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THE QUANTUM MECHANICAL THEORY OF COLLISIONS

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The Quantum Mechanical Theory of Collissions.

I.- In the present course we shall consider the quantum mechanical treatment of problems of particle interactions in which at least one of the particles is unbound and therefore able to travel large distances freely. In effect such particles are able to communicate the results of their interaction directly to macroscopic detection apparatus. The interpretation of the resulting data is in general the most direct way of forming conclusions about the interactions.

A considerable variety of physical phenomena involves unbound particles. Among the simplest are scattering processes ; in particular the deflection of particles from a collinated beam. More general collision processes which induce reactions of various sorts also lie within the class we shall examine. Our chief concern will be with the means of solving problems in which well-defined models have been postulated to describe the basic interactions. We shall restrict ourselves, in fact, to the treatment of fairly simple models, and shall discuss a number of approaches to the problems they raise.

We begin by discussing the scattering of particles by a simple potential field, fixed in space. The problem of two free particles with a potential between them of course assumes this form in the center-of-mass system. By imagining that a beam of particles of constant strenght is at all times being scattered by the potential, we may seek to describe the situation with the stationary-state Schrödinger equation.

$$\left(\nabla^2 + k^2 - \frac{2m}{\hbar^2} V(\vec{r})\right) \psi(\vec{r}) = 0 \tag{1}$$

Here $V(\vec{r})$ is the given potential function, $k^2 = \frac{2mE}{\hbar^2}$ with E the energy and m the mass (or reduced mass) of the incident particles. The solutions of this equation are not specified uniquely until further conditions are stated. As usual in quantum mechanics, we must require that the wave function $\psi(\vec{r})$ be quadratically integrable over any finite volume.

Assuming that the potential $V(\vec{r})$ is confined to a finite region, or decrease sufficiently rapidly with increasing radii r, we may, as a final condition on the wave function, specify the form it must assume outside the region of interaction. It will evidently be the superposition of a plane wave, representing the initial beam, and an outgoing, spherical wave representing the scattered particles. A wave function $\psi_{\vec{k}}(\vec{r})$ for which the incident beam is travelling in the direction $\vec{k}$ must, at large radii, assume the asymptotic form .

$$\psi_{\vec{k}}(\vec{r}) \sim e^{i\vec{k}\cdot\vec{r}} + f(\theta)\frac{e^{ikr}}{r} \tag{2}$$

where $|\vec{k}| = k$, and $f(\theta)$ is a complex-valued function which characterizes the distribution of particles scattered through the angle θ . The way in which it does so may be seen by a loose argument which we shall render more precise a little later. If the velocity of the incoming particles is $\vec{v} = \frac{\hbar\vec{k}}{m}$, then since the plane wave of (r) has unit amplitude, the incident flux is v particles per unit area per second. The number of particles scattered in the direction θ, per second, lying within the element of solid angle $d\Omega$ containing θ is $v|f(\theta)|^2 d\Omega$. The differential cross-section $d\sigma$ for scattering within this element is the ratio of this expression to the incident flux.

$$d\sigma = |f(\theta)|^2 \, d\Omega \tag{3}$$

Some general properties of the scattering amplitude.

The function $f(\theta)$ can only be found, in general, by actually solving the Schroedinger-equation (1), a procedure whose difficulty depends considerably on the nature of the potential $V(\vec{r})$, and on the incident energy. Before discussing the means by which this is done, we shall point out certain general relations that the scattering amplitude $f(\theta)$ must satisfy which are independent of both the potential and the incident energy, and which follow directly from the relations (1) and (2).

It will be convenient to replace the notation $f(\theta)$ for the scattering amplitude by one which contains both the initial and final directions of particle motion. We shall write $f(\vec{k}',\vec{k})$ to represent the amplitude for scattering from the direction $\vec{k}$ to the direction $\vec{k}'$. ($|\vec{k}'|=|k|=k$) The asy ptotic wave function (2) will then be written in the form

$$\psi_{\vec{k}}(\vec{r}) \sim e^{i\vec{k}\vec{r}} + f(\vec{k}_r, \vec{k})\frac{e^{ikr}}{r} \tag{4}$$

in which $\vec{k}_r$ is a propagation vector in the direction $\vec{r}$.

The wave equation (1) is satisfied equally well by wave functions having incident beams in all possible directions. In particular let us consider the equations satisfied by the wave functions $\psi_{\vec{k}}$ and $\psi_{-\vec{k}'}$ corresponding to incident beams in the directions $\vec{k}$ and $\vec{k}'$ respectively. If we multiply each of these equations by the other wave function and substract we have the identity

$$\psi_{-k'} \nabla^2 \psi_k - \psi_k \nabla^2 \psi_{-k'} = 0 \tag{5}$$

Integrating over the volume bounded by a sphere S we have, by Green's theorem.

$$\int_S \left(\psi_{-k'} \frac{\partial}{\partial r} \psi_k - \psi_k \frac{\partial}{\partial r} \psi_{-k'} \right) r^2 \, d\Omega = 0 \tag{6}$$

If now we give the sphere a sufficiently large radius the wave functions may be represented on its surface by the asymptotic form (4). Hence

$$0 = \int_S \left\{ \left(e^{-i\vec{k}'\cdot\vec{r}} + f(\vec{k}_r, -\vec{k}') \right) \frac{\partial}{\partial r} \left(e^{i\vec{k}\cdot\vec{r}} + f(\vec{k}_r, \vec{k}) \frac{e^{ikr}}{r} \right) - \left(e^{ik\cdot r} + f(k_r, k) \frac{e^{ikr}}{r} \right) \frac{\partial}{\partial r} \left(e^{-ik'r} + f(k_r, -k') \frac{e^{ikr}}{r} \right) \right\} d\Omega \tag{7}$$

The contributions of the pure plane wave terms to this integral vanish. This may be seen by writing them in the form

$$\frac{1}{r} \int (\vec{k} + \vec{k}') \cdot \vec{r} \; e^{i(\vec{k} \cdot \vec{k}') r} \, d\Omega \tag{8}$$

Since the vectors $\vec{k} - \vec{k}'$ and $\vec{k} + \vec{k}'$ are perpendicular, i.e. $(\vec{k} - \vec{k}') \cdot (\vec{k} + \vec{k}') = k^2 - k^2 = 0$, the average value of $(\vec{k} + \vec{k}') \cdot \vec{r}$ will vanish when the value of $(\vec{k} - \vec{k}') \cdot \vec{r}$ is fixed. The terms of (2) contributed entirely by the scattered waves will be $O\left(\frac{1}{r^3}\right)$ and we shall drop them. If we define μ_k to be the cosine of the angle between the vectors $\vec{r}$ and $\vec{k}$, and μ_k' to be the cosine of the angle between $\vec{r}$ and $\vec{k}'$, then the remaining terms which are $O\left(\frac{1}{r}\right)$ leave the relation

$$0=\int f(\vec{k}_r,-\vec{k}')(\mu_k-1)\,e^{ikr(\mu_k+1)}\,d\mu_k + \int f(\vec{k}_r,\vec{k})(\mu_k'+1)\,e^{-ikr(\mu_k'-1)}\,d\mu_k' \tag{9}$$

By performing integrations by parts, in which the exponentials are integrated first the asymptotic forms of these integrals are easily found. Only the integrated terms need be retained, the remaining integrals being a power r^{-1} smaller as may be shown by a further integration by parts . We then have apart from a factor $(ikr)^{-1}$

$$0=\Big[f(\vec{k}_r,-\vec{k}')(\mu_k-1)e^{ikr(\mu_k+1)}\Big]_{\mu_k=-1}^{1}-\Big[f(\vec{k}_r,\vec{k})(\mu_k'+1)e^{-ikr(\mu_k'-1)}\Big]_{\mu_k'=-1}^{1} \tag{10}$$

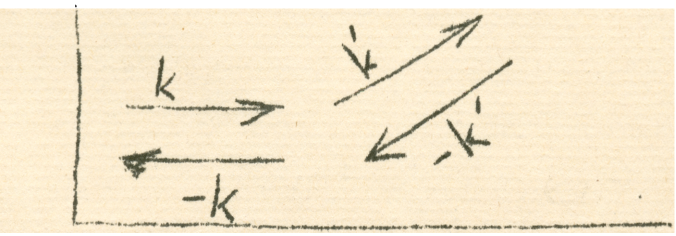
The upper limit in the first term, and the lower limit in the second term both contribute nothing. The resulting identity is

$$0=2\,f(-\vec{k},-\vec{k}')-2\,f(\vec{k}',\vec{k}) \tag{11}$$

or

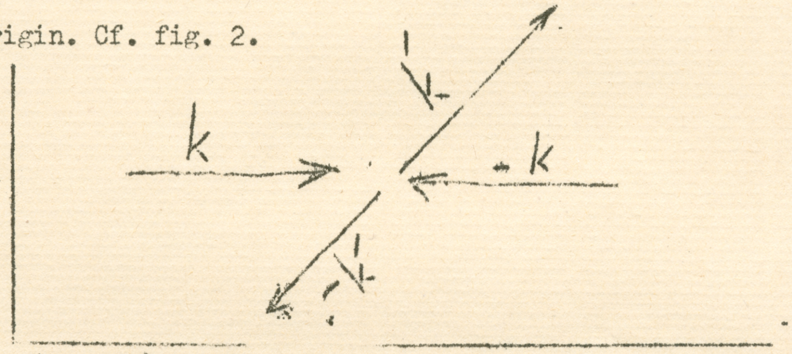
$$f(-\vec{k},-\vec{k}')=f(\vec{k}',\vec{k}) \tag{12}$$

This relation evidently expresses the reversibility of the scattering process, that is a beam has the same amplitude for scattering from the direction $-\vec{k}'$ to $-\vec{k}$ as from $\vec{k}$ to $\vec{k}'$. Cf. fig. 1



We have not yet employed any knowledge of the potential. In most problems of interest the potential has symmetry properties of its own. In particular, if it is invariant under inversion in the origin, $V(-\vec{r}) = V(\vec{r})$, we have another symmetry relation obeyed by the scattering amplitude. In that case the scattering amplitude must remain unchanged when both initial and final propagation vectors are inverted in the origin. Cf. fig. 2.

Fig. 2



$$f(-\vec{k}', -\vec{k}) = f(\vec{k}', \vec{k}) \qquad (13)$$

Combining this relation with the reversibility relation (12) we find that when inversion invariance prevails the scattering amplitude is a symmetric function of the two directions $\vec{k}$ and $\vec{k}'$

$$f(\vec{k}', \vec{k}) = f(\vec{k}, \vec{k}') \qquad (14)$$

Another important identity, independent of the potential may be obtained by a procedure similar to the derivation of the reversibility condition. This time we work with the wave function ψ_k and the complex conjugate wave function $\psi_{k'}^*$. By multiplying each wave equation by the other wave function and substracting we have

$$\psi_{k'}^* \nabla^2 \psi_k - \psi_k \nabla^2 \psi_{k'}^* = 0 \qquad (15)$$

an expression whose volume integral over a large sphere we again transform to a surface integral by Green's theorem.

$$\int_S \left(\psi_{k'}^{*} \frac{\partial}{\partial r} \psi_k - \psi_k \frac{\partial}{\partial r} \psi_{k'}^{*} \right) r^2 d\Omega = 0 \tag{16}$$

Once again, substituting the asymptotic wave functions we have

$$0 = \int \Big\{ \left(e^{-i\vec{k}'\cdot\vec{r}} + f^{*}(\vec{k}_r, \vec{k}') \frac{e^{-ikr}}{r} \right) \frac{\partial}{\partial r} \left(e^{i\vec{k}\cdot\vec{r}} + f(\vec{k}_r, \vec{k}) \frac{e^{ikr}}{r} \right) \tag{17}$$
$$- \left(e^{i\vec{k}\cdot\vec{r}} + f(\vec{k}_r, \vec{k}) \frac{e^{ikr}}{r} \right) \frac{\partial}{\partial r} \left(e^{-i\vec{k}'\cdot\vec{r}} + f^{*}(\vec{k}_r, \vec{k}') \frac{e^{-ikr}}{r} \right) \Big\} d\Omega$$

In this case as well the terms containing two plane wave factors contribute nothing since they are represented once more by the vanishing integral (8). A difference arises in treating the terms contributed purely by the scattered waves where a cancellation which took place in the derivation of (9) no longer occurs. Besides terms $O\left(\frac{1}{r^3}\right)$ which we neglect, the terms containing two scattering amplitudes contribute an integral $O\left(\frac{1}{r^2}\right)$ which, as we shall see, we must retain.

$$0 = \frac{2\pi i k}{r} \int f^{*}(\vec{k}_r, \vec{k}')(\mu_k + 1) e^{ikr(\mu_k - 1)} d\mu_k$$
$$+ \frac{2\pi i k}{r} \int f(\vec{k}_r, \vec{k})(\mu_{k'} + 1) e^{-ikr(\mu_{k'} - 1)} d\mu_{k'}$$
$$+ \frac{2ik}{r^2} \int f^{*}(\vec{k}_r, \vec{k}') f(\vec{k}_r, \vec{k})\, d\Omega \tag{18}$$

We require the last term, since as we have seen in deriving (10) plane wave factors in the integrands of the first two terms asymptotically contribute additional factors of r^{-1}.

Integrating the first two terms by parts and retaining only the integrated terms, which are the asymptotically dominant ones we have

$$0=\frac{2\pi}{r^2}\Big[f^*(k_r,k')(\mu_k+1)e^{ikr(\mu_k-1)}\Big]_{\mu_k=-1}^{1}-\frac{2\pi}{r^2}\Big[f(k_r,k)(\mu_{k'}+1)e^{-ikr(\mu_{k'}-1)}\Big]_{\mu_{k'}=-1}^{1}+\frac{2ik}{r^2}\int f^*(\vec{k}_r,\vec{k}')f(\vec{k}_r,\vec{k})\,d\Omega \tag{19}$$

Now, evaluating the integrated terms

$$0=4\pi\big[f^*(\vec{k},\vec{k}')-f(\vec{k}',\vec{k})\big]+2ik\int f^*(\vec{k}_r,\vec{k}')f(\vec{k}_r,\vec{k})\,d\Omega \tag{20}$$

The notation for the integration variable $\vec{k}_r$ may be improved by writting instead a propagation vector $\vec{k}''$ of the same magnitude $|\vec{k}''|=k$, and letting $d\Omega_{k''}$ be the corresponding element of solid angle. We then have the relation

$$\frac{1}{2i}\big[f(\vec{k}',\vec{k})-f^*(\vec{k},\vec{k}')\big]=\frac{k}{4\pi}\int f^*(\vec{k}'',\vec{k}')f(\vec{k}'',\vec{k})\,d\Omega_{k''} \tag{21}$$

The physical origin of this relation is most easily seen in the special case $\vec{k}'=\vec{k}$. Then equation (15), from which we have begun is simply the conservation condition in a stationary state for the quantum mechanical current vector,

$$\nabla\cdot\vec{j}=0 \tag{22}$$

where

$$\vec{j}=-\frac{i\hbar}{2m}\left(\psi^*\nabla\psi-\psi\nabla\psi^*\right) \tag{23}$$

The conditions (16) to (21) are then statements that the total flux through a large sphere must vanish. Obviously the pure plane weve terms in the asymptotic form of the current contribute no net flux. But the pure scattering terms do. The scattered flux must evidently be balanced by a term coming from the interference of the scattered wave with the plane wave, an effect which must account for the attenuation of the incident beam. We shall presently discuss this effection somewhat greater detail. Meanwhile it is clear that this balancing is expressed by the form assumed by (21) for $\vec{k}' = \vec{k}$, i.e.

$$\mathcal{I}m\, f(\vec{k},\vec{k}) = \frac{k}{4\pi}\int |f(\vec{k}'',\vec{k})|^2 d\Omega_{k''} \qquad (24)$$

in which $\mathcal{I}m$ means the imaginary part. The integral standing on the right which is proportional to the scattered flux is simply the total cross-section σ, whence we have the frequently useful relation

$$\sigma = \frac{4\pi}{k}\,\mathcal{I}m\, f(\vec{k},\vec{k}) \qquad (25)$$

The more general form assumed by (21) when $\vec{k} \neq \vec{k}'$ suffices to prove that the flux through a large sphere vanishes when the incident wave is a superposition of two or more plane waves. Somewhat more light is shed on the relation by noting that a quite analogous statement is made in the time-independent approach scattering problems. There the particle is considered as undergoing a transition in time from an initial state to its final one. Since the Hamiltonian is hermitian the operator S which effects this transition must be unitary, a condition which implies particle conservation and that orthogonal initial states lead to final ones that are orthogonal. In fact the relation (21) is simply the unitary condition $S^{+}S = 1$, for the matrix S whose representative is

$$(\vec{k}'|S|\vec{k}) = \delta(\vec{k}'-\vec{k}) + \frac{i}{2\pi}\frac{\delta(k-k')}{k} f(\vec{k}',\vec{k}) \qquad (26)$$

i.e. we have

$$\int (\vec{k}'|S^{+}|\vec{k}'')(\vec{k}''|S|\vec{k})\,d\vec{k}'' = \delta(\vec{k}'-\vec{k}) \qquad (27)$$

The relation (26) may be shown to follow from the time- dependent procedure.

We shall not, for the present at least, make any detailed exploration of the time-dependent approach. Since the temporal development of scattered waves is in fact never measured, introduction of the time is for most purposes a needless complication. The mathematical problem of finding the distributions of emergent particles is much more concisely stated in the stationary approach.

Never the less there are some simple questions of physical interpretation in the formulation of the stationary approach which are best clarified by a brief reference to the time-dependent one. In particular we should note that we have spoken rather loosely of the plane wave in the asymptotic form (2) as representing the beam of incident particles. This is of course an incorrect way of explaining that the total wave function is not normalized to unity. The function $\psi_k(\vec{r})$ can only describe a single particle. In order to secure a normalizable wave function for an incident particle we must use a superposition of waves ψ_k which renders the initial momentum slightly uncertain. Then since the problem is no longer monoenergetic the time-dependent Schrödinger equation must be used to describe the propagation of the wave packet. Viewed in this light, the stationary formulation is an idealization. The limiting case of precise specification of the initial momentum, in which the particle wave function becomes ψ_k apart from a normalization constant which vanishes in the limit.

A further formal difficulty in representing the incident particles by plane waves of infinite extent is that the scattered waves can never be separated entirely from the incident ones. The two parts of the wave function overlap and interfere at all points in space. Deriving the expression for the differential cross-section in terms of the scattering amplitude would then in principle require accounting for the interference effects in finding the current through an element of area, a calculation we omitted in deriving (3). The latter expression would in fact still be correct since at large distances the interference effect contributes terms which oscillate so rapidly with increasing scattering angle that their average value is quite effectively zero. Still, in defining the differential cross section, the use of wave packets is substantially more realistic.

If we were actually to carry out the scattering calculation using wave packets, it would convenient to choose an initial wave packet which represents a very small range of momenta in order to minimize the spreading of the packet. This would imply a rather extended packet on tha atomic scale of distances (we must in any case choose it much larger than the potential) but it may still be quite small, macroscopically speaking. This packet would be pictured as travelling toward the potential at the initial time cf. fig. 3. At a much later time, when the packet had passed the potential (cf. fig. 4) the wave function would contain in addition to the displaced packet, an outgoing spherical wave with an angle-dependent amplitude proportional to $f(\theta)$. There is thus no difficulty in showing for all directions save nearly the forward one that $\sigma_T = |f(0)|^2$ Near the forward direction, h however, the initial wave packet and the scattered wave are not always superposed (provided the scattered waves have not been greatly delayed within the potential, a point to which we shall later return.) It is easy to show, using asymptotic integrations quite analogous to those we have already used, that interference with the spherical wave leads to a decrease of probability that the particle is within the initial wave packet proportional to $\mathrm{Im}\,(0)$ so that particle conservation once again implies (25). We at least see more clearly from this approach that the interference effect which attenuates the initial beam can only involve the forward scattering amplitude.

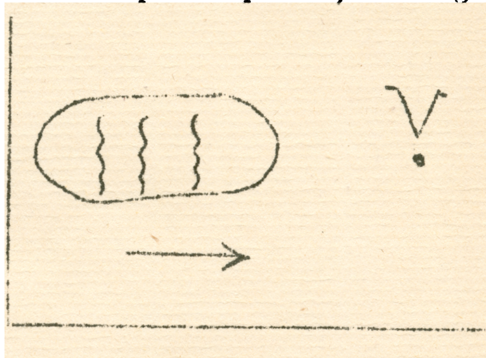
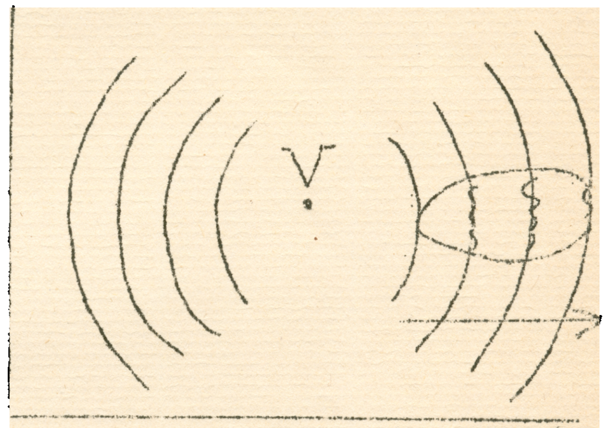


fig 3



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<u>Integral equation formulation.</u>

As the scattering problem has thus far been stated we must first find the solutions of the Schrödinger equation (1) and then select from among these the one having the asymptotic form.(2). For many purposes it is more convenient to impose the two conditions simultaneously by writing an integral equation for the wave function.

The Schrödinger equation we wish to solve is

$$(\nabla^2 + k^2)\psi_k(\vec{r}) = \frac{2m}{\hbar^2} V(\vec{r})\psi_k(\vec{r}) \tag{28}$$

Suppose we know a solution $G(\vec{r}, \vec{r}\,')$ to the much simpler in-homogeneous wave equation

$$(\nabla^2 + k^2) G(\vec{r}, \vec{r}\,') = -\delta(\vec{r} - \vec{r}\,') \tag{29}$$

Then the function $\chi(\vec{r}) = -\frac{2m}{\hbar^2}\int G(\vec{r}, \vec{r}\,') V(\vec{r}\,')\psi_k(\vec{r}\,') d\tau'$ evidently satisfies the equation

$$(\nabla^2 + k^2)\chi(\vec{r}) = \frac{2m}{\hbar^2} V(\vec{r})\psi_k(\vec{r}) \tag{30}$$

But $\chi(\vec{r})$ is not the most general solution to this equation. The most general solution is obtained by adding to $\chi(\vec{r})$ any solution $\varphi(\vec{r})$ of the homogenous wave equation $(\nabla^2 + k^2)\varphi = 0$ Since $\psi_k(\vec{r})$ is among the solutions it follows that ψ_k differs from $\chi(\vec{r})$ only by a free particle wave function $\varphi(\vec{r})$.

$$\psi_k(\vec{r}) = \varphi(\vec{r}) - \frac{2m}{\hbar^2}\int G(\vec{r}, \vec{r}\,') V(\vec{r}\,')\psi_k(\vec{r}\,') d\tau' \tag{31}$$

The ultimate determination of the functions φ and G depends on the asymptotic form we require ψ_k to take.

The determination of $G(\vec{r},\vec{r}')$ which is usually called the free particle Green's function may be undertaken as follows :

We note that we need only find a particular solution of equation (28) since the most general solution only differs from it by a solution of the homogenous equation. It suffices to choose a solution $G(\vec{r},\vec{r}')$ which depends only on the argument $\vec{r}-\vec{r}'$. We then represent the function as a fourier integral

$$G(r-r') = \frac{1}{(2\pi)^3}\int F(\vec{\lambda})\, e^{i\vec{\lambda}(\vec{r}-\vec{r}')}\, d\vec{\lambda} \qquad (32)$$

and, introducing the fourier integral representation of the δ -function

$$\delta(r-r') = \frac{1}{(2\pi)^3}\int e^{i\vec{\lambda}(\vec{r}-\vec{r}')}\, d\vec{\lambda}$$

and equating the transforms of both sides of equation (29) we have

$$-(\lambda^2-k^2)F(\vec{\lambda}) = -1 \qquad\qquad F(\lambda) = \frac{1}{\lambda^2-k^2}$$

and

$$G(\vec{r}-\vec{r}') = \frac{1}{(2\pi)^3}\int \frac{e^{i\vec{\lambda}\cdot(\vec{r}-\vec{r}')}}{\lambda^2-k^2}\, d\vec{\lambda} \qquad (33)$$

The angular part of this integration is easily performed by letting $\vec{r}-\vec{r}'$ be the polar direction in spherical coordinates and writing

$$\vec{\lambda}\cdot(\vec{r}-\vec{r}') = \lambda|\vec{r}-\vec{r}'|\cos\theta = \lambda|r-r'|\mu$$

$$d\vec{\lambda} = 2\pi\lambda^2\sin\theta\, d\lambda\, d\theta = -2\pi\lambda^2 d\lambda\, d\mu$$

$$G(r-r') = \frac{2}{(2\pi)^2 i}\frac{1}{|r-r'|}\int_0^{\infty}\frac{\sin\lambda|r-r'|}{\lambda^2-k^2}\lambda\,d\lambda$$

$$= \frac{1}{(2\pi)^2 i\,|r-r'|}\int_{-\infty}^{+\infty}\frac{e^{i\lambda|r-r'|}}{\lambda^2-k^2}\lambda\,d\lambda \qquad (34)$$

To give meaning to this integral we must carefully define the way the integration is to be performed in the neighborhoods of the poles $\lambda = \pm k$. The residuus at these points however are simply solutions of the homogenous equation, so that a variety of paths about the poles which in effect simply add or substract such solutions are possible (cf. fig. 5 and 6.) The contour must of course be closed in the upper half-plane. That of fig. 5 yields

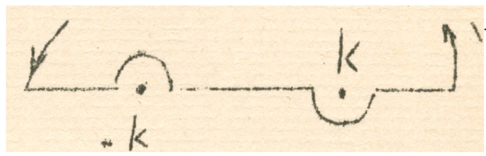

Fig. 5

$$G(r-r') = \frac{e^{ik|r-r'|}}{4\pi|r-r'|} \qquad (35)$$

while that of fig. 6 yields

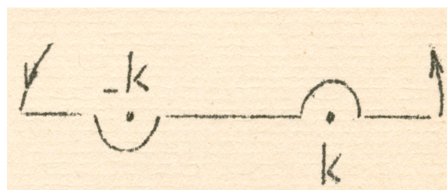

Fig. 6

$$G(r-r') = \frac{e^{-ik|r-r'|}}{4\pi|r-r'|} \qquad (36)$$

These indeed differ by $\frac{i\sin k|r-r'|}{2\pi|r-r'|}$, a solution of the homogenous equation. If we substitute (35) for example into equation (31) the asymptotic form of the integral $\int G(r-r')V(r')\psi_k(r')d\tau'$ for larger is easy to see. Since the potential is assumed to be localized to the neighborhood of the origin the integral will consist asymptotically of an outgoing wave $\frac{e^{ikr}}{r}$ with an angle-dependent amplitude. The choice (36) would fournish ingoing waves. By choosing (35) to represent the Green's function we need only choose $\varphi(\vec{r})$ to be the incident plane wave $e^{ik\cdot r}$ in equation (31) in order to guaranted the correct asymptotic behavior of ψ_k. We have then the integral equation for ψ_k.

$$\psi_k(r) = e^{ikr} - \frac{m}{2\pi\hbar^2}\int \frac{e^{ik|r-r'|}}{|r-r'|} V(r')\,\psi_k(r')\,d\tau' \quad (37)$$

To verify the asymptotic form of ψ_k, we expand the Green's function in powers of r'/r

$$\frac{e^{ik|r-r'|}}{4\pi|r-r'|} \sim \frac{e^{ik\left(r - \frac{\vec{r}\cdot\vec{r}'}{r^2}\right)}}{4\pi r} \quad (38)$$

Then we have

$$\psi_k \sim e^{ikr} + \frac{e^{ikr}}{r}\left(-\frac{m}{2\pi\hbar^2}\right)\int e^{-ik\frac{\vec{r}\vec{r}'}{r^2}} V(r')\,\psi_k(r')\,d\tau' \quad (39)$$

which in addition to exhibiting the correct behavior, furnishes an explicit expression for the scattering amplitude. If we lit k' be a propagation vector in the direction $\vec{r}$, $\vec{k}' = k\,\frac{\vec{r}}{r}$, then evidently

$$f(\vec{k}', \vec{k}) = -\frac{m}{2\pi\hbar^2}\int e^{-ik'r'} V(r')\,\psi_k(r')\,d\tau' \quad (40)$$

This relation involves the unknown wave function, but only within the volume occupied by the potential a region in which it may not, at times, be too difficult to approximate.

The Born approximations.

When the scattering potantial is everywhere quite weak the incident plane wave will be attend very little in its passage through the potential. We may then expect a good approximation to the scattering amplitude to result from substituting $e^{ik\cdot r}$ for the wave function in (40).

$$f(\vec{k}',\vec{k}) = -\frac{m}{2\pi\hbar^2}\int e^{-ik'r}V(r)e^{ikr}\,d\tau' \qquad (41)$$

This expression, the first Born approximation, sometimes gives a useful picture of the general behavior of cross-sections. Its frequent use has, however, been due more to its analytic simplicity than its accuracy, which is rarely adequate for any save the feeblest interactions.

The scattering amplitude (41), fulfills the reversibility condition (12). When the potential $V\ (r)$ is invariant under inversion, it further fulfills the summetry condition (14), which is equivalent to saying that the first Born- approximation scattering amplitude is real. It is clear, however, that the expression (41) can not satisfy the unitary relation (21). The expression $f(\vec{k}',\vec{k}) - f^{*}(\vec{k},\vec{k}')$ could not identically balance a term quadratic in the potential strenght. In fact it must vanish, and clearly does so. This means in particular that the first Born approximation does not conserve the number of particles in the system, a fact which can lead to grotesquely unphysical results when the potential is no longer weak. As a rather extreme example the cross section of a square-well of fixed radius would appear to increase without bound as the square of its depth. Unless the depth is quite small in fact, the absurdly large cross section that results is due to the spontaneous generation of particles by the Born approximation.

To secure more accurate results one may in principle compute corrections to (41) of higher order in the potential strenght. We may consider (41) as simply the lowest order term in a series development of the scattering amplitude in powers of the potential strenght. – The required expression for $\psi_k(r)$ is obtained as the Liouville-Neuman solution of the integral equation (37), or by iterated substitution of the incident plane wave

$$\psi_k(\vec{r}) = e^{ikr} - \frac{2m}{\hbar^2}\int G(r,r')V(r')e^{ikr'}d\tau' + \left(\frac{2m}{\hbar^2}\right)^2\int G(r,r')\cdot V(r')G(r',r'')V(r'')e^{ikr''}d\tau' d\tau'' - \ldots\ldots \qquad (42)$$

The resulting series for the scattering amplitude is

$$f(\vec{k}',\vec{k}) = -\frac{1}{4\pi}\left\{\frac{2m}{\hbar^2}\int e^{-ik'r}V(r)e^{ikr}d\tau - \left(\frac{2m}{\hbar^2}\right)^2\int e^{-ik'r}V(r)G(r,r')V(r')e^{ikr'}d\tau d\tau' + \left(\frac{2m}{\hbar^2}\right)^3\int e^{-ik'r}V(r)G(r,r')V(r')G(r',r'')e^{ikr''}d\tau d\tau' d\tau'' \ldots\right\} \qquad (43)$$

The approximation which summ only the first n terms is generally called the n th Born approximation, Each such approximation satisfies the reversibility and inversion invariance conditions. The second and higher approximations with an inversion-invariant potential are no longer real. The unitarity condition is only satisfied approximatly, with a relative error whose order is the power n - 1 of the potential strenght. The value of the power series (43) and of the entire procedure of successive Born approximations is of course limited to potential strenghts lying within its radius of convergence, a point to which we shall return. (For determinations of the radius of convergence in particular cases cf. W. Kohn, Phys. Rev. 87, 539 (1952), and forthcoming article in the Danish Journal)

Partial Wave Resolution

II.- The difficulty of solving directly the three dimensional Schrödinger equation(1), or the equivalent integral equation (37) is frequently formidable. By expressing the wave function, however, as a superposition of eigenfunctions for all possible angular momenta the three-dimensional problem may often be reducedto a sequence of much simpler one-dimensional ones.

We begin by resolving the incoming plane wave, $e^{ik.r}$, into its component angular momentum eigenfunctions. Since the wave is cylindrically symmetrical about the direction $\vec{k}$, which may be taken as the axis of quantization, only the eigenfunctions for magnetic quantum number zero, the Legendre polynomials, will occur. Letting μ be the cosine of the angle between $\vec{k}$ and $\vec{r}$ we write

$$e^{ik.r} = e^{ikr\mu} = \sum_{\ell} g_{\ell}(r)\, P_{\ell}(\mu) \tag{1}$$

where

$$g_{\ell}(r) = \frac{2l+1}{2} \int_{-1}^{+1} e^{ikr\mu} P_{\ell}(\mu)\, d\mu \tag{2}$$

Now for points far from the origin the asymptotic development of $g_{\ell}(r)$ may be begun by integrating by parts

$$g_{\ell}(r) \sim \frac{2l+1}{2ikr} \left[e^{ikr\mu} P_{\ell}(\mu) \right]_{-1}^{+1} + O\left(\frac{1}{r^2}\right)$$

$$g_{\ell}(r) \sim \frac{2l+1}{2ikr} \left(e^{ikr} - (-1)^{\ell} e^{-ikr} \right) \tag{3}$$

so that the asymptotic development of the incident plane wave is

$$e^{ik.r} \sim \frac{-1}{2ikr} \sum_{\ell} (2\ell + 1) \left((-1)^{\ell} e^{-ikr} - e^{ikr} \right) P_{\ell}(\mu) \quad (4)$$

The effect of the scattering center on the plane wave can only be to alter its outgoing part. We assume the interaction is at least cylindrically symmetric about the direction $\vec{k}$, so that the azimuthal quantum number is conserved and the scattering remains cylindrically symmetric. Then since the outgoing partial waves individually satisfy the Schrödinger equation for large r, the effect of scattering can only be to change their constant coefficients. This can be seen directly from the asymptotic form (I - 2), by developing the scattering amplitude $f(\theta)$ in Legendre polynomials.

Let us suppose that in the presence of a scattering center the asymptotic wave function is

$$\psi_k(r) \sim -\frac{1}{2ikr} \sum_{\ell} (2l + 1) \left((-1)^{\ell} e^{-ikr} - C_{\ell} e^{ikr} \right) P_{\ell}(\mu) \quad (5)$$

Then, by substracting (4) we have

$$f(\theta) = \frac{1}{2ik} \sum_{\ell} (2l + 1) (C_{\ell} - 1) P_{\ell}(\mu) \quad (6)$$

In the more general notation of (I - 4) this is

$$f(\vec{k}', \vec{k}) = \frac{1}{2ik} \sum_{\ell} (2l + 1) (C_{\ell} - 1) P_{\ell}(\vec{k}', \vec{k}) \quad (7)$$

where the latter Legendre function still depends only on the angle between $\vec{k}$ and $\vec{k}'$. By substituting this expression in the unitarity relation

(I _ 21) we obtain conditions on the coefficients C_ℓ. It is necessary to perform integrals of the form

$$\int P_\ell (\vec{k''}, \vec{k'}) \quad P_{\ell'}(\vec{k''}, \vec{k}) \quad d\,\Omega_{k''} \tag{8}$$

Since a spherical harmonic referred to one pole is a superposition of spherical harmonics of the same order when referred to any other pole, the integral vanishes for $\ell \neq \ell'$. For fixed $\vec{k}$ it is a spherical harmonic of order ℓ as a function of $\vec{k'}$, and furthermore depends only on the angle between $\vec{k}$ and $\vec{k'}$. It must in fact equal $P_\ell(\vec{k}, \vec{k'})$ apart from a constant factor which is fixed by setting $\vec{k'} = \vec{k}$.

$$\int P_\ell (\vec{k''}, \vec{k'}) \, P_{\ell'} (\vec{k''}, \vec{k}) \, d\,\Omega_{k''} = \frac{4\pi}{2\,l + 1} \, \delta_{\ell\ell'} \quad P_\ell(\vec{k'}, \vec{k}) \tag{9}$$

This is easily demonstrated using directly the addition theorem for spherical harmonics.

The unitarity relation (I - 21) then furnishes the condition

$$\sum_\ell \, (2 - C_\ell - C_\ell^*) \, P_\ell (\vec{k'}, \vec{k}) = \sum_\ell \, | \, C_\ell - 1 |^2 \, P_\ell (\vec{k'}\vec{k})$$

from which we have, for all C_ℓ

$$| C_\ell |^2 = 1 \tag{10}$$

It is customary to write $C_\ell = e^{2 i \delta_\ell}$, calling δ_ℓ the ℓ th phase shift. Since the unitarity condition we have used to derive (10) holds for interactions more general than static potential, the present analysis holds more generally as well.

In terms of the phase shifts we have the familiar results

$$\psi_k(r) \sim \frac{-1}{2ikr} \sum_{\ell} (2l+1) \left((-1)^{\ell} e^{-ikr} - e^{ikr + 2i\delta_\ell} \right) P_\ell(\mu) \tag{11}$$

$$\sim \frac{1}{kr} \sum_{\ell} (2l+1)\, i^{\ell} e^{i\delta_\ell} \sin\left(kr + \delta_\ell - \frac{\ell\pi}{2}\right) P_\ell(\mu) \tag{12}$$

and

$$f(\theta) = \frac{1}{2ik} \sum_{\ell} (2l+1)\left(e^{2i\delta_\ell} - 1\right) P_\ell(\mu) \tag{13}$$

from the last of which we obtain the differential cross section. The total cross section is

$$\sigma = \int |f|^2 \, d\Omega = \frac{4\pi}{k^2} \sum_{\ell} (2l+1) \sin^2 \delta_\ell \tag{14}$$

To find the phase shifts δ_ℓ we must, in general, solve the radial Schrödinger equations for each value of ℓ. If we assume an expansion of the form

$$\psi_k(\vec{r}) = \sum_{\ell} g_\ell(r)\, P_\ell(\mu) \tag{15}$$

which has cylindrical symmetry about the direction $\vec{k}$, we are led immediatly for the case of a spherically symmetric potential to the sequence of differential equations for the functions $g_\ell(r)$

$$\frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{dg_\ell}{dr}\right) + \left(k^2 - \frac{2m}{\hbar^2} V(r) - \frac{\ell(l+1)}{r^2}\right) g_\ell(r) = 0 \tag{16}$$

For asymetric potentials, the wave function ψ_k must be written as a more general expansion in spherical harmonics, and the equations (16) become coupled to one another for different values of ℓ and the magnetic quantum number. By substituting

$$g_{\ell}(r) = \frac{u_{\ell}(r)}{r} \tag{17}$$

we find somewhat simpler equations for the u_{ℓ} :

$$\frac{d^2}{dr^2} u_{\ell}(r) + \left\{k^2 - \frac{2m}{\hbar^2} V(r) - \frac{\ell(\ell+1)}{r^2}\right\} u_{\ell}(r) = 0 \tag{18}$$

It can easily be shown that for potentials for which $\lim_{r\to\infty} rV(r) = 0$, the solution at large distances from the origin is of the form $u_{\ell}(r) \sim \sin(kr + \text{const})$. This is indeed the form we have derived in (12), and the phase shift is to be found from the constant. If the wave function is not to be singular at the origin we must also require

$$u_{\ell}(0) = 0 \tag{19}$$

This condition, together with the asymptotic behavior which, apart from a normalization constant is

$$u_{\ell}(r) \sim \sin\left(kr + \delta_{\ell} - \frac{\ell\pi}{2}\right) \tag{20}$$

serves to determine both the wave function u_{ℓ} and the phase shift δ_{ℓ} . The normalization constant which corresponds to an incoming plane wave is given by (12).

For the particular case $V(r) = 0$, we evidently have $\psi_k(r) = e^{ik\cdot r}$, and the functions $g_{\ell}(r)$, properly normalized, are

$$g_{\ell}(r) = (2l+1)\, i^{\ell}\, j_{\ell}(kr) \tag{21}$$

where

$$j_{\ell}(x) = \sqrt{\frac{\pi}{2x}}\; J_{\ell+\frac{1}{2}}(x) \tag{22}$$

and for large x

$$j_{\ell}(x) \sim \frac{\sin\left(x - \frac{\ell\pi}{2}\right)}{x} \tag{23}$$

The phases δ_{ℓ} obviously vanish.

Integral equation formulation

As was the case in the more general three-dimensional formulation of the problem, it is for many purposes more convenient to combine the radial differential equations with the boundary conditions on their solutions by replacing them by integral equations. It is a simple matter to construct Green's functions for each of the equations (18). We define such functions as solutions of the equation

$$\left\{ \frac{d^2}{dr^2} + k^2 - \frac{\ell(l+1)}{r^2} \right\} G_{\ell}(r, r') = \delta(r - r') \tag{24}$$

subject to the condition $G_{\ell}(0, r') = 0$

Consider two linearly independent solutions v_{ℓ} and w_{ℓ} of the homogeneous equation

$$\left\{ \frac{d^2}{dr^2} + k^2 - \frac{\ell(l+1)}{r^2} \right\} \begin{pmatrix} v_{\ell} \\ w_{\ell} \end{pmatrix} = 0 \tag{25}$$

We may choose as two such solutions

$$v_\ell = kr\, j_\ell(kr) \qquad \text{and} \qquad w_\ell = kr\,\eta_\ell(kr) \tag{26}$$

where

$$j_\ell(x) = \sqrt{\frac{\pi}{2x}}\; J_{e+\frac{1}{2}}(x) \qquad \eta_\ell(x) = \sqrt{\frac{\pi}{2x}}\; Y_{\ell+\frac{1}{2}}(kr) \tag{27}$$

i.e. j_ℓ and η_ℓ are spherical Bessel functions. Near the origin we have

$$v_\ell \sim \frac{(kr)^{\ell+1}}{1.\,3.\,5\ldots(2\,1+1)} \qquad w_\ell \sim -\frac{1.\,3.\,5\ldots(2\,1-1)}{(kr)^{\ell}} \tag{28}$$

and for $kr \gg \ell$

$$v_\ell \sim \sin\left(kr - \frac{\ell\pi}{2}\right) \qquad w_\ell \sim -\cos\left(kr - \frac{\ell\pi}{2}\right) \tag{29}$$

We have further the Wronskian relation

$$v_\ell \frac{dw_\ell}{dr} - w_\ell \frac{d}{dr} v_\ell = k \tag{30}$$

for all values of r.

If we assume that $G_\ell(r, r')$ is bounded in the neighborhood of $r = r'$, then on integrating both sides of equation (24) from $r = r' - \mathcal{E}$ to $r = r' + \mathcal{E}$ we secure the condition

$$\lim_{\mathcal{E}\to 0} \frac{d}{dr} G_\ell(r, r')\Big|_{r'-\mathcal{E}}^{r'+\mathcal{E}} = 1 \tag{31}$$

Clearly the choice

$$G_{\ell}(r, r') = \frac{1}{k} \begin{cases} v_{\ell}(r)\, w_{\ell}(r') & r \leq r' \\ w_{\ell}(r)\, v_{\ell}(r') & r \geq r' \end{cases} \qquad (32)$$

in view of the relations (25) and (30), satisfies the conditions placed on the Green's functions.

To the integral $-\frac{2m}{\hbar^2}\int G_{\ell}(r,r')\, V(r')\, u_{\ell}(r')\, dr'$ which evidently satisfies the differential equation (18) we must add a solution of the free particle equation, the solution which would be present for $V(r) = 0$. The desired solution apart from a normalization constant is $v_{\ell}(r)$, and so we write

$$u_{\ell}(r) = v_{\ell}(r) + \int G_{\ell}(r,r')\, U(r')\, u_{\ell}(r')\, dr' \qquad (33)$$

where we have set

$$U(r) = -\frac{2m}{\hbar^2} V(r) \qquad (34)$$

The asymptotic form of the function u_{ℓ} which satisfies (33) is evidently

$$u_{\ell}(r) \sim \sin\left(kr - \frac{\ell\pi}{2}\right) - \cos\left(kr - \frac{\ell\pi}{2}\right) \frac{1}{k}\int v_{\ell}(r')\, U(r')\, u(r')\, dr' \qquad (35)$$

Now in view of (19), we expect the asymptotic form of $u_{\ell}(r)$ to differ from $\sin\left(kr + \delta_{\ell} - \frac{\ell\pi}{2}\right)$ only by a normalization constant. The normalization constant is evidently $(\cos\delta_{\ell})^{-1}$. By writing

$$u_{\ell}(r) \sim \frac{\sin\left(kr + \delta_{\ell} - \frac{\ell\pi}{2}\right)}{\cos\delta_{\ell}}$$

$$\sim \sin(kr + \delta_{\ell}) + \cos(kr + \delta_{\ell}) \tan\delta_{\ell} \qquad (36)$$

we immediately obtain the exact expression for tan δ_ℓ (

$$\tan \delta_\ell = -\frac{1}{k} \int_0^\infty v_\ell(r)\, U(r)\, u_\ell(r)\, dr \qquad (37)$$

By iterating the integral equation (33), one may generate a sequence of Born approximations to the wave functions u_ℓ. These expressions, substituted in (37) yield corresponding approximations to tan δ_ℓ. In the first approximation (37) reduces to

$$\delta_\ell \sim -\frac{1}{k} \int_0^\infty v_\ell^2(r)\, U(r)\, dr \qquad (38)$$

Another means of deriving integral equations for the radial functions consists in resolving the three-dimensional integral equation (I - 33) directly into partial waves. Writing

$$\psi_k(r) = \sum_\ell g_\ell(r)\, P_\ell(\mu)$$

and using the expansion previously developed for a plane wave the integral equation becomes

$$\sum_\ell g_\ell(r)\, P_\ell(\mu) = \sum_\ell (2l+1) i^\ell j_\ell(kr)\, P_\ell(\mu) - \frac{1}{4\pi} \int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}\, U(r') \sum_{\ell'} g_{\ell'}(r')\, P_{\ell'}(\mu')\, d\vec{r}' \qquad (39)$$

We now employ the expansion of the Green's function in spherical harmonics.

$$\frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} = ik \sum_{\ell, m} \mathcal{E}_m (2\, l + 1) \frac{(l - m)!}{(l + m)!} \cos m(\varphi - \varphi')\, P^m_{\ell}(\mu)\, P^m_{\ell}(\mu')$$

$$\begin{cases} j_{\ell}(kr)\, h_{\ell}(kr') & \text{for} \quad r \leqslant r' \\ h_{\ell}(kr)\, j_{\ell}(kr') & \text{for} \quad r \geqslant r' \end{cases} \qquad (40)$$

In this expression φ and φ' are azimuthal angles of $\vec{r}$ and $\vec{r}'$ respectively and μ and μ' are the cosines of their polar angles. Furthermore $\mathcal{E}_m = \begin{cases} 1 & m = 0 \\ 2 & m \neq 0 \end{cases}$ and the functions h_{ℓ} the spherical Hankel functions are defined by

$$h_{\ell}(x) = j_{\ell}(x) + i\, n_{\ell}(x) \qquad (41)$$

For $x \gg \ell$

$$h_{\ell}(x) \sim \frac{e^{ix}}{i^{\ell+1}\, x} \qquad (42)$$

By substituting the form ( ) for the Green's function into the integral equation (39), carrying out the angular integrations, and equating the coefficients of the corresponding Legendre polynomials on both sides of the resulting equation we find the relations

$$g_{\ell}(r) = (2\, l + 1)\, i^{\ell}\, j_{\ell}(kr) - ik \int j_{\ell}(kr_<)\, h_{\ell}(kr_>)\, U(r')\, g_{\ell}(r')\, r'^2 dr' \qquad (43)$$

in which we have used the abbreviation

$$j_{\ell}(kr_<)\, h_{\ell}(kr_>) = \begin{cases} j_{\ell}(kr)\, h_{\ell}(kr') & r \leqslant r' \\ h_{\ell}(kr)\, j_{\ell}(kr') & r \geqslant r' \end{cases} \qquad (44)$$

If we define the function

$$t_{\ell}(r) = kr\, g_{\ell}(r) \qquad (45)$$

the integral equation for $t_\ell(r)$ is

$$t_\ell(r) = (2l+1)i^\ell kr j_\ell(kr) - ikr \int j_\ell(kr_<) h_\ell(kr_>) U(r') t_\ell(r') r'dr' \tag{46}$$

This integral equation differs from (33) in the normalization of the inhomogeneous term, and in the choice of the free-particle solutions to (25) from which the Green's function is constructed. The choice of real functions for constructing the Green's function (32) was, in effect, a particularly simple one. The asymptotic form of the solutions $t_\ell(r)$ is evidently

$$t_\ell(r) \sim (2l+1)i^\ell \sin\left(kr - \frac{\ell\pi}{2}\right) - \frac{e^{ikr}}{i^\ell} \int j_\ell(r') U(r') t_\ell(r') r'dr' \tag{47}$$

In view of (12), it must be possible to write this expression in the form

$$t_\ell(r) \sim (2l+1) i^\ell e^{i\delta_\ell} \sin\left(kr + \delta_\ell - \frac{\ell\pi}{2}\right)$$

$$\sim (2l+1) i^\ell \left\{ \sin\left(kr - \frac{\ell\pi}{2}\right) + \frac{e^{ikr}}{2_i^{\ell+1}} \left(e^{2i\delta_\ell} - 1\right) \right\} \tag{48}$$

Now, on identifying the scattered waves in (47) and (48) we secure the relation

$$e^{2i\delta_\ell} - 1 = \frac{-2i}{(2l+1)i^e} \int j_\ell(r') U(r') t_\ell(r') r' dr' \tag{49}$$

By rewriting (46) as an integral equation for the function

$$\phi_\ell(r) = \frac{1}{(2l+1)i^\ell} t_\ell(r) \tag{50}$$

we simplify the normalization of the inhomogeneous term in the equation

$$s_\ell(r) = v_\ell(r) - ikr \int j_\ell(kr_<)\, h_\ell(kr_>)\, U(r')\, s_\ell(r')\, r'\, dr' \qquad (51)$$

We then have

$$e^{2i\delta_\ell} - 1 = -\frac{2i}{k} \int v_\ell(r)\, U(r)\, s_\ell(r)\, dr \qquad (52)$$

The functions $s_\ell(r)$ and $u_\ell(r)$ can, of course, only differ b a constant factor. It is evident from an examination of their asymptotic behaviors that

$$s_\ell(r) = e^{i\delta_\ell} \cos \delta_\ell\, u_\ell(r) \qquad (53)$$

and substitution of this relation in (52) immediately reduces it to (37). Nevertheless the integral equations (33) and (51) remain different, and the approximations secured for example by iterating them each a given number of times will generally differ. For the particular case, however, of the first Born approximation (52) evidently reduces to (38).

Variational Principles

The integral equation (33) may be used to construct another form of expression for tan δ_ℓ. By multiplying both sides of (33) by $u_\ell(r)\, U(r)$ and integrating over r we find

$$-k \tan \delta_\ell = \int v_\ell(r)\, U(r)\, u_\ell(r)\, dr \qquad (54)$$

$$-k \tan \delta_\ell = \int u_\ell^2(r)\, U(r)\, dr - \int u_\ell(r)\, U(r)\, G_\ell(r, r')\, U(r')\, u_\ell(r')\, dr\, dr' \qquad (55)$$

The identity obtained by dividing both sides of (55) by the squares of the corresponding expressions in (54) is

$$\frac{1}{k}\cot\delta_\ell = -\frac{\int u_\ell^2(r)\, U(r)\, dr - \int u_\ell(r)\, U(r)\, G_\ell(r, r')\, U(r')\, u_\ell(r')\,dr\,dr'}{\left(\int v_\ell(r)\, U(r)\, u_\ell(r)\, dr\right)^2} \tag{56}$$

This expression is evidently independent of the normalization chosen for the function u_ℓ. It is easy to verify that it is stationary with respect to small variations of the function $u_\ell(r)$ about the correct solution to the integral equation (33). Conversely the condition that the expression be stationary implies that the function about which variations are taken satisfies the integral equation.

In practice since the expression (56) involves only the solutions within the region occupied by the potential, it furnishes a most convenient means of treating potential of short range. One substitutes for $u_\ell(r)$ a trial function containing adjustable parameters, and corresponding to what physical knowledge we have of the solution, e.g. knowing the behavior of $u_\ell(r)$ near the origin we might write

$$u_\ell(r) \sim \sum_{j=\ell+1}^{N} C_j\, r^j \tag{57}$$

The adjustement of the parameters to secure a stationary value for the expression (56) will then provide an estimate of $\cot\delta_\ell$. While the accuracy of this estimate will generally increase rapidly with the number of parameters used, it is often sufficiently great with the use of only the crudest of trial functions. A similar variational principle may be constructed analogously for the quantity $e^{2i\delta_e} - 1$.

The scattering amplitude in 3 dimensions $f(\vec{k}', \vec{k})$ may also be represented by a stationary expression. We multiply the integral equation (I - 37) by $\psi_{-k'}(r)\, U(r)$, where $\vec{k}'$ is some direction other than $\vec{k}$, and integrate over $\vec{r}$, finding the expression :

$$- 4\pi\, f(-\vec{k}, -\vec{k}') = \int e^{ik.r}\, U(r)\, \psi_{-k'}(r)\, d\vec{r} \tag{58}$$

$$-4\pi\, f(-\vec{k}, -\vec{k}') = \int \psi_{-k'}(r)\, U(r) \psi_k(r)\, d\vec{r} + \int \psi_{-k'}(r)\, U(r)\, G(r,r')\, U(r')\, \psi_k(r')\, d\vec{r}\, d\vec{r}' \tag{59}$$

Now the reversibility relation is

$$f(-\vec{k}, -\vec{k}') = f(\vec{k}', \vec{k})$$

$$= - \frac{1}{4\pi} \int e^{-ik'.r}\, U(r)\, \psi_k(r)\, d\vec{r} \tag{60}$$

Now dividing the product of the two forms (58) and (60) for $- 4\pi f(\vec{k}', \vec{k})$ by the expression (59) we obtain

$$4\pi f(\vec{k}', \vec{k}) = - \frac{\int e^{-ik'.r}\, U(r)\psi_k(r)\, d\vec{r} \cdot \int e^{ik.r'} U(r')\, \psi_{-k'}(r')\, d\vec{r}'}{\int \psi_{-k'}(r)\, U(r)\, \psi_k(r)\, d\vec{r} + \int \psi_{-k'}(r)\, U(r)\, G(r,r')\, U(r')\psi_k(r')\, d\vec{r}\, d\vec{r}'} \tag{61}$$

This expression is independent of the normalizations of both $\psi_k(r)$ and $\psi_{-k'}(r)$, and it exhibits explicitly the symmetry expressed by the reversibility relation. One easily verifies that the expression is stationary with respect to independent variations of the two functions

ψ_k and ψ_{-k}, about the correct solutions to their respective integral equations. Conversely if the expression is stationary for variations about two such functions, then they satisfy their integral equations. The latter fact, together with the symmetry of (61) constitutes an alternative proof of the reversibility relation.

Since (61), like (56), involves the wave functions only within the region occupied by the potential, it is well suited for use with short-range potentials. Some simple illustrations of the use of these principles, first derived by Schwinger, have been given by G. Chew, Phys. Rev. 93, 341 (1954). Two other forms of variational principles for the finding of phase shifts have been given by G. Hulthèn, (cf. Mott and Massey, second edition, p. 128) and by W. Kohn, Phys. Rev., 74, 1763, (1948). Some calculations made for the purpose of comparing the various methods are reported by S. Altschuler, Phys. Rev. 89, 1278, 1953).

The fact that the interaction energy between two nucleons is quite large at close range leads one to expect that relatively small variations in the kinetic energies of the incident nucleons will not lead to very noticeable changes in the parts of their wave functions lying within the potential. Since the binding energy of the deuteron is much smaller than the two-nucleon interaction energy, we may expect the part of the deuteron wave function within the potential to be quite similar in form to the corresponding part of the wave function for neutron-proton scattering at zero energy. We may further expect that this similarity will be approximately preserved for scattering wave functions up to energies of several million volts. In this case a convenient trial function to substitute in the variational principle (56), written for the S-wave phase shift, is the wave function corresponding to zero energy. This procedure leads to the well-known effective range formula for cot δ_0, and constituted its first derivation, by Schwinger. The method is described in detail by J. Blatt and J.D. Jackson, Phys. Rev., 76, 18, 1949. A much more compact, although subsequent, derivation is given by Bethe in the same journal Phys. Rev., 76, 38, (1949).