\mathfrak{z}$, with $\mathfrak{z}$ the atom-particle axis and $\mathfrak{x}$ for convenience in the xy plane. Then

$$\begin{aligned} \mathfrak{x} &= y\cos\varphi - x\sin\varphi \\ \mathfrak{y} &= -(x\cos\varphi + y\sin\varphi)\cos\theta + z\sin\theta \\ \mathfrak{z} &= (x\cos\varphi + y\sin\varphi)\sin\theta + z\cos\theta \end{aligned} \qquad (95)$$

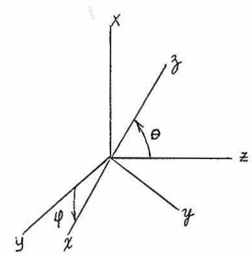


fig. 5

Transformed to the fixed system

$$\chi_n = \chi_n(r, \mathfrak{x}\mathfrak{y}\mathfrak{z}) = \chi_n(r, \theta\varphi, xyz)$$

and
$$\begin{aligned} \frac{\partial}{\partial\theta}\chi_n(r\theta\varphi xyz) &= \left(\frac{\partial\mathfrak{x}}{\partial\theta}\frac{\partial}{\partial\mathfrak{x}} + \frac{\partial\mathfrak{y}}{\partial\theta}\frac{\partial}{\partial\mathfrak{y}} + \frac{\partial\mathfrak{z}}{\partial\theta}\frac{\partial}{\partial\mathfrak{z}}\right)\chi_n(r\mathfrak{x}\mathfrak{y}\mathfrak{z}) \\ &= \left(\mathfrak{z}\frac{\partial}{\partial\mathfrak{y}} - \mathfrak{y}\frac{\partial}{\partial\mathfrak{z}}\right)\chi_n(r,\mathfrak{x}\mathfrak{y}\mathfrak{z}) \\ &= -i P_{\mathfrak{x}}\chi_n \end{aligned} \qquad (96)$$

and further
$$\frac{\partial^2}{\partial\theta^2}\chi_n = (-iP_{\mathfrak{x}})^2\chi_n$$

where $P_{\mathfrak{x}}$ is the angular momentum operator for the axis of $\mathfrak{x}$.

Similarly
$$\frac{\partial}{\partial\varphi}\chi_n = -i\left[\cos\theta\, P_{\mathfrak{z}} + \sin\theta\, P_{\mathfrak{y}}\right]\chi_n \qquad (97)$$

$$\frac{\partial^2}{\partial\varphi^2}\chi_n = -\left[\cos\theta\, P_{\mathfrak{z}} + \sin\theta\, P_{\mathfrak{y}}\right]^2\chi_n$$

where $P_{\mathfrak{x}}$, $P_{\mathfrak{y}}$, and $P_{\mathfrak{z}}$ are the angular momentum operators for axes $\mathfrak{x}$, $\mathfrak{y}$, and $\mathfrak{z}$, respectively. Then

$$\nabla_r\chi_n = \vec{i}_r\frac{\partial\chi_n}{\partial r} + \vec{i}_\theta\frac{1}{r}(-iP_{\mathfrak{x}})\chi_n + \vec{i}_\varphi\frac{1}{r\sin\theta}\left[\sin\theta(-iP_{\mathfrak{y}}) + \cos\theta(-iP_{\mathfrak{z}})\right]\chi_n \qquad (98)$$

and, with $iP_{\mathfrak{x}} = P_{\mathfrak{y}}P_{\mathfrak{z}} - P_{\mathfrak{z}}P_{\mathfrak{y}}$,

$$\nabla_r^2\chi_n = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\chi_n - \frac{1}{r^2}(P_{\mathfrak{x}}^2 + P_{\mathfrak{y}}^2)\chi_n - \frac{\cos^2\theta}{r^2\sin^2\theta}P_{\mathfrak{z}}^2\chi_n - \frac{2\cos\theta}{r^2\sin\theta}P_{\mathfrak{y}}P_{\mathfrak{z}}\chi_n \qquad (99)$$

Since the central field of the charged particle does not alter the φ_1-state of χ_n , which in complex form is $e^{i\sigma\varphi_1}$, the particle-oriented momentum component of the complex χ_n

has the constant, integral value σ , so

$$P_z \chi_{n(\sigma)} = \sigma \chi_{n(\sigma)} \qquad (100)$$

The eigenvalues of the operator $(P_x^2+P_y^2)\chi_n$ are, in general, functions of the separation r . Since the σ-value of $\chi_{n(\sigma)}$ is not altered by the operators P_z and $P_x^2+P_y^2$, but is changed by a unit by the operators P_x and P_y , the elements $\int \chi_n^* \nabla_r \chi_m d\tau_a$ and $\int \chi_n^* \nabla_r^2 \chi_m d\tau_a$ vanish, according to (98) and (99), unless the σ-values of χ_n and χ_m are the same or differ by ± 1 ; so each equation (94) connects only states $\chi_{n(\sigma)}$ for which $\Delta\sigma = 0, \pm 1$.

Because of the persistence of the φ_1-state over the range of separations, the two states $\chi_{n(+\sigma)}$ and $\chi_{n(-\sigma)}$ are degenerate and hence allow combinations $a_\pm(\chi_{n(+\sigma)} \pm \chi_{n(-\sigma)})$ yielding real forms of χ_n , written as $\chi_n^{(i)}$. In this mixture of $|\sigma|$ states, the distinction between $+\sigma$ and $-\sigma$ momenta is lost, and (100) must be replaced by

$$P_z^2 \chi_n^{(i)} = \sigma^2 \chi_n^{(i)} \qquad (101)$$

The real form of χ_n , although inconstant in σ , has the advantage of simplifying the equations of motion, for $\int \chi_n \nabla_r \chi_n d\tau_a \equiv 0$. In terms of real states, the elements $\int \chi_n^{(i)} \nabla_r \chi_n^{(j)} d\tau_a$ and $\int \chi_n^{(i)} \nabla_r^2 \chi_n^{(j)} d\tau_a$ vanish unless the $|\sigma|$-values of $\chi_n^{(i)}$ and $\chi_m^{(j)}$ are the same or differ by a unit. Consequently, each equation (94) connects only the real states $\chi_n^{(i)}$ for which $\Delta\sigma^2 = 0, 1$. Although the operators (98) and (99) cannot connect the degenerate states $\chi_{n(+\sigma)}$ and $\chi_{n(-\sigma)}$, since $\Delta\sigma > 1$, the coefficient of $\vec{i}_\varphi$ in the operator ∇_r can connect the degenerate states of the real form.

(c) the operators of the equation of motion

In terms of real stationary states, the left member of (94) may, with the introduction of (98) and (99), be written in the form

$$-\frac{\hbar^2}{2M}\nabla_r^2 F_n + \left[\mathcal{E}_n(r) - E\right]F_n - \frac{\hbar^2}{2M}\left[\int \chi_n \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\chi_n d\tau_a\right]F_n +$$
$$+ \frac{\hbar^2}{2Mr^2}\left[\int \chi_n (P_x^2 + P_y^2)\chi_n d\tau_a\right]F_n + \frac{\hbar^2}{2Mr^2}\left[\frac{\cos^2\theta}{\sin^2\theta}\sigma^2\right]F_n \qquad (102)$$

which represents the interrelation of F_n and χ_n, since the right member of (94) depends on the connection of χ_n with other states of the atom. The first term of (102) is the energy of relative motion, $\mathcal{E}_n(r)$ is the energy of the stationary state χ_n, and E is the total energy of the system; the fourth term represents an inertia effect of the changing χ_n state, and the remaining two terms are gyroscopic coupling energies which represent the coupling of the electronic angular momentum and the motion of the atom particle axis since these terms derive from the angular parts of the operator ∇_r^2. Of the two terms, the first represents the coupling of the precession of the state χ_n about the atom-particle axis with the motion of the axis, to which it imparts a resistence with an effectiveness depending on the moment of inertia of the system $(\frac{1}{2}Mr^2)$ and hence diminishing with increasing mass and separation r. The term $\frac{\hbar^2}{2Mr^2}\int \chi_n(P_x^2+P_y^2)\chi_n d\tau_a$ is a spherically symmetric function of r and has the form of a repulsive potential. The last term, a function of the particle-oriented angular momentum component σ, is the gyroscopic coupling energy involved in the conservation of angular momentum.

Although the relative angular momentum in the collision is not certain, it has no component in the incident direction for an initial state of vanishing σ-value, and this property must be conserved in any transition to excited states of non-vanishing σ-value. The last term of (102) vanishes at $\theta=\frac{\pi}{2}$ in which direction has no $\vec{\sigma}$-component, and has the effect, in the factor $\frac{1}{\sin^2\theta}$, of excluding the z-axis to the probability distribution of the relative state F_n. The effect of the σ-coupling on the relative depends on the moment of inertia of the system, but where increasing separation diminishes the effect of the precession coupling, as it correspondingly weakens the stationary coupling of χ_n to the particle, it cannot entirely overcome the singularity of the σ-coupling in the incident direction.*

(d) approximate equations of motion for low relative velocity

If the relative motion of an atom and particle is so slow that the atomic system remains in a ground stationary S state, coupled to the moving particle, then the vanishing of (102) defines the state of relative motion or

$$-\frac{\hbar^2}{2M}\nabla_r^2 F_0 + \left[\mathcal{E}_0(r) - E - \frac{\hbar^2}{2M}\int \chi_0 \nabla_r^2 \chi_0 \, d\tau_a\right] F_0 = 0 \qquad (103)$$

* The vanishing expression (102) is the equation of motion of a stable molecule with the electronic state strongly coupled to the atom-particle axis, if a stable molecule is possible. For such a system the spatial extent of the stationary states is effectively limited by the stationary orbits of the bound particle. The angle-dependent terms of (102) describe a state of quantized total angular momentum in some fixed direction $\theta=0$, with the direction $\theta=0$ excluded to the precessing atom-particle axis which carries the angular momentum σ.

with $$F_0 \sim e^{ik_0 z} + \frac{e^{ik_0 r}}{r} f_0(\theta,\varphi) \tag{104}$$

which is an elastic collision and scattering for a coupled atomic state.* Excitation at low velocities is then a perturbation of the state $F_0 \chi_0$, such that $\sum_{n\neq 0} F_n^* F_n \ll F_0^* F_0$, and neglecting all terms on the right of (94) except those involving F_0 , F_n is defined by

$$\frac{-\hbar^2}{2M}\nabla_r^2 F_n + \left[\mathcal{E}_n(r) - E - \frac{\hbar^2}{2M}\int \chi_n \nabla_r^2 \chi_n \, d\tau_a\right] F_n = \frac{\hbar^2}{2M}\int \chi_n (2\nabla_r F_0 \cdot \nabla_r \chi_0 + F_0 \nabla_r^2 \chi_0)\, d\tau_a \tag{105}$$

and $$F_n \sim \frac{e^{ik_n r}}{r} f_n(\theta,\varphi)$$

Accordingly, the excitations $F_n \chi_n$ exist independently, and are also coupled states of the system.

Degenerate states are not connected in the neglected terms of (94) since the connection appears only with the operator $\frac{\partial}{\partial\varphi}$ in (98) and, since from (104) there are no initial φ-motions, none appear. Consequently, the states that are connected in neglected terms differ in the coefficient of F_n in the equation (105) and hence are not coherent. According to the operator forms (98) and (99), only states with $\sigma^2 = 0,1$ are excited in the first order of approximation since the σ-value of χ_0 vanishes.

The approximation (105) corresponds to the impact parameter form (81); but, without path distinctions, the validity of (105) depends on a relative velocity sufficiently low to ensure the coupling of the atomic states to the particle within the range of interaction. Equations (103) and (105) are the perturbation equations of Mott and Massey.[7]

* For asymptotically-degenerate ground states, (103) must be replaced by the set of equations connecting the states $F_0^{(i)}$.

The solution of (105) may be evaluated by expressing F_n and the right member in terms of a complete set of functions appropriate to the operator of F_n. If $\int \chi_n \nabla_r^2 \chi_n d\tau_a$ is a spherically symmetric function of r, which according to (99) occurs for $\sigma = 0$, the solution may be expressed in terms of Legendre functions.

(e) an asymptotic solution for a spherically symmetric behavior of $\int \chi_n \nabla_r^2 \chi_n d\tau_a$

For functions $\int \chi_n \nabla_r^2 \chi_n d\tau_a$ that are spherically symmetric in r, and for functions $\mathcal{E}_n(r) - E_n$ and $\int \chi_n \nabla_r^2 \chi_n d\tau_a$ that diminish more steeply than $\frac{1}{r}$ as $r \to \infty$, the asymptotic value of the solution of (105) then has the familiar form[8]

$$F_n(r, \theta_n) \sim \frac{e^{ik_n r}}{r} \frac{1}{4\pi} \int \mathcal{F}(r', \pi - \Theta)\, \chi_n' \left(2\nabla_r F_0 \cdot \nabla_r \chi_0 + F_0 \nabla_r^2 \chi_0\right)' d\tau_a \, d\tau' \qquad (106)$$

where $\vec{r}$ is converted to $\vec{r}\,'$ in the integral, and

$$\cos\Theta = \cos\theta_n \cos\theta' + \sin\theta_n \sin\theta' \cos(\varphi_n - \varphi')$$

and where $\mathcal{F}_n(r, \theta)$ is the solution of

$$-\frac{\hbar^2}{2M} \nabla_r^2 \mathcal{F}_n + \left[\mathcal{E}_n(r) - E - \frac{\hbar^2}{2M} \int \chi_n \nabla_r^2 \chi_n d\tau_a\right] \mathcal{F}_n = 0 \qquad (107)$$

with the asymptotic behavior

$$e^{ik_n z} + \frac{e^{ik_n r}}{r} f_n(\theta, \varphi) \qquad (108)$$

As asymptotic forms, the solutions (106) are not measures of the sufficient smallness of F_n. If $\int \chi_n \nabla_r^2 \chi_n d\tau_a$ is not a spherically symmetric function of r, such a reduction as (106) is not available.

(f) the approximate equations of motion for low velocities and weak interactions

If the stationary states are represented as perturbations of asymptotic states, the solution may be reduced as in the impact parameter formulation, but where the impact parameter reduction may be limited to paths sufficiently distant to admit the approximation, the wave interaction cannot be confined; and, here, the perturbation representation is admissible only if the stationary interaction is sufficiently weak over the range of separations, and this depends on a sufficiently weak incident charge. Thus, with perturbation representations of χ_n, the equations (105) are approximate descriptions of the collision if the interaction is sufficiently weak and if the relative motion is sufficiently slow.

In terms of the particle-oriented states $(\psi_n)_1$, and to the first order in V_{nm},

$$\begin{aligned}\chi_0(\vec{r},\vec{r}_a) &= \psi_0(\vec{r}_a) + \sum_{m\neq 0}\frac{V^{(1)}_{m0}(r)}{E_0-E_m}(\psi^{(1)}_m)_1+\cdots\\ \chi^{(i)}_n(\vec{r},\vec{r}_a) &= (\psi^{(i)}_n)_1 + \sum\frac{V^{(i)}_{mn}(r)}{E_n-E_m}(\psi^{(i)}_m)_1+\cdots\end{aligned}\tag{109}$$

and with the energy balance

$$\begin{aligned}E &= E_0+\frac{\hbar^2k_0^2}{2M} = E_n+\frac{\hbar^2k_n^2}{2M}\\ \mathcal{E}^{(i)}_n(r)-E &= -\frac{\hbar^2k_n^2}{2M}+V^{(i)}_{nn}+\cdots\end{aligned}\tag{110}$$

where the superscript (i) denotes non-φ_1 states.

Thus, in terms of the angular momentum operators of (98), the approximate equations of motion (105) become

$$\nabla_r^2 F_0 + \left[k_0^2 - \frac{2M}{\hbar^2} V_{00}(r)\right] F_0 = 0 \tag{111}$$

$$\nabla_r^2 F_n^{(i)} + \left[k_n^2 - \frac{2M}{\hbar^2} V_{nn}^{(i)}(r) - \frac{1}{r^2}\int (\psi_n^{(i)})_1 (P_x^2+P_y^2)(\psi_n^{(i)})_1 d\tau_a - \frac{\cos^2\theta}{r^2\sin^2\theta}(\sigma^2)_n^{(i)}\right] F_n^{(i)} =$$

$$= \frac{-\delta^{(i)(1)}}{E_0-E_n}\left[2\nabla_r F_0 \cdot \nabla_r V_{n0}^{(1)}(r) + F_0 \nabla_r^2 V_{n0}^{(1)}(r) - F_0 \frac{V_{n0}^{(1)}}{r^2}\int (\psi_n^{(1)})_1 (P_x^2+P_y^2)(\psi_n^{(1)})_1 d\tau_a\right] - \tag{112}$$

$$-2\nabla_r F_0 \cdot \sum_{m\neq 0} \frac{V_{m0}^{(1)}(r)}{(E_0-E_m)r}\int (\psi_n^{(i)})_1 \left[\vec{i}_\theta(-iP_x) + \vec{i}_\varphi(-iP_y)\right](\psi_m^{(1)})_1 d\tau_a$$

where $\delta^{(i)(1)} = 0$ unless $\chi^{(i)} = \chi^{(1)}$, a non-φ_1 state with $\sigma=0$.

(g) an approximate form of F_0 for large relative momentum

If the reduced mass of the system is sufficiently large that the magnitude of the relative momentum is much greater than the change of momentum in the collision, the term $\frac{\hbar^2 k_0^2}{2M}$ dominates the expression

$$\frac{\hbar^2 k_0^2}{2M} - (\mathcal{E}_0(r) - E_0) + \frac{\hbar^2}{2M}\int \chi_0 \nabla_r^2 \chi_0 d\tau_a$$

of (103), and the approximate solution of (103) is the plane wave $e^{ik_0 z}$ satisfying the initial boundary condition.

As a refinement of this approximate solution, consider the variation of F_0 to be predominantly in the variable z, so that (103) may be written in the approximate form

$$\frac{d^2F_0}{dz^2} + \left[k_0^2 - \frac{2M}{\hbar^2}(\mathcal{E}_0 - E_0) + \int \chi_0 \nabla_r^2 \chi_0 d\tau_a\right] F_0 = 0$$

with the approximate WKB solution

$$F_0 \simeq \frac{k_0^{1/2}}{\left[k_0^2 - \frac{2M}{\hbar^2}(\mathcal{E}_0 - E_0) + \int \chi_0 \nabla_r^2 \chi_0 d\tau_a\right]^{1/4}} e^{i\int^z \sqrt{k_0^2 - \frac{2M}{\hbar^2}(\mathcal{E}_0 - E_0) + \int \chi_0 \nabla_r^2 \chi_0 d\tau_a}\, dz}$$

or with sufficiently large mass M ,

$$F_0 \simeq e^{ik_0 z - i\frac{1}{\hbar v_0}\int^z (\mathcal{E}_0 - E_0)\, dz} + \cdots \tag{113}$$

The ground state of the system for these approximations takes the form

$$F_0 \chi_0 e^{-\frac{i}{\hbar}Et} = \chi_0 e^{-\frac{i}{\hbar v_0}\int^z \mathcal{E}_0 dz} e^{\frac{i}{\hbar v_0}E_0 z} e^{ik_0 z} e^{-\frac{i}{\hbar}Et} \tag{114}$$

which agrees with (2), with (4) and (40).

For weak interactions (113) becomes

$$F_0 \approx e^{ik_0 z - i\frac{1}{\hbar v_0}\int^z V_{00}(r)\, dz} + \cdots \tag{115}$$

which, together with (109), reduces (114) to a form proportional to (38).

(h) the approximate solution for S state excitation with low velocity and weak interaction

For the excitation of an S state, $(\sigma^2)_S = 0$ and $\int \psi_S (P_x^2 + P_y^2) \psi_S \, d\tau_a = 0$ so that the equation of motion (112) becomes

$$\nabla_r^2 F_S + \left[k_S^2 - \frac{2M}{\hbar^2} V_{SS}(r)\right] F_S = \frac{1}{E_S - E_0}\left[2\nabla_r F_0 \cdot \nabla_r V_{S0} + F_0 \nabla_r^2 V_{S0}\right] \tag{116}$$

and, since V_{SS} is spherically symmetric, the asymptotic solution, according to (106), is

$$F_S \sim -\frac{e^{ik_S r}}{r}\frac{1}{4\pi}\int \mathcal{F}_S(\vec{r}, \pi - \Theta)\frac{1}{E_S - E_0}\left[2\nabla_r F_0 \cdot \nabla_r V_{S0} + F_0 \nabla_r^2 V_{S0}\right] d\tau \tag{117}$$

where, to the same order of approximation, $\mathcal{F}_S$ is the solution of

$$\nabla_r^2 \mathcal{F}_S + \left[k_S^2 - \frac{2M}{\hbar^2} V_{SS}(r)\right] \mathcal{F}_S = 0 \tag{118}$$

Writing the integrand of (117) in the form $\nabla_r^2(F_0 V_{s0}) - V_{s0}\nabla_r^2 F_0$, transferring the operator ∇_r^2 to $\mathcal{F}_s$, and substituting from (111), (118), and (110), the solution (117) becomes

$$F_s \sim -\frac{e^{ik_s r}}{r}\frac{M}{2\pi\hbar^2}\int \mathcal{F}_s\left[1+\frac{V_{ss}-V_{00}}{E_s-E_0}\right]V_{s0}F_0\,d\tau \tag{119}$$

If, in addition to the conditions necessary for this approximate solution, the reduced mass is large enough that the relative motions F_0 and $\mathcal{F}_s$ remain predominantly plane waves, then $e^{-i\vec{k}_s\cdot\vec{r}}$ and $e^{i\vec{k}_0\cdot\vec{r}}$ replace $\mathcal{F}_s$ and F_0 in (119), and the total excitation probability becomes

$$I_s = \frac{k_s}{k_0}\left(\frac{M}{2\pi\hbar^2}\right)^2\int\left|\int V_{s0}(r)\left[1+\frac{V_{ss}-V_{00}}{E_s-E_0}\right]e^{i(\vec{k}_0-\vec{k}_s)\cdot\vec{r}}\,d\tau\right|^2 \sin\theta\,d\theta\,d\varphi \tag{120}$$

For a momentum $\hbar k_0$ that is sufficiently large (120) reduces to the impact parameter approximation of (85) with (56). Although proof[9] of the reduction is complex, it begins from the development of the exponent of (120) in the form $i(k_0-k_s)z +$ $ik_s \times$ function of the scattering angles, and the first term retains its form in the reduction. Using (110), it may be written as $\frac{i}{\hbar v}(E_s-E_0)z$ with $v=\frac{1}{2}(v_0+v_s)$, and the elaboration of (115) for (111) and (118) extends this to $\frac{i}{\hbar v}\int^z(E_s-E_0+V_{ss}-V_{00})dz$ which is the impact parameter exponent. If $1+\frac{V_{ss}-V_{00}}{E_s-E_0}\simeq 1$, the solution (120) becomes identical with the Born approximation.

(i) the approximate solution for P state excitation with low velocity and weak interaction

For the excitation of a P state of a single electron atom, the total electronic angular momentum becomes $\sqrt{l(l+1)}=\sqrt{2}$, with components

$$(\sigma)_p^{(1)} = 0 \qquad \text{and} \qquad \int (\psi_p^{(1)})_1 \left(P_x^2 + P_y^2\right)(\psi_p^{(1)})_1 \, d\tau_a = 2$$
$$(\sigma^2)_p^{(i)} = 1 \qquad \text{and} \qquad \int (\psi_p^{(i)})_1 \left(P_x^2 + P_y^2\right)(\psi_p^{(i)})_1 \, d\tau_a = 1 \quad (i=2,3) \tag{121}$$

With the operations

$$(-iP_x)(\psi_p^{(1)})_1 = (\psi_p^{(2)})_1 \qquad \text{and} \qquad (-iP_y)(\psi_p^{(1)})_1 = (\psi_p^{(3)})_1$$

the approximate equations of motion (112) become

$$\nabla_r^2 F_p^{(1)} + \left[k_p^2 - \frac{2M}{\hbar^2} V_{pp}^{(1)}(r) - \frac{2}{r^2}\right] F_p^{(1)} = \frac{1}{E_p - E_0}\left[2\nabla_r F_0 \cdot \nabla_r V_{p0} + F_0 \nabla_r^2 V_{p0} - 2F_0 \frac{V_{p0}}{r^2}\right]$$
$$\nabla_r^2 F_p^{(2)} + \left[k_p^2 - \frac{2M}{\hbar^2} V_{pp}^{(2)}(r) - \frac{1}{r^2} - \frac{\cos^2\theta}{r^2 \sin^2\theta}\right] F_p^{(2)} = \frac{1}{E_p - E_0}\left[\frac{2V_{p0}^{(1)}}{r^2} \frac{\partial}{\partial\theta} F_0\right] \tag{122}$$
$$\nabla_r^2 F_p^{(3)} + \left[k_p^2 - \frac{2M}{\hbar^2} V_{pp}^{(2)}(r) - \frac{1}{r^2} - \frac{\cos^2\theta}{r^2 \sin^2\theta}\right] F_p^{(3)} = \frac{1}{E_p - E_0}\left[\frac{2V_{p0}^{(1)}}{r^2 \sin\theta} \frac{\partial}{\partial\varphi} F_0\right]$$

These equations are distinguished by the dependence of excitation and scattering on coupling of atomic state and particle, which is expressed in the spherical symmetry of the potential interaction $V_{pp}^{(i)}(r)$ and in the angular-momentum coupling terms that appear in the coefficient of $F_p^{(i)}$.

Since the initial wave F_0, according to (111) and (104), is independent of φ, the right member of the last equation vanishes and hence $F_p^{(3)} \equiv 0$. Because of the difference in coefficients of $F_p^{(1)}$ and $F_p^{(2)}$ in (122), the remaining two excited states of the system are not coherent. Excitation of $\chi_p^{(1)}$ depends on radial gradients of relative motion and upon the precession coupling of $F_0 \frac{V_{p0}}{r^2}$. Excitation of $\chi_p^{(2)}$ depends, as in the impact parameter description, on the angular gradients of the relative motion, which connects angular momentum states of the particle-coupled χ_0 and $\chi_p^{(2)}$.

The first equation of (122) is spherically symmetric in the coefficient of $F_p^{(1)}$, and hence, the asymptotic solution according to (106) and (107) is

$$F_p^{(1)} \sim -\frac{e^{ik_p r}}{r}\frac{1}{4\pi}\int \mathcal{F}_p(r,\pi-\theta)\frac{1}{E_p-E_o}\left[2\nabla_r F_o\cdot\nabla_r V_{po}^{(1)} + F_o\nabla_r^2 V_{po}^{(1)} - 2F_o\frac{V_{po}^{(1)}}{r^2}\right]d\tau \tag{123}$$

where $\mathcal{F}_p^{(1)}$ is the solution of

$$\nabla_r^2\mathcal{F}_p^{(1)} + \left[k_p^2 - \frac{2M}{\hbar^2}V_{pp}^{(1)}(r) - \frac{2}{r^2}\right]\mathcal{F}_p^{(1)} = 0 \tag{124}$$

with asymptotic behavior (108). Writing the integrand in the form $\left[\nabla_r^2(F_o V_{po}^{(1)}) - V_{po}^{(1)}\nabla_r^2 F_o - 2F_o\frac{V_{po}^{(1)}}{r^2}\right]$, transferring the operator ∇_r^2 to $\mathcal{F}_p^{(1)}$, and introducing (111), (124), and (110), (123) becomes

$$F_p^{(1)} \sim -\frac{e^{ik_p r}}{r}\frac{M}{2\pi\hbar^2}\int \mathcal{F}_p^{(1)}\left[1 + \frac{V_{pp}^{(1)}-V_{oo}}{E_p-E_o}\right]V_{po}^{(1)}F_o\,d\tau \tag{125}$$

If the reduced mass is sufficiently large that the relative motion states F_o and $\mathcal{F}_p^{(1)}$ of (111) and (124) remain predominantly plane waves in the form (115), the total excitation probability (93) for the $\chi_p^{(1)}$ state approaches the impact parameter value of (85) with (79).

In terms of unmodified plane waves, (125) becomes

$$F_p^{(1)} \sim -\frac{e^{ik_p r}}{r}\frac{M}{2\pi\hbar^2}\int V_{po}^{(1)}(r)\left[1 + \frac{V_{pp}^{(1)}-V_{oo}}{E_p-E_o}\right]e^{i(\vec{k}_o-\vec{k}_p)\cdot\vec{r}}\,d\tau \tag{126}$$

which has the same form as the S state solution (119), for, with the condition of large momentum, the precession coupling of (124) has a negligible effect. Although the P state solution (126) has the same appearance as the Born approximation, the element $V_{po}^{(1)}(r)$ is a spherically symmetric function of r, whereas the interaction element of the Born approximation depends on the angle between $\vec{r}$ and the fixed orientation of the P states $(\psi_p^{(1)})_a$. Since this orientation is arbitrary it may be taken to be the direction of $\vec{K} = \vec{k}_0 - \vec{k}_p$, for which the Born approximation has the form

$$\frac{e^{ik_p r}}{r} \frac{M}{2\pi\hbar^2} \int V^{(1)}_{p0}(r) \cos\theta_K \, e^{iKr\cos\theta_K} d\tau \tag{127}$$

and this is the complete solution since the integral for the remaining elements $V^{(1)}_{p0}(r) \sin\theta_K \cos\varphi_K$ and $V^{(1)}_{p0}(r) \sin\theta_K \sin\varphi_K$ (see (31) with $\varpi \to \theta_K$ and $\varphi \to \varphi_K$) vanish in the integration over φ_K .

Since $V^{(1)}_{p0}(r)$, $V^{(1)}_{pp}(r)$, and $V_{00}(r)$ are spherically symmetric functions of r , the stationary state approximation (126) may be reduced to the form

$$F^{(1)}_p \sim -\frac{e^{ik_p r}}{r} \frac{2M}{\hbar^2} \int_0^\infty V^{(1)}_{p0}(r) \left[1 + \frac{V^{(1)}_{pp} \, V_{00}}{E_p - E_0} \right] \frac{\sin Kr}{Kr} r^2 dr \tag{128}$$

where $K = |\vec{k}_0 - \vec{k}_p|$.

The second equation of (122) is complicated by the presence of the angle-dependent term in the coefficient of $F^{(2)}_p$, which precludes the form (106) and requires a detailed development of the solution. The θ-dependent parts of the left member of (122) have the eigenfuntions $\frac{1}{r^2} \mathcal{J}_n(\theta)$ with eigenvalues $\frac{(n+1)(n+2) - 1}{r^2}$, where $\mathcal{J}_n$ is the Jacobi polynomial, defined by

$$\mathcal{J}_n(\theta) = \sqrt{\frac{(n+2)!(2n+3)}{2 \cdot n! \, (n+1)!^2}} \, \frac{1}{\sin\theta} \, \frac{1}{2^{n+1}} \frac{d^n}{d\cos\theta^n} \left(-\sin^2\theta\right)^{n+1} \quad \text{and} \quad \int_0^\pi \mathcal{J}_n(\theta) \mathcal{J}_m(\theta) \sin\theta \, d\theta = \delta_{nm} \tag{129}$$

The functions $\mathcal{J}_n(\theta)$ are proportional to $\sin\theta$. Since F_0 is independent of φ , the right member of (122) and $F^{(2)}_p$ may be expanded in terms of the orthonormal set $\mathcal{J}_n(\theta)$,

$$\frac{2V^{(1)}_{po}(r)}{(E_p-E_o)r^2}\frac{\partial F_o}{\partial\theta} = \sum_n A^{(2)}_n(r)\mathcal{J}_n(\theta)$$

$$F^{(2)}_p = \sum_n B^{(2)}_n(r)\mathcal{J}_n(\theta) \tag{130}$$

and these expansions, substituted in (122), yield the equation

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + k_p^2 - \frac{2M}{\hbar^2}V^{(2)}_{pp}(r) - \frac{(n+1)(n+2)}{r^2}\right]B^{(2)}_n(r) = A^{(2)}_n(r) \tag{131}$$

for $B^{(2)}_n(r)$.

If the asymptotic decline of $V^{(2)}_{pp}(r)$ is steeper than $\frac{1}{r}$, an asymptotic solution may be obtained in the form[10]

$$F^{(2)}_p \sim -\frac{e^{ik_pr}}{r}\sum e^{-i\frac{\pi}{2}(n+1)+i\delta^{(2)}_n}\left(\int_0^\infty L^{(2)}_n(r)A_n(r)r^2dr\right)\mathcal{J}_n(\theta) \tag{132}$$

where $L^{(2)}_n(r)$ is the solution of

$$\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}L^{(2)}_n + \left[k_p^2 - \frac{2M}{\hbar^2}V^{(2)}_{pp}(r) - \frac{(n+1)(n+2)}{r^2}\right]L^{(2)}_n = 0$$

or of

$$\frac{d^2}{dr^2}(rL^{(2)}_n) + \left[k_p^2 - \frac{2M}{\hbar^2}V^{(2)}_{pp}(r) - \frac{(n+1)(n+2)}{r^2}\right](rL^{(2)}_n) = 0 \tag{133}$$

with the asymptotic behavior

$$L^{(2)}_n \sim \frac{\sin\left(k_pr - \frac{\pi}{2}(n+1) + \delta^{(2)}_n\right)}{k_pr} \tag{134}$$

The corresponding development for the $F^{(1)}_p$ solution takes the form

$$F^{(1)}_p \sim -\frac{e^{ik_pr}}{r}\sum_n e^{-i\frac{\pi}{2}\nu^{(1)}_n + i\delta^{(1)}_n}\left(\int_0^\infty L^{(1)}_n(r)A^{(1)}_n(r)\,r^2dr\right)P_n(\cos\theta) \tag{135}$$

where $P_n(\cos\theta)$ is the Legendre function, $A^{(1)}_n$ is the coefficient of P_n in the expansion of the right member of (122), and $L^{(1)}_n$ is the solution of

$$\frac{d^2}{dr^2}(rL^{(1)}_n) + \left[k_p^2 - \frac{2M}{\hbar^2}V^{(1)}_{pp}(r) - \frac{n(n+1)+2}{r^2}\right](rL^{(1)}_n) = 0 \tag{136}$$

with the asymptotic behavior

$$L_n^{(1)} \sim \frac{\sin\left(k_p r - \frac{\pi}{2}\nu_n^{(1)} + \delta_n^{(1)}\right)}{k_p r} \tag{137}$$

where
$$\nu_n^{(1)} = \frac{1}{2}\left(\sqrt{4n^2+4n+9}\right) - 1 \,)$$

In the forms (134) and (137), $\delta_n^{(1)}$ and $\delta_n^{(2)}$ are the phases depending on $V_{pp}^{(1)}$ and $V_{pp}^{(2)}$.

The incoherence of the states of motion (135) and (132) for $\chi_p^{(1)}$ and $\chi_p^{(2)}$, respectively, is expressed in the difference of the coefficients of $rL_n^{(1)}$ and $rL_n^{(2)}$ in (136) and (133). For the condition of a large relative momentum, gained at low velocity by a sufficiently large reduced mass, and for separations r not too near zero, the WKB approximations of (136) and (133) take the forms

$$rL_n^{(1)} \simeq \frac{1}{\sqrt{k_p}\left[k_p^2 - \frac{2M}{\hbar^2}V_{pp}^{(1)} - \frac{n^2+n+2}{r^2}\right]^{1/4}}\left\{e^{i\int^r\sqrt{k_p^2 - \frac{2M}{\hbar^2}V_{pp}^{(1)} - \frac{n^2+n+2}{r^2}}\,dr} - e^{-i\int^r\sqrt{k_p^2 - \frac{2M}{\hbar^2}V_{pp}^{(1)} - \frac{n^2+n+2}{r^2}}\,dr}\right\}\frac{1}{2i}$$

$$rL_n^{(2)} \simeq \frac{1}{\sqrt{k_p}\left[k_p^2 - \frac{2M}{\hbar^2}V_{pp}^{(2)} - \frac{n^2+3n+2}{r^2}\right]^{1/4}}\left\{e^{i\int^r\sqrt{k_p^2 - \frac{2M}{\hbar^2}V_{pp}^{(2)} - \frac{n^2+3n+2}{r^2}}\,dr} - e^{-i\int^r\sqrt{k_p^2 - \frac{2M}{\hbar^2}V_{pp}^{(2)} - \frac{n^2+3n+2}{r^2}}\,dr}\right\}\frac{1}{2i}$$

which, for the large momentum $\hbar k_p = Mv_p$, may be written in the approximate form

$$L_n^{(1)} \simeq \frac{1}{k_p r\left[1 - \frac{2M}{\hbar^2 k_p^2}V_{pp}^{(1)} - \frac{n^2+n+2}{k_p^2 r^2}\right]^{1/4}}\left\{e^{ik_p r - \frac{i}{\hbar v_p}\int^r V_{pp}^{(1)}(r)\,dr + \cdots} - e^{-ik_p r + \frac{i}{\hbar v_p}\int^r V_{pp}^{(1)}(r)\,dr + \cdots}\right\}\frac{1}{2i}$$

$$L_n^{(2)} \simeq \frac{1}{k_p r\left[1 - \frac{2M}{\hbar^2 k_p^2}V_{pp}^{(2)} - \frac{n^2+3n+2}{k_p^2 r^2}\right]^{1/4}}\left\{e^{ik_p r - \frac{i}{\hbar v_p}\int^r V_{pp}^{(2)}(r)\,dr + \cdots} - e^{-ik_p r + \frac{i}{\hbar v_p}\int^r V_{pp}^{(2)}(r)\,dr + \cdots}\right\}\frac{1}{2i}$$

so the incoherence of the states $F_p^{(1)}$ and $F_p^{(2)}$ appears, for this system, in the difference $\frac{1}{\hbar v_p}\int^r\left(V_{pp}^{(1)} - V_{pp}^{(2)}\right)dr$ at sufficiently low velocity, which is of the same form as the impact parameter development (80).

The neglected terms of (94) that connect the states $\chi_p^{(1)}$, $\chi_p^{(2)}$, and $\chi_p^{(3)}$ are, to the first order in this approximation with $\chi_p^{(i)} \simeq (\psi_p^{(i)})_1$, and using (98) or (58) with $\varpi \to \theta$,

$$
\begin{aligned}
&+ \frac{2\cos\theta}{r^2\sin\theta} F_p^{(2)} + \frac{2}{r^2}\frac{\partial}{\partial\theta} F_p^{(2)} + \frac{2}{r^2\sin\theta}\frac{\partial}{\partial\varphi} F_p^{(3)} \\
&\qquad - \frac{2}{r^2}\frac{\partial}{\partial\theta} F_p^{(1)} + \frac{2\cos\theta}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi} F_p^{(3)} \\
&\qquad\qquad - \frac{2}{r^2\sin\theta}\frac{\partial}{\partial\varphi} F_p^{(1)} - \frac{2\cos\theta}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi} F_p^{(2)}
\end{aligned}
\qquad (138)
$$

for the right members of (122), respectively. Of these terms $F_p^{(3)}$ vanishes in the first order, and $F_p^{(1)}$ and $F_p^{(2)}$ are not functions of φ, which leaves the terms in $F_p^{(2)}$ for the $F_p^{(1)}$ equation and the term in $F_p^{(1)}$ for the $F_p^{(2)}$ equation. At low velocities $F_p^{(1)}$ and $F_p^{(2)}$ are not coherent and both are small compared to F_0.

(j) the effect of atom-particle coupling at low relative velocities

In the excitation of atoms by collision, the probability distribution of the excitation varies over the members of an asymptotically-degenerate set of atomic states, with the consequence that associated with the intensity distribution of scattered waves is a distribution of atomic orientations. With the appearance of the atom-particle coupling at low relative velocities, according to the stationary state approximation, the relative probability distribution of atomic orientation is directly proportional to the intensity distribution of the scattered wave.

This behavior contrasts markedly with that of the Born approximation, appropriate at high velocities, where the probability distribution of orientation of the vanishing-momentum-component state $(\sigma=0)$ is proportional to the intensity distribution of the momentum change, that is, to the relative probability distribution of momentum change associated with the intensity distribution of the scattered wave.

Consequently, for large relative momenta with little scattering, the predominant orientation of excited atomic states is in the incident direction, according to the stationary state approximation, and normal to the incident direction, according to the Born approximation. For a vanishing final momentum (incident relative energy of motion near the threshold energy of excitation), the stationary state orientation distribution is uniform, whereas the Born distribution is confined to the incident direction, which is the direction of the momentum change. This difference in orientation distributions should be revealed in the measured polarization of the subsequent radiation.

7. Summary of the development

The principal conclusions of the foregoing development are: (1) that in the excitation of S states from an S state by collision the asymptotic state or Born solution is a valid approximation at low velocities for weak interactions of atomic state and charged particle, but in the excitation of states that form a degenerate group, the Born approximation requires a coherence of the group throughout the collision, and, because of differences in the interactions of the states with the incident charge, the coherence is lost in the extended collision period at low relative velocity; (2) that at sufficiently low velocity of relative motion, according to the equation of motion in terms of stationary states, the atomic states of the system are coupled to the moving particle, and differences in coupling energy produce an incoherence of states of the system; (3) that excitation at low velocities is an interaction of particle-coupled atomic states, and this coupling orients excited states to the direction of scattering.

On the basis of the equation of motion for the collision expressed in terms of asymptotic or isolated atom states and in terms of the stationary states, the thesis introduces: the velocity-dependent conditions (27), (72), and (83) on the coherence of asymptotically-degenerate states in the collision; the approximate equations of motion (60) and (122) with (138) which include the interaction of asymptotically-degenerate states; and the approximate solutions (79), (84), (125), and (132) for sufficiently low velocities of relative motion; and establishes regions of agreement of the various approximate representations of the solution.

Improvement in the description of the low velocity theory would be gained by an exact solution of equations (60) and of (122) with (138) in order to show the nature of transition between the approximate solutions of high and low relative velocity; and also by a detailed stationary state solution at low velocity for a simple collision system, together with an experimental measurement of cross sections and radiation polarizations for the same system.

8. A review of theories of low velocity collisions

(a) the impact parameter form

In Mott's development[11] of the low velocity theory of excitation in the impact parameter form, the stationary states as functions of time are taken to be of the first form of (40) or $\chi_n e^{-\frac{i}{\hbar}\mathcal{E}_n t}$ (in the notation used here) for which the equations of motion become (48) with $\dot{c}_n$ replaced by $\dot{c}_n - \frac{i}{\hbar}\frac{\partial \mathcal{E}_n}{\partial t} t\, c_n$. This second term is discarded by Mott as relatively negligible, although this is not justified, and the equations of motion then gain the form of (48) but with $e^{\frac{i}{\hbar}(\mathcal{E}_n-\mathcal{E}_m)t}$ in place of $e^{\frac{i}{\hbar}\int^t(\mathcal{E}_n-\mathcal{E}_m)dt}$.

The approximation for the perturbation of a ground state is written as

$$C_n(t) = -\int_{-\infty}^{t}\left(\int \chi_n^* \frac{\partial \chi_0}{\partial t}\, d\tau_a\right) e^{i\frac{\mathcal{E}_n-\mathcal{E}_0}{\hbar}t}\, dt \tag{α}$$

For the weak interaction of distant paths, Mott then makes the approximation

$$\chi_0(\vec{r},\vec{r}_a) = \psi_0(\vec{r}_a) + \sum_{n\neq 0}\frac{V_{no}(\vec{r})}{E_0-E_n}\psi_n(\vec{r}_a) + \cdots \tag{β}$$

$$\chi_n(\vec{r},\vec{r}_a) = \psi_n(\vec{r}_a) + \sum_{m\neq n}\frac{V_{mn}(\vec{r})}{E_n-E_m}\psi_m(\vec{r}_a) + \cdots \tag{γ}$$

for which the solution (α) reduces to

$$C_n(t) = -\int_{-\infty}^{t}\frac{\partial V_{no}(r)}{\partial t}\,\frac{1}{E_0-E_n}\, e^{i\frac{E_n-E_0}{\hbar}t}\, dt \tag{δ}$$

and the final value, integrating by parts, becomes

$$C_n(\infty) = \frac{1}{i\hbar}\int_{-\infty}^{\infty} V_{no}(\vec{r})\, e^{i\frac{E_n-E_0}{\hbar}t}\, dt$$

or the Born approximation, which Mott concludes to be a general result. However, for other than S states, the approximation (γ) neglects infinite terms that connect degenerate states. Or, if $\psi_n(\vec{r}_a)$ of (β) and (γ) are assumed to represent particle-oriented states, then the reduction (δ) is incomplete and does not agree with the Born approximation.

In Frame's application (12) of Mott's approximate solution (α) to the collision of a Lithium ion Li^{++} and an α-particle, the ground state χ_0 is developed in the form $A(r)e^{-\frac{Z_1}{a_0}r_1 - \frac{Z}{a_0}f(r)|\vec{r}-\vec{r}_1|}$ with the value of $f(r)$ adjusted to obtain a minimum value of $\mathcal{E}_0(r)$. The excited P states are taken, without comment, to be the particle-oriented states $(\psi_P)_1$. The solution (α) is evaluated in the equivalent form (using (41))

$$C_P^{(1)}(\infty) = \int_{-\infty}^{\infty} \frac{1}{\mathcal{E}_P - \mathcal{E}_0}\left[(\psi_P^{(1)})_1 \frac{\partial V(\vec{r},\vec{r}_1)}{\partial z} \chi_0(\vec{r},\vec{r}_1)\, d\tau_a\right] e^{i\frac{\mathcal{E}_P-\mathcal{E}_0}{\hbar v}z}\, dz$$

which, except for the exponent, is the correct low velocity approximation. The calculation, however, is carried out for velocities between 4.7 and 18.8 x 10^8 cm/sec., or, since this collision corresponds to the calculations of figures 2 and 3, for values of $\left(\frac{\omega_{P0} a_0}{Z_1 v}\right)^{-1}$ between 2 and 8 which, with $\frac{Z}{Z_1} = \frac{2}{3}$, borders on the region of the Born approximation where the connection of the states $(\psi_P^{(1)})_1$ and $(\psi_P^{(2)})_1$ cannot be neglected. The impression is gained that the difference of Frame's solution and the Born approximation is considered to be a result of the development of χ_0 and $\mathcal{E}_0$, although a major contribution is the form taken for the excited states.

(b) the wave motions of collision and scattering

Mott and Massey's perturbation solution[13] for stationary states is the form (105). In approximation, however, the excited states are taken to be of the form (γ), which is not admissible as a stationary state discipline, and hence the reduction, by use of (106), to the Born approximation as a general result for weak interactions and low velocities is erroneous. In using (γ), the important first order terms of $\int \chi_n \nabla_i^2 \chi_n d\tau_a$ do not appear in the equation of motion.

In the application by Massey and Smith[14] to the P-state excitation of a helium atom by a proton, the excited states are taken to be the asymptotic states $(\psi_p^{(i)})_0$ of fixed orientation which is a repetition of the error contained in the approximate forms of the general theory.

(c) the correction embodied in the thesis

The foregoing theories and applications overlook the effect of the phase relations of asymptotically-degenerate states in the collision and the importance of atom-particle coupling at low relative velocity. According to the thesis development, the Born approximation requires a coherence, and the stationary state approximation a sufficient incoherence, of the states of the system that are asymptotically-degenerate, and, since the phase relations in the collision depend on the velocity as well as the interaction, in the manner indicated in figures 2 and 3, the Born approximation, except for S state excitations, cannot be extended to arbitrarily small velocities nor the stationary state approximation to arbitrarily large velocities of relative motion.

(d) electrons as incident particles

The measured total cross sections of the inelastic collision of an electron and helium atom agree with the calculated Born approximation over the range of velocities for an S state excitation, but is considerably less than the calculated value for a P state excitation in the region adjacent the threshold energy of relative motion. Mott and Massey[15] attribute this difference in the effectiveness of the Born approximation to the difference in the behavior of the interaction element $V_{no}(\bar{r})$ which, at large separations, diminishes like $e^{-\alpha r}$ for the S state and like $\frac{1}{r^2}$ for the P state, and the greater scattering effect of the P state requires the consideration of relative motions more accurate than the Born plane waves. In contrast to this explanation is that suggested by the principles developed in the thesis, according to which, the failure of the Born approximation for the P state excitation is due to the incoherence of the degenerate asymptotic P states at the vanishing and low velocities that appear for excitation near the threshold energy. Although the impact parameter development does not strictly apply near the threshold, the condition (27) is the form of the limitation on the Born approximation for the P state excitation.

The polarization of radiation from atoms excited by electrons vanishes at or near the threshold energy of relative motion which cannot be explained by the Born approximation[16] and is called "anomalous". This behavior may be due to the coupling of the excited atomic state to the slowly moving electron and the consequent uniform distribution of orientation that follows from the uniform distribution of scattered electrons near the threshold energy.

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