than would reasonably be expected from statistical fluctuations.

It was estimated from Fig. 1 that at 240 days after irradiation the long-lived activity contributed about one-fourth of the total gamma-count. Even if the chemical separations were only 50 percent efficient so that this contribution was reduced from one-fourth to one-eighth, it was calculated that the counting rate ratios should change by about 20 percent in two months. The absence of such variations in any of the three samples was considered as proof that the long-lived activity was not carried by any of the other elements and must therefore be associated with a cerium isotope.

The evidence for the presence of Ce^{139} consists in: (1) The existence of a half-life of greater than 120 days in the photon component of the irradiated cerium, (2) the greater contributions of soft radiation corresponding to x-rays following K capture in this activity, and (3) the impossibility of separating the activity chemically from cerium, by removal of the most likely impurities.

III. ESTIMATE OF CROSS SECTION RATIO

An estimate of the ratio of cross sections of (Ce^{138}/Ce^{140}) should now be possible from the fact mentioned above, that at 240 days after a 30-day irradiation the counting activity of the long-lived gammas was one-third of that for the short-lived activity which Shepard estimated to occur in 70 percent of the disintegrations of Ce^{141}. Then, estimating the counting efficiency for Ce^{139} radiation to be twice as great as that for Ce^{141} because of the larger fraction of x-rays of about 30 kev energy,[8] the ratio of the disintegration rates 139/141 at this time would be 0.12. Using the half-life values of 140 and 28 days this ratio would have been 1.1×10^{-3} at the end of irradiation. For a 30-day bombardment, and using the isotopic abundances of 0.250 and 88.48 percent given by Ingham, Hayden, and Hess,[9] the ratio of the cross sections was calculated to be: $\sigma(138)/\sigma(140) \approx 1.4$.

[8] H. Maier-Liebnitz, Zeits. f. Naturforsch. 1, 243 (1946).
[9] Ingham, Hayden, and Hess, Phys. Rev. 72, 967 (1947).

Variational Principles for Scattering Processes. I

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A systematic treatment is presented of the application of variational principles to the quantum theory of scattering.

Starting from the time-dependent theory, a pair of variational principles is provided for the approximate calculation of the unitary (collision) operator that describes the connection between the initial and final states of the system. An equivalent formulation of the theory is obtained by expressing the collision operator in terms of an Hermitian (reaction) operator; variational principles for the reaction operator follow. The time-independent theory, including variational principles for the operators now used to describe transitions, emerges from the time-dependent theory by restricting the discusson to stationary states. Specialization to the case of scattering by a central force field establishes the connection with the conventional phase shift analysis and results in a variational principle for the phase shift.

As an illustration, the results of Fermi and Breit on the scattering of slow neutrons by bound protons are deduced by variational methods.

I. INTRODUCTION

ALTHOUGH variational methods have long been applied to eigenvalue problems in many fields of physics, no systematic use had been made of variational procedures in connection with scattering processes until the period 1942–1946 when variational techniques, among others, were extensively employed in the solution of electromagnetic wave guide problems.[1] Variational formulations have also been devised for the treatment of neutron diffusion,[2] acoustical and optical diffraction,[3] and quantum-mechanical scattering problems.[4] Indeed,

[1] "Notes on Lectures by Julian Schwinger: Discontinuities in Waveguides," prepared by David S. Saxon, MIT Radiation Laboratory Report, February 1945.

[2] J. Schwinger, unpublished; R. E. Marshak, Phys. Rev. 71, 688 (1947).
[3] H. Levine and J. Schwinger, Phys. Rev. 74, 958 (1948); 75, 1423 (1949).
[4] J. Schwinger, "Lectures on Nuclear Physics," Harvard University, 1947; J. Schwinger, Phys. Rev. 72, 742 (1947); J. M. Blatt, Phys. Rev. 74, 92 (1948); W. Kohn, Phys. Rev. 74, 1763 (1948); J. M. Blatt and J. D. Jackson, Phys. Rev. 76, 18 (1949). Variational principles for scattering problems have also been independently developed by L. Hulthén, see Mott and Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), 2nd ed., p. 128, and I. Tamm, J. Exp. Theor. Phys. USSR 18, 337 (1948); 19, 74 (1949).

such methods are applicable in any branch of physics where the fundamental equations can be derived from an extremum principle.

It is the purpose of this paper to describe the quantum mechanical time-dependent scattering theory and its variational reformulation. As a simple illustration of these methods, we consider the scattering of slow neutrons by protons bound in a molecule. This was first discussed by Fermi[5] in terms of an equivalent potential used in conjunction with the Born approximation. A more exact integral equation treatment was given by Breit,[6] with quite small ensuing corrections[7] to Fermi's theory. We shall show that the results of Fermi and Breit are easily derived from a variational treatment. Although one could consider, without difficulty, the scattering by any number of nuclei, the discussion will be restricted to the spin-dependent scattering by a single proton in an otherwise inert molecule of arbitrary mass. An extension to two protons, and in particular to the hydrogen molecule, is contained in an accompanying paper by one of us. Also included is an estimate of the error in the para-hydrogen scattering cross section calculated by Fermi's method.

II. TIME-DEPENDENT SCATTERING THEORY

We are concerned with the development in time of a system consisting of two interacting parts, which are such that the interaction energy approaches zero as the two parts are separated spatially. Correspondingly, the Hamiltonian is decomposed into the unperturbed Hamiltonian H_0, describing the two independent parts, and H_1, the energy of interaction. Since the problem is to describe the effect of H_1, it is convenient to remove the time dependence associated with H_0 from the Schrodinger equation

$$i\hbar[\partial\Psi'(t)/\partial t] = (H_0 + H_1)\Psi'(t). \tag{1.1}$$

This is accomplished by the unitary transformation

$$\Psi'(t) = \exp(-iH_0 t/\hbar)\Psi(t) \tag{1.2}$$

which yields

$$i\hbar[\partial\Psi(t)/\partial t] = H_1(t)\Psi(t), \tag{1.3}$$
$$H_1(t) = \exp(iH_0 t/\hbar)H_1 \exp(-iH_0 t/\hbar).$$

The initially non-interacting parts of the system are characterized by the state vector $\Psi(-\infty)$. On following the course of the interaction and the eventual separation of the two parts, we are led to the state vector $\Psi(+\infty)$, representing the final state of the system. This description can be made independent of the particular initial state by regarding the time development as the unfolding of a unitary transformation:

$$\Psi(t) = U_+(t)\Psi(-\infty), \quad U_+^+(t)U_+(t) = 1. \tag{1.4}$$

[5] E. Fermi, Ricerca Scient. **VII–II**, 13 (1936).
[6] G. Breit, Phys. Rev. **71**, 215 (1947).
[7] G. Breit and P. R. Zilsel, Phys. Rev. **71**, 232 (1947); Breit, Zilsel, and Darling, Phys. Rev. **72**, 576 (1947).

In particular,

$$\Psi(\infty) = S\Psi(-\infty), \quad S = U_+(\infty) \tag{1.5}$$

defines the collision operator, which generates the final state of the system from an arbitrary initial state. The operator $U_+(t)$ is to be obtained as the solution of the differential equation

$$i\hbar[\partial U_+(t)/\partial t] = H_1(t)U_+(t) \tag{1.6}$$

subject to the boundary condition

$$U_+(-\infty) = 1. \tag{1.7}$$

It is also useful to introduce a unitary operator $U_-(t)$, which generates the state vector $\Psi(t)$ from the final state $\Psi(\infty)$,

$$\Psi(t) = U_-(t)\Psi(\infty) = U_-(t)S\Psi(-\infty). \tag{1.8}$$

Since the two operators are related by

$$U_+(t) = U_-(t)S \tag{1.9}$$

the operator $U_-(t)$ is evidently the solution of the equations

$$i\hbar[\partial U_-(t)/\partial t] = H_1(t)U_-(t), \quad U_-(\infty) = 1. \tag{1.10}$$

Furthermore,

$$U_-(-\infty) = S^{-1} \tag{1.11}$$

which is the operator generating the initial state vector from the final state vector.

The differential equation for $U_+(t)$ can be replaced by the integral equation

$$U_+(t) = 1 - (i/\hbar)\int_{-\infty}^{t} H_1(t')U_+(t')dt'$$
$$= 1 - (i/\hbar)\int_{-\infty}^{\infty} \eta(t-t')H_1(t')U_+(t')dt' \tag{1.12}$$

which incorporates the boundary condition (1.7). Here

$$\eta(t-t') = 1; \quad t > t'.$$
$$= 0; \quad t < t'. \tag{1.13}$$

Similarly, $U_-(t)$ obeys the integral equation

$$U_-(t) = 1 + (i/\hbar)\int_{t}^{\infty} H_1(t')U_-(t')dt'$$
$$= 1 + (i\hbar/)\int_{-\infty}^{\infty} dt' H_1(t')U_-(t')\eta(t'-t). \tag{1.14}$$

By considering the limit as $t \to \infty$ in (1.12) and $t \to -\infty$ in (1.14), we obtain

$$S = 1 - (i/\hbar)\int_{-\infty}^{\infty} H_1(t)U_+(t)dt \tag{1.15}$$

and

$$S^{-1} = 1 + (i/\hbar) \int_{-\infty}^{\infty} H_1(t) U_-(t) dt \qquad (1.16)$$

which are, of course, connected by (1.9).

The differential and integral equations characterizing $U_+(t)$ and $U_-(t)$ will now be replaced by equivalent variational principles from which the fundamental equations are obtained as conditions expressing the stationary property of a suitable expression. Furthermore, the stationary value of this quantity is just S, the collision operator. Hence the variational formulation of the problem also yields a practical means of approximate calculation, since errors in the construction of S will be minimized by employing a stationary expression.

We first consider

$$`S' = U_+(\infty) - \int_{-\infty}^{\infty} U_-^+(t) \left(\frac{\partial}{\partial t} + \frac{i}{\hbar} H_1(t) \right) U_+(t) dt, \quad (1.17)$$

which is regarded as a function of the operator $U_+(t)$, subject only to the restriction (1.7), and of the Hermitian conjugate of the arbitrary operator $U_-(t)$. The change induced in $`S'$ by small, independent, variations of U_+ and U_- is

$$\delta `S' = (1 - U_-(\infty))^+ \delta U_+(\infty)$$

$$- \int_{-\infty}^{\infty} \delta U_-^+(t) \left(\frac{\partial}{\partial t} + \frac{i}{\hbar} H_1(t) \right) U_+(t) dt$$

$$+ \int_{-\infty}^{\infty} \left[\left(\frac{\partial}{\partial t} + \frac{i}{\hbar} H_1(t) \right) U_-(t) \right]^+ \delta U_+(t) dt. \quad (1.18)$$

The requirement that $`S'$ be stationary with respect to arbitrary variations of $U_+$ and $U_-$, apart from the restriction (1.7), thus leads to the differential equations (1.6), (1.10) and the boundary condition (1.10) for $U_-(t)$. It is also evident from (1.17) that the stationary value of $`S'$ is the collision operator S, according to (1.5). A somewhat more symmetrical version of (1.17) is

$$`S' = \tfrac{1}{2}(U_+(\infty) + U_-^+(-\infty))$$

$$- \int_{-\infty}^{\infty} \left[\frac{1}{2} U_-^+(t) \frac{\partial U_+(t)}{\partial t} - \frac{1}{2} \frac{\partial U_-^+(t)}{\partial t} U_+(t) \right.$$

$$\left. + \frac{i}{\hbar} U_-^+(t) H_1(t) U_+(t) \right] dt \quad (1.19)$$

subject to the restrictions

$$U_+(-\infty) = U_-(\infty) = 1. \qquad (1.20)$$

It is easily verified that $`S'$ is stationary with respect to variations of $U_+$ and $U_-$ about the solutions of the differential equations (1.6) and (1.10), subject to the boundary conditions (1.20), and that the stationary value of $`S'$ is S.

A variational basis for the integral equations (1.12) and (1.14) is provided by the expression

$$'S = 1 - \frac{i}{\hbar} \int_{-\infty}^{\infty} [U_-^+(t) H_1(t) + H_1(t) U_+(t)] dt$$

$$+ \frac{i}{\hbar} \int_{-\infty}^{\infty} U_-^+(t) H_1(t) U_+(t) dt$$

$$+ \left(\frac{i}{\hbar} \right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} U_-^+(t) H_1(t) \eta(t-t')$$

$$\times H_1(t') U_+(t') dt dt'. \quad (1.21)$$

Thus,

$$\delta 'S = \frac{i}{\hbar} \int_{-\infty}^{\infty} dt \, \delta U_-^+(t) H_1(t) \left[U_+(t) - 1 \right.$$

$$+ \frac{i}{\hbar} \int_{-\infty}^{\infty} \eta(t-t') H_1(t') U_+(t') dt' \right]$$

$$+ \frac{i}{\hbar} \int_{-\infty}^{\infty} dt \left[U_-(t) - 1 - \frac{i}{\hbar} \int_{-\infty}^{\infty} dt' H_1(t') \right.$$

$$\times U_-(t') \eta(t'-t) \right]^+ H_1(t) \delta U_+(t), \quad (1.22)$$

which is indeed zero if U_+ and U_- satisfy their defining integral equations. It is also evident that the stationary value of $'S$ is just the collision operator, in the form (1.15).

This variational principle differs from (1.17), or (1.19), in that no restrictions are imposed on U_+ and U_-, and that every integral contains the interaction operator H_1. The latter property implies that an adequate approximation to U_+ and U_- is required only during the actual process of interaction. Furthermore, the second type of variational principle will yield more accurate results than the first if the same approximate operators U_+ and U_- are employed. This is indicated by the results of inserting the simple but crude approximation

$$U_+(t) = U_-(t) = 1 \qquad (1.23)$$

in (1.17) and (1.21). The former yields

$$S \simeq 1 - (i/\hbar) \int_{-\infty}^{\infty} H_1(t) dt \qquad (1.24)$$

which is equivalent to the first Born approximation, while (1.21) gives

$$S \simeq 1 - (i/\hbar) \int_{-\infty}^{\infty} H_1(t) dt + (i/\hbar)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} H_1(t)$$

$$\times \eta(t-t') H_1(t') dt dt' \quad (1.25)$$

the second Born approximation.

These approximate expressions for S illustrate a disadvantage of the variational principles thus far discussed; the unitary property is not guaranteed for an inexact S. It follows from (1.24), for example, that

$$S^+S \simeq 1 + (1/\hbar^2)\left(\int_{-\infty}^{\infty} H_1(t)dt\right)^2. \qquad (1.26)$$

A version of the theory that meets this objection is obtained on replacing the unitary operators $U_+(t)$ and $U_-(t)$ by

$$V(t) = U_+(t)2/(1+S) = U_-(t)2/(1+S^{-1}). \qquad (1.27)$$

Note that

$$\begin{aligned} V(-\infty) &= 2/(1+S); \\ V(\infty) &= 2/(1+S^{-1}) = 2S/(1+S), \end{aligned} \qquad (1.28)$$

whence

$$\tfrac{1}{2}(V(\infty) + V(-\infty)) = 1 \qquad (1.29)$$

and

$$V(\infty) = V^+(-\infty). \qquad (1.30)$$

The property (1.29) leads us to write

$$V(\infty) = 1 - \tfrac{1}{2}iK; \quad V(-\infty) = 1 + \tfrac{1}{2}iK \qquad (1.31)$$

while (1.30) supplies the information

$$K^+ = K \qquad (1.32)$$

the so-called reaction operator K is Hermitian. On remarking that

$$S = V(\infty)/V(-\infty) \qquad (1.33)$$

we obtain

$$S = (1 - \tfrac{1}{2}iK)/(1 + \tfrac{1}{2}iK) \qquad (1.34)$$

which represents the unitary S in terms of the Hermitian K. We shall now construct a variational principle for K in which the Hermitian property is assured.

Consider the operator $`K'$, defined by

$$\begin{aligned} `K' = -\frac{i}{2} \int_{-\infty}^{\infty} \left(V^+(t)\frac{\partial V(t)}{\partial t} - \frac{\partial V^+(t)}{\partial t}V(t) \right)dt \\ + \frac{1}{\hbar} \int_{-\infty}^{\infty} V^+(t)H_1(t)V(t)dt \\ + \frac{i}{2}[(V(\infty) - V(-\infty)) \\ - (V^+(\infty) - V^+(-\infty))] \qquad (1.35) \end{aligned}$$

which is evidently Hermitian for arbitrary $V(t)$. The effect of a small variation in $V(t)$ and $V^+(t)$ is indicated

by

$$\begin{aligned} \delta`K' = -\frac{1}{\hbar} \int_{-\infty}^{\infty} \left[\delta V^+(t)\left(i\hbar\frac{\partial}{\partial t} - H_1(t) \right)V(t) \right. \\ + \left[\left(i\hbar\frac{\partial}{\partial t} - H_1(t) \right)V(t) \right]^+ \delta V(t) \right]dt \\ - \frac{i}{2}\left[(V^+(\infty) - V^+(-\infty))\delta\left(\frac{V(\infty) + V(-\infty)}{2} \right) \right. \\ + \left(\frac{V^+(\infty) + V^+(-\infty)}{2} - 1 \right)\delta(V(\infty) - V(-\infty)) \\ - \delta\left(\frac{V^+(\infty) + V^+(-\infty)}{2} \right)(V(\infty) - V(-\infty)) \\ - \delta(V^+(\infty) - V^+(-\infty)) \\ \left. \times \left(\frac{V(\infty) + V(-\infty)}{2} - 1 \right) \right]. \qquad (1.36) \end{aligned}$$

If, therefore, $V(t)$ is restricted by the mixed boundary condition (1.29), $`K'$ is stationary with respect to variations about the solution of the differential equation

$$\left(i\hbar\frac{\partial}{\partial t} - H_1(t) \right)V(t) = 0 \qquad (1.37)$$

and the stationary value of $`K'$ equals K, according to (1.31) and (1.32).

The integral equation satisfied by $V(t)$ can be constructed from that obeyed by $U_+(t)$, or directly in the following manner. On integrating the differential equation (1.37) from $-\infty$ to t, and from ∞ to t, we obtain

$$\begin{aligned} V(t) &= V(-\infty) - \frac{i}{\hbar}\int_{-\infty}^{t} H_1(t')V(t')dt', \\ V(t) &= V(\infty) + \frac{i}{\hbar}\int_{t}^{\infty} H_1(t')V(t')dt' \end{aligned} \qquad (1.38)$$

The addition of these equations yields, in consequence of the boundary condition (1.29),

$$V(t) = 1 - \frac{i}{2\hbar}\int_{-\infty}^{\infty} \epsilon(t-t')H_1(t')V(t')dt' \qquad (1.39)$$

where

$$\begin{aligned} \epsilon(t-t') &= 1; \quad t > t'. \\ &= -1; \quad t < t'. \end{aligned} \qquad (1.40)$$

Conversely, the differential equation and boundary condition obeyed by $V(t)$ can be deduced from the integral equation. Note also that

$$K = i(V(\infty) - V(-\infty)) = \frac{1}{\hbar}\int_{-\infty}^{\infty} H_1(t)V(t)dt. \qquad (1.41)$$

A variational principal formulation of this integral equation is provided by the expression

$$`K' = \frac{1}{\hbar} \int_{-\infty}^{\infty} (H_1(t)V(t) + V^+(t)H_1(t))dt$$

$$-\frac{1}{\hbar} \int_{-\infty}^{\infty} V^+(t)H_1(t)V(t)dt$$

$$-\frac{i}{2\hbar^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} V^+(t)H_1(t)\epsilon(t-t')H_1(t')$$

$$\times V(t')dtdt' \quad (1.42)$$

which is obviously Hermitian for arbitrary $V(t)$. Now

$$\delta`K' = -\frac{1}{\hbar} \int_{-\infty}^{\infty} \delta V^+(t)H_1(t)\left[V(t) - 1 \right.$$

$$\left. + \frac{i}{2\hbar} \int_{-\infty}^{\infty} \epsilon(t-t')H_1(t')V(t')dt' \right] dt$$

$$-\frac{1}{\hbar} \int_{-\infty}^{\infty} \left[V(t) - 1 + \frac{i}{2\hbar} \int_{-\infty}^{\infty} \epsilon(t-t')H_1(t') \right.$$

$$\left. \times V(t')dt' \right] + H_1(t)\delta V(t)dt \quad (1.43)$$

which is indeed zero if $V(t)$ satisfies the integral equation (1.39). Furthermore, the stationary value of $`K'$ is just (1.41), the correct reactor operator.

The abstract theory thus far developed can be made more explicit by introducing eigenfunctions, Φ_a, for the separated parts of the system, which will describe the initial and final states. Thus, since $S\Phi_a$ is the final state that emergies from the initial state Φ_a, the probability that the system will be found eventually in the particular state Φ_b, is

$$W_{ba} = |(\Phi_b, S\Phi_a)|^2 = |S_{ba}|^2. \quad (1.44)$$

It is slightly more convenient to deal with the operator

$$T = S - 1, \quad (1.45)$$

which generates the change in the state vector produced by the interaction process. The unitary property of S implies that

$$T^+T = -(T + T^+) \quad (1.46)$$

and the probability that the system will be found in a particular final state differing from the initial one is

$$b \neq a; \quad W_{ba} = |T_{ba}|^2. \quad (1.47)$$

Now, according to (1.15),

$$T_{ba} = -(i/\hbar) \int_{-\infty}^{\infty} dt(\Phi_b, H_1(t)U_+(t)\Phi_a),$$

$$= -(i/\hbar) \int_{-\infty}^{\infty} dt(\Phi_b, \exp(iH_0 t/\hbar)H_1$$

$$\times \exp(-iH_0 t/\hbar)U_+(t)\Phi_a). \quad (1.48)$$

It should be noted that Φ_b cannot be an exact eigenfunction of H_0, since a superposition of momentum states (wave packet) is required to produce the spatial localizability involved in the definite separation of the two parts of the system. An equivalent description is obtained, however, by introducing eigenfunctions of H_0,

$$H_0\Phi_b = E_b\Phi_b \quad (1.49)$$

and simulating the cessation of interaction, arising from the separation of the component parts of the system, by an adiabatic decrease in the interaction strength as $t \to \pm \infty$. The latter can be represented by the factor $\exp(-\epsilon|t|/\hbar)$ where ϵ is arbitrarily small. Accordingly, (1.48) becomes

$$T_{ba} = -(i/\hbar)(\Phi_b, H_1\Psi_a^{(+)}(E_b)) \quad (1.50)$$

where

$$\Psi_a^{(+)}(E) = \int_{-\infty}^{\infty} dt \exp(i(E - H_0)t/\hbar)$$

$$\times \exp(-\epsilon|t|/\hbar)U_+(t)\Phi_a. \quad (1.51)$$

Formula (1.16) for $S^{-1} - 1 = T^+$ leads, in a similar way, to

$$(T^+)_{ba} = (i/\hbar)(\Phi_b, H_1\Psi_a^{(-)}(E_b)) \quad (1.52)$$

or equivalently,

$$T_{ab} = -(i/\hbar)(\Psi_a^{(-)}(E_b), H_1\Phi_b) \quad (1.53)$$

in which

$$\Psi_a^{(-)}(E) = \int_{-\infty}^{\infty} dt \exp(i(E - H_0)t/\hbar)$$

$$\times \exp(-\epsilon|t|/\hbar)U_-(t)\Phi_a. \quad (1.54)$$

Determining equations for $\Psi_a^{(+)}(E)$ and $\Psi_a^{(-)}(E)$ can be obtained from (1.12) and (1.14), the integral equations for $U_+(t)$ and $U_-(t)$. Thus

$$\Psi_a^{(+)}(E) = \int_{-\infty}^{\infty} dt \exp(i(E - E_a)t/\hbar) \exp(-\epsilon|t|/\hbar)\Phi_a$$

$$-(i/\hbar)\int_0^{\infty} d\tau \exp(i(E - H_0)\tau/\hbar)$$

$$\times \exp(-\epsilon\tau/\hbar)H_1\Psi_a^{(+)}(E) \quad (1.55)$$

and

$$\Psi_a^{(-)}(E) = \int_{-\infty}^{\infty} dt \exp(i(E - E_a)t/\hbar) \exp(-\epsilon|t|/\hbar)\Phi_a$$

$$+(i/\hbar)\int_0^{\infty} d\tau \exp(-i(E - H_0)\tau/\hbar)$$

$$\times \exp(-\epsilon\tau/\hbar)H_1\Psi_a^{(-)}(E), \quad (1.56)$$

where $\tau = |t - t'|$. Now

$$\mp \frac{i}{\hbar} \int_0^\infty d\tau \, \exp(\pm i(E - H_0)\tau/\hbar) \, \exp(-\epsilon\tau/\hbar)$$

$$= \frac{1}{E \pm i\epsilon - H_0} = \frac{E - H_0}{(E - H_0)^2 + \epsilon^2} \mp i \frac{\epsilon}{(E - H_0)^2 + \epsilon^2}$$

$$= P\frac{1}{E - H_0} \mp i\pi\delta(E - H_0). \quad (1.57)$$

The last expression is a symbolic statement of the following integral properties possessed by the real and imaginary parts of (1.57) in the limit as $\epsilon \to 0$.

$$\underset{\epsilon \to 0}{\text{Lim}} \int_{-\infty}^\infty \frac{x}{x^2 + \epsilon^2} f(x) dx = P \int_{-\infty}^\infty \frac{f(x)}{x} dx,$$

$$\underset{\epsilon \to 0}{\text{Lim}} \frac{1}{\pi} \int_{-\infty}^\infty \frac{\epsilon}{x^2 + \epsilon^2} f(x) dx = f(0), \quad (1.58)$$

where P denotes the principal part of the integral and $f(x)$ is an arbitrary function. Therefore

$$\Psi_a^{(\pm)}(E) = 2\pi\hbar\delta(E - E_a)\Phi_a$$

$$+ \frac{1}{E \pm i\epsilon - H_0} H_1\Psi_a^{(\pm)}(E) \quad (1.59)$$

and, on writing

$$\Psi_a^{(\pm)}(E) = 2\pi\hbar\delta(E - E_a)\Psi_a^{(\pm)} \quad (1.60)$$

we obtain

$$\Psi_a^{(\pm)} = \Phi_a + \frac{1}{E_a \pm i\epsilon - H_0} H_1\Psi_a^{(\pm)}. \quad (1.61)$$

These equations provide a time-independent formulation of the scattering problem, in which the small positive or negative imaginary addition to the energy serves to select, automatically, outgoing or incoming scattered waves.

A matrix element of the operator T can now be expressed as

$$T_{ba} = -2\pi i\delta(E_a - E_b)\mathbf{T}_{ba} \quad (1.62)$$

where

$$\mathbf{T}_{ba} = (\Phi_b, H_1\Psi_a^{(+)}) = (\Psi_b^{(-)}, H_1\Phi_a) \quad (1.63)$$

are equivalent forms for an element of the association matrix $\mathbf{T}$, which is defined only for states of equal energy. The resulting formula for the transition probability,

$$W_{ba} = 4\pi^2[\delta(E_a - E_b)]^2 |\mathbf{T}_{ba}|^2 \quad (1.64)$$

is to be interpreted by replacing one factor, $\delta(E_a - E_b)$, by its defining time integral

$$\delta(E_a - E_b) = \frac{1}{2\pi\hbar} \int_{-\infty}^\infty \exp(i/(E_a - E_b)t/\hbar)$$

$$\times \exp(-\epsilon|t|/\hbar)dt; \quad \epsilon \to 0 \quad (1.65)$$

in which $E_a - E_b$ must be placed equal to zero, in view of the second delta-function factor. The expression thus obtained

$$W_{ba} = \frac{2\pi}{\hbar}\delta(E_a - E_b)|\mathbf{T}_{ba}|^2 \int_{-\infty}^\infty dt, \quad (1.66)$$

evidently describes the fact that transitions occur only between states of equal energy for the separated system, and with an intensity proportional to the total time of effective interaction. In the idealized limit $\epsilon \to 0$, the latter is infinitely large. However, we infer from (1.66) that the rate at which the transition probability increases is

$$w_{ba} = (2\pi/\hbar)\delta(E_a - E_b)|\mathbf{T}_{ba}|^2. \quad (1.67)$$

A somewhat more satisfactory derivation of this result follows from the evaluation of

$$w_{ba} = \frac{\partial}{\partial t}|(\Phi_b, U_+(t)\Phi_a)|^2 \quad (1.68)$$

which expresses the increase, per unit time, of the probability that the system, known to be initially in the state a, will be found at time t in the state b. Now

$$w_{ba} = \frac{i}{\hbar}(H_1(t)U_+(t)\Phi_a, \Phi_b)$$

$$\times (\Phi_b, U_+(t)\Phi_a) + \text{complex conjugate}$$

$$= \frac{1}{\hbar^2} \int_{-\infty}^t dt'(\exp(i/(E_b - H_0)t/\hbar)U_+(t)\Phi_a, H_1\Phi_b)$$

$$\times (\Phi_b, H_1 \exp(i(E_b - H_0)t'/\hbar)$$

$$\times U_+(t')\Phi_a) + \text{c.c.} \quad (1.69)$$

in which we have employed (1.12), and assumed that $b \neq a$. This can be simplified by noting that (1.51) and (1.60),

$$\int_{-\infty}^\infty dt \exp(i(E - H_0)t/\hbar) \exp(-\epsilon|t|/\hbar)U_+(t)\Phi_a$$

$$= 2\pi\hbar\delta(E - E_a)\Psi_a^{(+)} \quad (1.70)$$

imply that

$$\exp(-iH_0t/\hbar)U_+(t)\Phi_a = \exp(-iE_at/\hbar)\Psi_a^{(+)} \quad (1.71)$$

which is just the state vector, in the Schrödinger representation, of our idealized stationary state. Hence

$$w_{ba} = \frac{1}{\hbar^2}|\mathbf{T}_{ba}|^2 \int_{-\infty}^t \exp(i(E_a - E_b)(t - t')/\hbar)dt' + \text{c.c.}$$

$$= \frac{2\pi}{\hbar}|\mathbf{T}_{ba}|^2\delta(E_a - E_b). \quad (1.72)$$

A simple expression for the total rate of transition from the initial state follows from the general property

of the operator T contained in (1.46). On writing a matrix element of this operator relation and substituting (1.62), we obtain

$$4\pi^2 \sum_b \delta(E_a - E_b)\mathbf{T}_{ba}{}^*\delta(E_b - E_c)\mathbf{T}_{bc}$$
$$= 2\pi i\delta(E_a - E_c)(\mathbf{T}_{ac} - \mathbf{T}_{ca}{}^*). \quad (1.73)$$

The factor $\delta(E_a - E_c)$ can be canceled and (1.73) then yields, for the special situation, $c = a$,

$$4\pi^2 \sum_b \delta(E_a - E_b)|\mathbf{T}_{ba}|^2 = -4\pi Im(\mathbf{T}_{aa}) \quad (1.74)$$

or

$$\sum_b w_{ba} = -(2/\hbar)\, Im(\mathbf{T}_{aa}). \quad (1.75)$$

The left side of this formula is not exactly the total rate of transition out of the state a, since $b = a$ is included in the summation. However, a single state makes no contribution to such a summation; a group of states is required. A relation of the type (75) is characteristic of a wave theory, in which the reduction in intensity of a plane wave passing through a scattering medium is accounted for by destructive interference between the original wave and the secondary waves scattered in the direction of propagation.

A variational formulation of Eq. (1.61) by means of a stationary expression for $\mathbf{T}_{ba}$ can be obtained from the variational principle (1.21). A matrix element of this operator equation reads

$$`T'_{ba} = -\frac{i}{\hbar}\int_{-\infty}^{\infty} dt[(\exp(i(E_a - H_0)t/\hbar)U_-(t)\Phi_b, H_1\Phi_a)$$

$$+ (\Phi_b, H_1 \exp(i(E_b - H_0)t/\hbar)U_+(t)\Phi_a)]$$

$$+ \frac{i}{\hbar}\int_{-\infty}^{\infty} dt(\exp(-iH_0t/\hbar)U_-(t)\Phi_b,$$

$$\times H_1 \exp(-iH_0t/\hbar)U_+(t)\Phi_a)$$

$$+ \left(\frac{i}{\hbar}\right)^2 \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt'(\exp(-iH_0t/\hbar)U_-(t)\Phi_b,$$

$$\times H_1 \exp(-iH_0(t - t')/\hbar)$$

$$\times H_1 \exp(-iH_0t'/\hbar)U_+(t')\Phi_a) \quad (1.76)$$

in which the adiabatic reduction of H_1 for large $|t|$ has not been indicated explicitly. We now restrict ourselves to the class of stationary states, according to the assumption

$$\exp(-iH_0t/\hbar)U_{\pm}(t)\Phi_a = \exp(-iE_at/\hbar)\Psi_a{}^{(\pm)}. \quad (1.77)$$

The result of performing the time integrations is expressed by

$$`T'_{ba} = (\Psi_b{}^{(-)}, H_1\Phi_a) + (\Phi_b, H_1\Psi_a{}^{(+)})$$

$$- (\Psi_b{}^{(-)}, H_1\Psi_a{}^{(+)})$$

$$+ \left(\Psi_b{}^{(-)}, H_1\frac{1}{E + i\epsilon - H_0}H_1\Psi_a{}^{(+)}\right), \quad (1.78)$$

where E is the common energy of states a and b. We shall verify directly that (1.78) has the required properties. Thus

$$\delta`T'_{ba} = \left(\delta\Psi_b{}^{(-)}, H_1\left(\Phi_a + \frac{1}{E + i\epsilon - H_0}H_1\Psi_a{}^{(+)}\right.\right.$$

$$\left.\left. - \Psi_a{}^{(+)}\right)\right) + \left(\left(\Phi_b + \frac{1}{E - i\epsilon - H_0}H_1\Psi_b{}^{(-)}\right.\right.$$

$$\left.\left. - \Psi_b{}^{(-)}\right), H_1\delta\Psi_a{}^{(+)}\right) \quad (1.79)$$

which is indeed zero for variations about the solutions of (1.61). Furthermore, it is a consequence of the latter equations that

$$(\Psi_b{}^{(-)}, H_1\Psi_a{}^{(+)}) - \left(\Psi_b{}^{(-)}, H_1\frac{1}{E + i\epsilon - H_0}H_1\Psi_a{}^{(+)}\right)$$

$$= (\Psi_b{}^{(-)}, H_1\Phi_a) = (\Phi_b, H_1\Psi_a{}^{(+)}) \quad (1.80)$$

so that the stationary value of $`T'_{ba}$ is $\mathbf{T}_{ba}$, according to (1.63).

A similar theory can be developed for the matrix elements of the operator K. It is easily shown that

$$\mathbf{K}_{ba} = 2\pi\delta(E_a - E_b)\mathbf{K}_{ba}, \quad (1.81)$$

where

$$\mathbf{K}_{ba} = (\Phi_b, H_1\Psi_a{}^{(1)}) = (\Psi_b{}^{(1)}, H_1\Phi_a). \quad (1.82)$$

The time-independent state vector $\Psi_a{}^{(1)}$ describes a stationary state, according to the relation

$$\exp(-iH_0t/\hbar)V(t)\Phi_a = \exp(-iE_at/\hbar)\Psi_a{}^{(1)} \quad (1.83)$$

and obeys the equation

$$\Psi_a{}^{(1)} = \Phi_a + P\left(\frac{1}{E_a - H_0}\right)H_1\Psi_a{}^{(1)}. \quad (1.84)$$

A variational basis for (1.82) and (1.84) is provided by

$$`K'_{ba} = `K'_{ab}{}^* = (\Psi_b{}^{(1)}, H_1\Phi_a)$$

$$+ (\Phi_b, H_1\Psi_a{}^{(1)}) - (\Psi_b{}^{(1)}, H_1\Psi_a{}^{(1)})$$

$$+ \left(\Psi_b{}^{(1)}, H_1 P\left(\frac{1}{E - H_0}\right)H_1\Psi_a{}^{(1)}\right). \quad (1.85)$$

The connection between the matrices $\mathbf{T}$ and $\mathbf{K}$ is obtained from

$$T = S - 1 = -iK/(1 + \tfrac{1}{2}iK) \quad (1.86)$$

on rewriting the latter as

$$T + \tfrac{1}{2}iKT = -iK. \quad (1.87)$$

Non-vanishing matrix elements of this operator relation are restricted to states of equal energy, according to

(1.62) and (1.81), whence

$$T_{ba} + i\pi \sum_c K_{bc} \delta(E_c - E) T_{ca} = K_{ba}, \quad (1.88)$$

where E is the common energy states a and b. An effective way to solve this equation is to construct the eigenfunctions of K, which are defined by the eigenvalue equation

$$\sum_a K_{ba} \delta(E_a - E) f_{aA} = K_A f_{bA}. \quad (1.89)$$

Since K is an Hermitian matrix, the eigenvalues K_A are real, the eigenfunctions f_{aA} are orthogonal, and may be normalized according to

$$\sum_a f_{aA}^* \delta(E_a - E) f_{aB} = \delta_{AB}. \quad (1.90)$$

The matrix elements of K can be exhibited in terms of the eigenfunctions and eigenvalues of K

$$K_{ba} = \sum_A f_{bA} K_A f_{aA}^*. \quad (1.91)$$

Equation (1.88) for T will then be satisfied by

$$T_{ba} = \sum_A f_{bA} T_A f_{aA}^*, \quad (1.92)$$

where

$$T_A + i\pi K_A T_A = K_A \quad (1.93)$$

or

$$T_A = K_A / (1 + i\pi K_A). \quad (1.94)$$

This is only to say that T is a function of K and therefore possesses the same eigenfunctions, while its eigenvalues are determined by those of K. These eigenvalues can be conveniently expressed by introducing the real angles δ_A, according to

$$K_A = -(1/\pi) \tan\delta_A \quad (1.95)$$

so that

$$T_A = -(1/\pi) \sin\delta_A e^{i\delta_A}. \quad (1.96)$$

The resulting expression for the transition probability per unit time is

$$w_{ba} = (2/\pi\hbar) |\sum_A \sin\delta_A e^{i\delta_A} f_{bA} f_{aA}^*|^2 \delta(E_a - E_b) \quad (1.97)$$

and the total probability per unit time for transitions from a particular state is given by

$$\sum_b w_{ba} = (2/\pi\hbar) \sum_A \sin^2\delta_A |f_{aA}|^2 \quad (1.98)$$

according to (1.97) or (1.75). Finally, the sum of the total transition probability per unit time over all initial states of the same energy is expressed by

$$\sum_{b,a} w_{ba} \delta(E_a - E) = (2/\pi\hbar) \sum_A \sin^2\delta_A. \quad (1.99)$$

These results are generalizations of familiar formulas obtained in the conventional phase shift analysis of the scattering of a particle by a central field of force. In the latter situation, the eigenfunctions of K are evident from symmetry considerations, namely the invariance of K_{ba} under a simultaneous rotation of k_a and k_b, the

propagation vectors that define the initial and final states. It may be inferred that the f_{aA} are spherical harmonics, considered as a function of the angles that define the direction of k_a,

$$f_{aA} = CY_l^m(k_a); \quad A \equiv l, m, \quad (1.100)$$

and that the eigenvalues of K depend only upon the order of the spherical harmonics, i.e., $\delta_A \equiv \delta_l$. The constant C is fixed by the normalization convention contained in (1.90), which now reads,

$$|C|^2 \int Y_l^{m*}(k) Y_{l'}^{m'}(k) \rho d\Omega = \delta_{ll'} \delta_{mm'}. \quad (1.101)$$

Here $\rho d\Omega$ is the number of states, per unit energy range, associated with motion within the solid angle $d\Omega$. This occurs as a weight factor in a summation over states with equal energy, replacing the summation over all states as restricted by the factor $\delta(E_a - E)$. Explicitly,

$$\rho = \frac{p^2 dp}{8\pi^3 \hbar^3 dE} = \frac{1}{8\pi^3 \hbar} \frac{k^2}{v}, \quad (1.102)$$

if we consider a unit spatial volume. The second form in (1.102) expresses ρ in terms of the wave number k and v, the speed of the particle. With spherical harmonics that are normalized on a unit sphere (1.101) requires that

$$|C|^2 = 1/\rho = 8\pi^3 \hbar v / k^2. \quad (1.103)$$

We may now compute from (1.97) the probability, per unit time, that the particle is scattered from the direction of k_a into the solid angle $d\Omega$ around the direction of k_b,

$$w = (2/\pi\hbar) |\sum_{l,m} \sin\delta_l e^{i\delta_l} |C|^2 Y_l^m(k_b) Y_l^{m*}(k_a)|^2 \rho d\Omega. \quad (1.104)$$

We then obtain the well-known expression of the differential cross section for scattering through an angle ϑ,

$$d\sigma(\vartheta) = (1/k^2) |\sum_l (2l+1) \sin\delta_l e^{i\delta_l} P_l(\cos\vartheta)|^2 d\Omega \quad (1.105)$$

on dividing w by v, which measures the flux of incident particles, and employing the spherical harmonics addition theorem,

$$\sum_{m=-l}^{l} Y_l^m(k_b) Y_l^{m*}(k_a) = [(2l+1)/4\pi] P_l(\cos\vartheta), \quad (1.106)$$

where the Legendre polynomial $P_l(\cos\vartheta)$ is a function of ϑ, the angle between k_a and k_b. The total scattering cross section is obtained from (1.98),

$$\sigma = (2/\pi\hbar v) \sum_{l,m} \sin^2\delta_l |C|^2 |Y_l^m(k_a)|^2$$

$$= (4\pi/k^2) \sum_l (2l+1) \sin^2\delta_l \quad (1.107)$$

in consequence of

$$\sum_m |Y_i^m(\mathbf{k}_a)|^2 = (2l+1)/4\pi. \qquad (1.108)$$

Since the total cross section is independent of the incidence direction, the same result follows immediately from (1.99).

We consider finally, the variational formulation of problems possessing the general character of the scattering by a central force field; namely, those in which the eigenfunctions of $\mathbf{K}$ are determined by symmetry considerations, and the basic question is to obtain the eigenvalues $\mathbf{K}_A$, or the phase angles δ_A. For this purpose, we notice that the inverse of (1.91) is

$$\sum_{b,a} f_{bB}{}^*\delta(E_b-E)\mathbf{K}_{ba}f_{aA}\delta(E_a-E) = \mathbf{K}_A\delta_{AB}. \quad (1.109)$$

On introducing the state vectors

$$\sum_a \Phi_a f_{aA}\delta(E_a-E) = \Phi_A, \qquad (1.110)$$

and

$$\sum_a \Psi_a^{(1)} f_{aA}\delta(E_a-E) = \Psi_A^{(1)}, \qquad (1.111)$$

the variational principle (1.85) becomes

$$\frac{1}{\pi}\tan\delta'_A\delta_{AB} = (\Psi_B^{(1)}, H_1\Phi_A)$$
$$+ (\Phi_B, H_1\Psi_A^{(1)}) - (\Psi_B^{(1)}, H_1\Psi_A^{(1)})$$
$$+ \left(\Psi_B^{(1)}, H_1 P\left(\frac{1}{E-H_0}\right)H_1\Psi_A^{(1)}\right). \quad (1.112)$$

Note that Φ_A, or more exactly written $\Phi_{A,E}$, has the following orthogonality-normalization property:

$$(\Phi_{A,E}, \Phi_{B,E'}) = \sum_a f_{aA}{}^*\delta(E_a-E)f_{AB}\delta(E_a-E')$$
$$= \delta(E-E')\sum_a f_{aA}{}^*\delta(E_a-E)f_{aB}$$
$$= \delta_{AB}\delta(E-E') \qquad (1.113)$$

and that the inverses of (1.110), (1.111) are

$$\Phi_a = \sum_A f_{aA}{}^*\Phi_A, \quad \Psi_a^{(1)} = \sum_A f_{aA}{}^*\Psi_A^{(1)} \quad (1.114)$$

which are expansions of these state vectors in eigenvectors of $\mathbf{K}$.

III. NEUTRON SCATTERING BY A BOUND PROTON

As an application of the variational methods discussed in the first section, we consider the scattering of slow neutrons by a proton bound in an otherwise inert molecule. If the momentum associated with the center of gravity of the whole system is assumed to be zero, the unperturbed Hamiltonian consists of two parts, one describing the relative motion of the neutron and the molecular center of gravity, the other being the Hamiltonian of the internal molecular motion,

$$H_0 = (\mathbf{p}_n^2/2\mu) + H_m. \qquad (2.1)$$

Here

$$\mu = AM/(A+1) \qquad (2.2)$$

is the reduced mass for relative motion of the neutron and molecule, while A is the molecular mass in units of M, the mass of the neutron. The perturbation is the neutron-proton interaction energy,

$$H_1 = V(\mathbf{r}_n - \mathbf{r}_p) \qquad (2.3)$$

which also depends upon the spin operators of neutron and proton, $\boldsymbol{\sigma}_n$ and $\boldsymbol{\sigma}_p$. The simplifying feature in this problem arises from the short range and large magnitude of the nuclear potential contrasted with the long range, weak molecular forces. The variational principle (1.78) requires a knowledge of the wave function representing the state vector only within the region of nuclear interaction, where the molecular force on the proton is negligible. Thus, the basic problem is the scattering of a neutron by a free proton, with essentially zero energy of relative motion. We therefore first consider some properties of the latter system.

The unperturbed Hamiltonian for a neutron and a free proton, in the system in which the center of gravity is at rest, is

$$\mathfrak{H}_0 = \mathbf{p}^2/M, \qquad (2.4)$$

where $\mathbf{p}$ is the relative momentum of the particles. If we temporarily omit the spin coordinates, the wave function φ, representing the unperturbed state vector Φ_a, is simply a constant in the limit of zero energy. This constant can be chosen as unity, corresponding to a unit spatial volume. The wave function representing the state vectors $\Psi_a^{(+)}$ and $\Psi_a^{(-)}$ will be denoted by $\psi(\mathbf{r})$. There is no distinction between outgoing and incoming waves in the limit of zero energy. Since the scattering is necessarily isotropic, $\mathbf{T}_{ba}$ is simply a constant, denoted by $\mathbf{t}$. According to (1.63), $\mathbf{t}$ is given by

$$\mathbf{t} = (\varphi, V\psi) = \int V(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}, \qquad (2.5)$$

where ψ obeys the integral equation (1.61).

$$\psi + (1/\mathfrak{H}_0)V\psi = \varphi. \qquad (2.6)$$

The connection between $\mathbf{t}$ and the S phase shift is obtained from (1.92) and (1.96),

$$\mathbf{t} = -|f|^2 ka/\pi, \qquad (2.7)$$

in which we have employed the zero energy limiting form,

$$\sin\delta \to ka; \quad k \to 0 \qquad (2.8)$$

thereby introducing the scattering amplitude a. The constant f is fixed by the normalization condition (1.90),

$$|f|^2 4\pi\rho = 1 \qquad (2.9)$$

where, (1.102),

$$4\pi\rho = k^2/2\pi^2\hbar v = kM/4\pi^2\hbar^2. \qquad (2.10)$$

The second form of (2.10) follows from $\hbar k = \frac{1}{2}Mv$, the relation between the relative momentum and the relative velocity. Finally,

$$\mathbf{t} = -4\pi\hbar^2 a/M. \qquad (2.11)$$

If the neutron-proton interaction operator is spin-dependent, **t** must be replaced by a matrix in the spin quantum numbers. The eigenfunctions of this spin matrix are those of the triplet and singlet states of resultant spin angular momentum. The associated eigenvalues of **t** are related to the triplet and singlet scattering amplitudes,

$$t_{1,0} = -4\pi\hbar^2 a_{1,0}/M. \qquad (2.12)$$

As in (1.92), the matrix **t** can be constructed as a linear combination of its eigenvalues, multiplied by coefficients which are the matrix elements of projection operators for the corresponding eigenvalues. The projection operators for the triplet and singlet states are well known to be

$$P_1 = \tfrac{1}{4}(3 + \boldsymbol{\sigma}_n \cdot \boldsymbol{\sigma}_p), \quad P_0 = \tfrac{1}{4}(1 - \boldsymbol{\sigma}_n \cdot \boldsymbol{\sigma}_p). \qquad (2.13)$$

Hence, to include spin dependent interactions it is sufficient to regard **t** in (2.11) as a spin operator, with

$$a = a_1 P_1 + a_0 P_0 = \tfrac{1}{4}(3a_1 + a_0) + \tfrac{1}{4}(a_1 - a_0)\boldsymbol{\sigma}_n \cdot \boldsymbol{\sigma}_p. \qquad (2.14)$$

We shall now perform an approximate but highly accurate evaluation of $\mathbf{T}_{ba}$, which describes the scattering of a neutron by a bound proton. For this purpose, (1.78) is written

$$`\mathbf{T}'_{ba} = (\Psi_b{}^{(-)}, V\Phi_a) + (\Phi_b, V\Psi_a{}^{(+)})$$

$$- (\Psi_b{}^{(-)}, V\Psi_a{}^{(+)}) - \left(\Psi_b{}^{(-)}, V\frac{1}{\mathfrak{IC}_0}V\Psi_a{}^{(+)}\right)$$

$$+ \left(\Psi_b{}^{(-)}, V\left(\frac{1}{E+i\epsilon-H_0} + \frac{1}{\mathfrak{IC}_0}\right)V\Psi_a{}^{(+)}\right), \qquad (2.15)$$

In treating the spin dependent interactions, it is convenient to suppress spin functions and thus regard $\mathbf{T}_{ba}$ as a spin operator. The first approximation to be introduced concerns the wave function representing the state vector Φ_a, say $\Phi_a(\mathbf{r}_n, \mathbf{r})$. Here $\mathbf{r}_n$ is the neutron coordinate relative to the molecular center of gravity, while **r** symbolizes the set of internal molecular coordinates, including $\mathbf{r}_p$, the proton position vector relative to the molecular center of gravity. This wave function, describing the independent motion of the neutron and molecule, will have the form

$$\Phi_a(\mathbf{r}_n, \mathbf{r}) = \exp(i\mathbf{k}_a \cdot \mathbf{r}_n) \cdot \chi_a(\mathbf{r}) \qquad (2.16)$$

in which $\chi_a(\mathbf{r})$ is an internal molecular wave function. Now $\Phi_a(\mathbf{r}_n, \mathbf{r})$ in (2.15), only occurs multiplied by the short range nuclear potential $V(\mathbf{r}_n - \mathbf{r}_p)$. We shall therefore replace $\Phi_a(\mathbf{r}_n, \mathbf{r})$ by

$$\Phi_a(\mathbf{r}_p, \mathbf{r}) = F_a(\mathbf{r}). \qquad (2.17)$$

The error thereby incurred is of the order $(kr_0)^2$, where r_0 is a measure of the nuclear force range. Since the influence of molecular binding is only of interest for slow neutrons, $(kr_0)^2 \gtrsim 10^{-6}$, and we need not introduce a correction to compensate for this replacement.

A second approximation involves the last term of (2.15), which is small in comparison with the other terms, since molecular energies are negligible in comparison with the practically equal kinetic energies of neutron and proton during the nuclear interaction process. If we initially ignore the last term of (2.15) the latter reads

$$`\mathbf{T}'_{ba} = (\Psi_b{}^{(-)}, VF_a) + (F_b, V\Psi_a{}^{(+)})$$

$$- (\Psi_b{}^{(-)}, V\Psi_a{}^{(+)}) - \left(\Psi_b{}^{(-)}, V\frac{1}{\mathfrak{IC}_0}V\Psi_a{}^{(+)}\right). \qquad (2.18)$$

The condition that $`\mathbf{T}'_{ba}$ be stationary is that $\Psi_a{}^{(\pm)}$ satisfy the relation

$$\Psi_a{}^{(\pm)} + (1/\mathfrak{IC}_0)V\Psi_a{}^{(\pm)} = F_a(\mathbf{r}). \qquad (2.19)$$

On comparison with (2.6), it is evident that

$$\Psi_a{}^{(\pm)} = \psi(\mathbf{r}_n - \mathbf{r}_p)F_a(\mathbf{r}) \qquad (2.20)$$

and the stationary value of $`\mathbf{T}'_{ba}$, an approximation to the correct $\mathbf{T}_{ba}$, is given by

$$\mathbf{T}_{ba} \simeq (F_b, V\Psi_a{}^{(+)}) = (F_b, V\psi F_a)$$

$$= \mathbf{t}\int F_b{}^*(\mathbf{r})F_a(\mathbf{r})d\mathbf{r} \qquad (2.21)$$

according to (2.5). This result,

$$\mathbf{T}_{ba} \simeq -\frac{4\pi\hbar^2}{M}a\int \exp[i(\mathbf{k}_a - \mathbf{k}_b)\cdot\mathbf{r}_p]\cdot$$

$$\times \chi_b{}^*(\mathbf{r})\chi_a(\mathbf{r})d\mathbf{r} \qquad (2.22)$$

is the Fermi approximation.

To include the last term in (2.15), we observe that it may be written, in terms of wave functions, as

$$\int \Psi_b{}^{(-)*}(\mathbf{r}_n, \mathbf{r})V(\mathbf{r}_n - \mathbf{r}_p)$$

$$\times \left(\mathbf{r}_n, \mathbf{r}\left|\frac{1}{E+i\epsilon-H_0} + \frac{1}{\mathfrak{IC}_0}\right|\mathbf{r}_n', \mathbf{r}'\right)V(\mathbf{r}_n' - \mathbf{r}_p')$$

$$\times \Psi_a{}^{(+)}(\mathbf{r}_n', \mathbf{r}')d\mathbf{r}_n d\mathbf{r} d\mathbf{r}_n' d\mathbf{r}'. \qquad (2.23)$$

We shall again introduce an approximation which exploits the short range of V in comparison with molecular dimensions, namely, the replacement of (2.23) by

$$\int \Psi_b{}^{(-)*}(\mathbf{r}_n, \mathbf{r})V(\mathbf{r}_n - \mathbf{r}_p)K^{(+)}(\mathbf{r}, \mathbf{r}')V(\mathbf{r}_n' - \mathbf{r}_p')$$

$$\times \Psi_a{}^{(+)}(\mathbf{r}_n', \mathbf{r}')d\mathbf{r}_n d\mathbf{r} d\mathbf{r}_n' d\mathbf{r}', \qquad (2.24)$$

where

$$K^{(\pm)}(\mathbf{r}, \mathbf{r}') = \left(\mathbf{r}_p, \mathbf{r}\left|\frac{1}{E\pm i\epsilon-H_0} + \frac{1}{\mathfrak{IC}_0}\right|\mathbf{r}_p', \mathbf{r}'\right). \qquad (2.25)$$

The conditions that $`T'_{ba}`$ be stationary are then expressed by

$$\Psi_a{}^{(\pm)}+\frac{1}{\mathfrak{IC}_0}V\Psi_a{}^{(\pm)}=F_a(\mathbf{r})+\int K^{(\pm)}(\mathbf{r},\ \mathbf{r}')$$

$$\times V(\mathbf{r}_n{}'-\mathbf{r}_p{}')\Psi_a{}^{(\pm)}(\mathbf{r}_n{}',\ \mathbf{r}')d\mathbf{r}_n{}'d\mathbf{r}' \quad (2.26)$$

which, in virtue of (2.5) and (2.6), imply that

$$\Psi_a{}^{(\pm)}=\psi(\mathbf{r}_n-\mathbf{r}_p)G_a{}^{(\pm)}(\mathbf{r}) \quad (2.27)$$

where $G_a{}^{(\pm)}(\mathbf{r})$ obeys the integral equation

$$G_a{}^{(\pm)}(\mathbf{r})-\mathbf{t}\int K^{(\pm)}(\mathbf{r},\ \mathbf{r}')G_a{}^{(\pm)}(\mathbf{r}')d\mathbf{r}'=F_a(\mathbf{r}). \quad (2.28)$$

This is a generalization of the integral equation obtained by Breit.

The stationary value of $`T'_{ba}`$ is given by

$$\mathbf{T}_{ba}\simeq(F_b,\ V\Psi_a{}^{(+)})=\mathbf{t}\int F_b{}^*(\mathbf{r})G_a{}^{(+)}(\mathbf{r})d\mathbf{r}. \quad (2.29)$$

The integral equation for $G_a{}^{(+)}(\mathbf{r})$ can be solved by successive substitutions,

$$G_a{}^{(+)}(\mathbf{r})=F_a(\mathbf{r})+\mathbf{t}\int K^{(+)}(\mathbf{r},\ \mathbf{r}')F_a(\mathbf{r}')d\mathbf{r}'$$

$$+\mathbf{t}^2\int K^{(+)}(\mathbf{r},\ \mathbf{r}')K^{(+)}(\mathbf{r}',\ \mathbf{r}'')$$

$$\times F_a(\mathbf{r}'')d\mathbf{r}'d\mathbf{r}''+\cdots, \quad (2.30)$$

which is evidently a power series expansion in a/l, where l is a characteristic molecular dimension. Since $a/l\sim10^{-3}$, the series converges rapidly and it is quite sufficient to retain only the first term beyond $F_a(\mathbf{r})$ to obtain an accurate estimate of the correction to Fermi's approximation. Therefore,

$$\mathbf{T}_{ba}\simeq\mathbf{t}\int F_b{}^*(\mathbf{r})F_a(\mathbf{r})d\mathbf{r}+\mathbf{t}^2\int F_b{}^*(\mathbf{r})K^{(+)}(\mathbf{r},\ \mathbf{r}')F_a(\mathbf{r}')$$

$$\times d\mathbf{r}d\mathbf{r}'. \quad (2.31)$$

To construct $K^{(+)}(\mathbf{r},\ \mathbf{r}')$, we observe that

$$\left(\mathbf{r}_n,\ \mathbf{r}\left|\frac{1}{E+i\epsilon-H_0}\right|\mathbf{r}_n{}',\ \mathbf{r}'\right)$$

$$=\sum_c \Phi_c(\mathbf{r}_n,\ \mathbf{r})\frac{1}{E+i\epsilon-E_a}\Phi_c{}^*(\mathbf{r}_n{}',\ \mathbf{r}')$$

$$=\sum_\gamma \int \frac{d\mathbf{k}}{(2\pi)^3}\exp(i\mathbf{k}\cdot\mathbf{r}_n)\cdot\chi_\gamma(\mathbf{r})$$

$$\times\frac{1}{E+i\epsilon-(\hbar^2k^2/2\mu)-W_\gamma}$$

$$\times\exp(-i\mathbf{k}\cdot\mathbf{r}_n{}')\chi_\gamma{}^*(\mathbf{r}'). \quad (2.32)$$

In the second version, the summation over the states of the system molecule plus free neutron is explicitly performed over the independent states of the molecule and of the neutron. For the evaluation of the corresponding matrix element of $1/\mathfrak{IC}_0$, it must be realized that the latter operator refers to the relative motion of neutron and proton only. Thus

$$\left(\mathbf{r}_n,\ \mathbf{r}\left|\frac{1}{\mathfrak{IC}_0}\right|\mathbf{r}_n{}',\ \mathbf{r}'\right)=\int \frac{d\mathbf{k}}{(2\pi)^3}\exp(i\mathbf{k}\cdot(\mathbf{r}_n-\mathbf{r}_p))\left(\frac{M}{\hbar^2k^2}\right)$$

$$\times\exp(i\mathbf{k}\cdot(\mathbf{r}_n{}'-\mathbf{r}_p{}'))$$

$$\times\delta\left(\frac{\mathbf{r}_n+\mathbf{r}_p}{2}-\frac{\mathbf{r}_n{}'+\mathbf{r}_p{}'}{2}\right)\delta(\mathbf{s}-\mathbf{s}'), \quad (2.33)$$

where $\mathbf{s}$ symbolizes the set of internal molecular coordinates, omitting $\mathbf{r}_p$. We are actually interested in (2.33) as $\mathbf{r}_n\rightarrow\mathbf{r}_p$ and $\mathbf{r}_n{}'\rightarrow\mathbf{r}_p{}'$. In this limit, $\delta(\mathbf{r}_n+\mathbf{r}_p/2-\mathbf{r}_n{}'+\mathbf{r}_p{}'/2)$ becomes $\delta(\mathbf{r}_p-\mathbf{r}_p{}')$ and we may employ the completeness relation for the molecular eigenfunctions,

$$\delta(\mathbf{r}_p-\mathbf{r}_p{}')\delta(\mathbf{s}-\mathbf{s}')=\delta(\mathbf{r}-\mathbf{r}')=\sum_\gamma \chi_\gamma(\mathbf{r})\chi_\gamma{}^*(\mathbf{r}'). \quad (2.34)$$

One can now combine (2.32) and (2.33) to form

$$K^{(+)}(\mathbf{r},\ \mathbf{r}')=\sum_\gamma \int \frac{d\mathbf{k}}{(2\pi)^3}\exp(i\mathbf{k}\cdot\mathbf{r}_p)\chi_\gamma(\mathbf{r})$$

$$\times\left[\frac{1}{E+i\epsilon-(\hbar^2k^2/2\mu)-W_\gamma}+\frac{1}{(\hbar^2k^2/M)}\right]$$

$$\times\exp(-i\mathbf{k}\cdot\mathbf{r}_p{}')\chi_\gamma{}^*(\mathbf{r}')$$

$$=\frac{M}{\hbar^2}\sum_\gamma \int \frac{d\mathbf{k}}{(2\pi)^3}\exp(i\mathbf{k}\cdot(\mathbf{r}_p-\mathbf{r}_p{}'))$$

$$\times\left[\frac{2\mu/M}{k_\gamma{}^2+i\eta-k^2}+\frac{1}{k^2}\right]\chi_\gamma(\mathbf{r})\chi_\gamma{}^*(\mathbf{r}'). \quad (2.35)$$

Here

$$k_\gamma{}^2=(2\mu/\hbar^2)(E-W_\gamma) \quad (2.36)$$

and $\eta=(2\mu/\hbar^2)\epsilon$. The $\mathbf{k}$ integration in (2.35) involves the well-known integrals

$$\int \frac{d\mathbf{k}}{(2\pi)^3}\frac{\exp(i\mathbf{k}\cdot(\mathbf{r}_p-\mathbf{r}_p{}'))}{k^2-k_\gamma{}^2-i\eta}=\frac{\exp(ik_\gamma|\mathbf{r}_p-\mathbf{r}_p{}'|)}{4\pi|\mathbf{r}_p-\mathbf{r}_p{}'|} \quad (2.37)$$

and

$$\int \frac{d\mathbf{k}}{(2\pi)^3}\frac{\exp(i\mathbf{k}\cdot(\mathbf{r}_p-\mathbf{r}_p{}'))}{k^2}=\frac{1}{4\pi|\mathbf{r}_p-\mathbf{r}_p{}'|}, \quad (2.38)$$

where

$$k_\gamma = +\left(\frac{2\mu}{\hbar^2}(E-W_\gamma)\right)^{\frac{1}{2}}; \quad W_\gamma < E$$

$$= +i\left(\frac{2\mu}{\hbar^2}(W_\gamma - E)\right)^{\frac{1}{2}}; \quad W_\gamma > E \quad (2.39)$$

the propagating or attenuating nature of the spherical wave corresponding to whether or not the excitation of the molecular state γ is energetically possible. Finally, then

$$K^{(+)}(\mathbf{r}, \mathbf{r}') = -\frac{M}{4\pi\hbar^2}\sum_\gamma \chi_\gamma(\mathbf{r})\chi_\gamma^*(\mathbf{r}')$$

$$\times \frac{2\mu}{M}\frac{\exp(ik_\gamma|\mathbf{r}_p - \mathbf{r}_p'|) - 1}{|\mathbf{r}_p - \mathbf{r}_p'|} \quad (2.40)$$

and

$$\mathbf{T}_{ba} \simeq -\frac{4\pi\hbar^2}{M}a\left[\int F_b^*(\mathbf{r})F_a(\mathbf{r})d\mathbf{r}\right.$$

$$+ a\sum_\gamma \int F_b^*(\mathbf{r})\chi_\gamma(\mathbf{r})\chi_\gamma^*(\mathbf{r}')$$

$$\left.\times\frac{(2\mu/M)\exp(ik_\gamma|\mathbf{r}_p - \mathbf{r}_p'|) - 1}{|\mathbf{r}_p - \mathbf{r}_p'|}F_a(\mathbf{r}')d\mathbf{r}d\mathbf{r}'\right]. \quad (2.41)$$

The ratio $2\mu/M$ ranges from unity, referring to a free proton, to 2, which applies to a proton bound in an infinitely heavy molecule. Our results for these situations are in agreement with those of Breit. In particular, for a free proton $k_\gamma = k$, since there is no internal molecular motion, and (2.41) reduces to

$$\mathbf{T}_{ba} = \mathbf{t}' = -\frac{4\pi\hbar^2}{M}a(1 + ika). \quad (2.42)$$

This is simply the exact version of (2.7)

$$\mathbf{t}' = -\frac{1}{\pi}|f|^2\sin\delta e^{i\delta} = -\frac{4\pi\hbar^2}{M}\frac{1}{k}\frac{\tan\delta}{1 - i\tan\delta} \quad (2.43)$$

with $\tan\delta$ replaced by ka, the low energy limiting form, but retaining the complex factor $1/(1 - i\tan\delta) \simeq 1 + ika$. The latter has a negligible effect on transition probabilities in the energy range of interest, but is necessary to preserve the general conservation theorem (1.74). We shall, indeed, verify (1.74) for the more general expression (2.41). It is most evident from (2.31) and (2.32) that

$$-\frac{1}{\pi}Im\mathbf{T}_{aa} = \mathbf{t}^2\sum_c \int F_a^*(\mathbf{r})F_c(\mathbf{r})\delta(E - E_c)$$

$$\times F_c^*(\mathbf{r}')F_a(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

$$= \sum_c |\mathbf{T}_{ca}|^2\delta(E - E_c) \quad (2.44)$$

in which $\mathbf{T}_{ca}$ on the right side is computed from the Fermi approximation. This is in accordance with the approximate nature of (2.41).