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THE SCATTERING OF ELECTRONS BY NEUTRAL ATOMS

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ABSTRACT

A recent reformulation of the theory of electron scattering by atoms--in which those scatterings, real or virtual, that leave the state of the atom unchanged are separated off from the remainder--has been generalized to include the effects of the Pauli principle. The case where the Hartree approximation suffices to describe the atom is considered in detail, including a calculation of the "scattering potential" to second order.

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I. INTRODUCTION

Recently, a new method was introduced for handling atomic scattering problems.[1] The novel element was a rearrangement of the perturbation series for the scattering so that a "scattering potential" was obtained for all interactions not changing the state of the atom. The scattered particle was assumed not to be an electron, so there was no need to consider the Pauli principle.

The purpose of this discussion is to extend the method of I to include the effects of the Pauli principle; that is, we now assume that the scattered particle is an electron. Previously, methods have been developed for handling exchange corrections for electron-atom scattering within the framework of the Hartree-Fock approximation.[2,3] From such studies one concludes that although exchange corrections are not of paramount importance for scattering by heavy atoms, they are not really negligible, at least for low-energy scattering.[4]

II. THE SCATTERING OF A PARTICLE BY A SYSTEM OF SIMILAR PARTICLES

We consider the scattering of an electron by a neutral atom having z electrons. The essence of the Pauli principle is that all the electrons are equivalent, so we shall adapt our notation to express this symmetry.

Thus, we label the electrons $0, 1, \ldots z$. Then, with $\underset{\sim}{p}_\ell$, $\underset{\sim}{x}_\ell$ as the momentum and coordinate operators for the ℓth electron, and $\sum_i$ meaning an unrestricted summation from 0 to z, the Hamiltonian is[5]

$$H = K + V_N + V \,, \tag{2.1}$$

where

$$K = \sum_i K_i = \sum_i \frac{\underset{\sim}{p}_i^2}{2m} \,,$$

$$V_N = \sum_i v_N(\underset{\sim}{x}_i) = \sum_i - \frac{ze^2}{|\underset{\sim}{x}_i|} \,,$$

and

$$V = \sum_{i<j} v_{ij} = \sum_{i<j} \frac{e^2}{|\underset{\sim}{x}_i - \underset{\sim}{x}_j|} \,. \tag{2.2}$$

When an arbitrary electron, say the ℓth, moves freely while the remaining electrons are bound to the nucleus, we shall write the Hamiltonian as

$$H_\ell = h_\ell + K_\ell \,. \tag{2.3}$$

Here, K_ℓ has been defined above, and we have

$$h_\ell = \sum_i^{(\ell)} \{ K_i + v_N(\underset{\sim}{x}_i) \} + \sum_{i<j}^{(\ell)} v_{ij} \,, \tag{2.4}$$

where $\sum_i^{(\ell)}$ means summation from 0 to z excluding ℓ.

The Hamiltonian H_ℓ differs from H by the interaction between electron ℓ and the rest of the system. Calling this interaction $\overline{V}_\ell$, we have

$$H = H_\ell + \overline{V}_\ell ,$$

and (2.5)

$$\overline{V}_\ell = v_N(\underset{\sim}{x}_\ell) + \sum_i^{(\ell)} v_{i\ell} = v_N(\underset{\sim}{x}_\ell) + V_\ell ,$$

thereby also defining V_ℓ.

We turn now to the definitions of the basis eigenvectors of the problem. If we assume that electron 0 is the incident particle, the atom is described by the Schrödinger equation,

$$h_0 \phi_n = W_n \phi_n , \tag{2.6}$$

where $\phi_n(0) \equiv \phi_n(x_1 \ldots x_z)$ is the (antisymmetric) eigenvector and W_n the energy belonging to the atomic state n. To simplify the notation, we shall assume that the electron-spin variables are included with the coordinates $\underset{\sim}{x}_i$ by writing x_i, etc.

If electron ℓ is incident, we operate on Eq. (2.6) with $\mathcal{P}_{0\ell}$, the operator that interchanges electrons 0 and ℓ; because we have

$$h_\ell = \mathcal{P}_{0\ell} h_0 \mathcal{P}_{0\ell} ,$$

we find

$$h_\ell \phi_n(\ell) = W_n \phi_n(\ell) , \tag{2.7}$$

where $\phi_n(\ell) \equiv \mathcal{P}_{0\ell} \phi_n = \phi_n(x_1 \ldots x_0(\ell) \ldots x_z)$. The symbol $x_0(\ell)$ indicates that x_0 now occupies the position formerly belonging to x_ℓ.

The eigenvector that describes electron ℓ, moving freely with energy $\epsilon_{p_0} = p_0^2/2m$ is $\lambda_{p_0}(x_\ell)$, where

$$K_\ell \lambda_{p_0}(x_\ell) = \epsilon_{p_0} \lambda_{p_0}(x_\ell) \tag{2.8}$$

and

$$\langle x_\ell \mid \lambda_{p_0}(x_\ell) \rangle = (2\pi)^{-3/2} e^{i\underset{\sim}{p}_0 \underset{\sim}{x}_\ell} . \tag{2.9}$$

For the system comprising an atom plus the ℓth electron incident moving without interaction, we have the description

$$H_\ell \mid p_0 n_0 \rangle_\ell = E \mid p_0 n_0 \rangle_\ell \tag{2.10}$$

with

$$E = \epsilon_{p_0} + W_{n_0}$$

and

$$\mid p_0 n_0 \rangle_\ell \equiv \lambda_{p_0}(x_\ell) \phi_{n_0}(\ell) = \lambda_{p_0}(x_\ell) \phi_{n_0}(x_1 \ldots x_0(\ell) \ldots x_z). \tag{2.11}$$

We observe that

$$H_\ell = \mathcal{P}_{0\ell} H_0 \mathcal{P}_{0\ell} ,$$

so that, as expected,

$$\mid p\, n \rangle_\ell = \mathcal{P}_{0\ell} \mid p\, n \rangle_0 .$$

Finally, the Schrödinger equation, including all interactions, is

$$(E - H)\Psi = 0 . \tag{2.12}$$

Here, Ψ is antisymmetric in all pairs of electrons.

A boundary condition must be added to Eq. (2.12), to fix Ψ uniquely. The physics of the problem dictates the boundary condition: as $\underset{\sim}{x}_\ell$ approaches ∞, for ℓ arbitrary, Ψ approaches the asymptotic form

$$\Psi \underset{(x_\ell \to \infty)}{\sim} \delta_\ell \mid p_0\, n_0 \rangle_\ell + (\text{electron } \ell \text{ outgoing scattered waves}). \qquad (2.13)$$

$$(\ell = 0, \ldots z)$$

Here, $p_0 n_0$ labels the incident wave, while the factor δ_ℓ, given by

$$\delta_\ell = 1 \quad \text{for} \quad \ell = 0$$
$$= -1 \quad \text{for} \quad \ell \neq 0 \,, \qquad (2.14)$$

insures that the first term of Eq. (2.13) is antisymmetric in all pairs of electrons. We should, perhaps, write Ψ as $\Psi_{p_0 n_0}$, to show which incident wave is the source function, but we prefer to leave the subscripts understood.

The basis vectors $\mid p\, n \rangle_0$ are orthonormal,

$$\underset{0}{\langle} p'\, n' \mid p\, n \rangle_0 = \delta_{pp'}\, \delta_{nn'} \,,$$

and form a complete set for the expansion of any vector, e.g. $L(x_0;\, x_1 \ldots x_z)$, which is antisymmetric in any pair $x_1 \ldots x_z$ but has arbitrary symmetry in x_0 :

$$L(x_0;\, x_1 \ldots x_z) = \sum_{pn} \mid p\, n \rangle_0\, C_{pn} \,.$$

In what follows, we shall often wish to form antisymmetric expressions from the $\mid p\, n \rangle_0$. This can be accomplished by using the δ_ℓ defined above

and the $\mathcal{P}_{0\ell}$ defined previously. For example, let $Q(x_0; x_1 \ldots x_z)$ be symmetric in any pair $x_1 \ldots x_z$ but of arbitrary symmetry in x_0. Then, if $\phi(x_1 \ldots x_z)$ is antisymmetric in any pair of variables, it is easily verified that

$$\begin{aligned} f(x_0 x_1 \ldots x_z) &= \sum_\ell \delta_\ell \mathcal{P}_{0\ell}\, Q(x_0; x_1 \ldots x_z)\phi(x_1 \ldots x_z) \\ &= \sum_\ell \delta_\ell\, Q(x_\ell; x_1 \ldots x_0(\ell) \ldots x_z)\phi(x_1 \ldots x_0(\ell) \ldots x_z) \end{aligned} \tag{2.15}$$

is antisymmetric in any pair of its $z + 1$ variables.

The use of Ψ to calculate scattering cross sections has been discussed by Takeda and Watson,[6] who show that since Ψ is antisymmetrized we need calculate the flux of scattered 0 electrons only. That is, all particles enter the problem symmetrically, hence each particle has the same flux, and the total flux is $z + 1$ times the flux of any one. This holds for both the incident and scattered fluxes; therefore, since only the ratio appears in the cross section, this may be computed by calculating the flux of particle 0 alone. Or, we may regard 0 as a distinguishable particle in obtaining the scattering cross section from Ψ.

The flux of 0 electrons scattered is calculated from

$$\lim_{x_0 \to \infty} \sum_{p,n} |\, p\, n \,\rangle_0 \; {}_0\langle\, p\, n \,|\, \Psi \,\rangle \;, \tag{2.16}$$

where Ψ contains both incident and (outgoing) scattered waves. The contribution of the latter to Eq. (2.16) is

$$- \sum_n \frac{e^{ik_n x_0}}{x_0}\, T_n(\hat{x}_0)\, \phi_n$$

where n labels the atomic state, k_n is the momentum carried by the scattered particle, and T_n is the scattering amplitude. Let the incident flux of 0 electrons be p_0/m ; then the scattering cross section for leaving the atom in the state n is

$$\frac{d\sigma}{d\Omega} = \frac{k_n}{p_0} S \left| T_n(\hat{x}_0) \right|^2 , \tag{2.17}$$

where S represents the appropriate sum and average over final and initial spin states.

It is apparent from Eq. (2.16), that we may obtain the cross section from

$$\psi(p\ n) \equiv {}_0\langle\ p\ n \mid \Psi\ \rangle \ . \tag{2.18}$$

That is, we may use a representation that treats particle 0 as distinguishable from the other particles. (It will turn out to be a matter of practical convenience to use this representation.)

Because Ψ is antisymmetric, the function $\psi(p\ n)$ satisfies a number of important symmetry relations. Indeed, these represent sufficient conditions that a wave function has been obtained that is consistent with the Pauli principle. First, we have, for $\ell = 0, 1, 2, \ldots z$,

$${}_0\langle\ p\ n \mid \Psi\ \rangle = \delta_{\ell\ \ell}\langle\ p\ n \mid \Psi\ \rangle \ . \tag{2.18A}$$

From this, we find trivially that, for $j, \ell = 0, 1, 2 \ldots z$,

$${}_j\langle\ p\ n \mid \Psi\rangle = \delta_j\ \delta_{\ell\ \ell}\langle\ p\ n \mid \Psi\rangle \ . \tag{2.18B}$$

From (2.18A) we obtain the important relation

$$\sum_{p'n'} {}_j\langle\, p\, n \mid p'\, n' \rangle_\ell \;\; \psi(p'\, n') = \delta_j\, \delta_\ell\, \psi(p\, n) \quad . \tag{2.18C}$$

When it is sufficient to use Hartree wave functions as approximations to the ϕ_n , we can considerably simplify our formulae. Let, then

$$\phi_n = \frac{1}{\sqrt{z!}} \sum_{\mathcal{P}} \epsilon_{\mathcal{P}}\, \mathcal{P}\, g_{\nu_1}(x_1) \ldots g_{\nu_z}(x_z) \; . \tag{2.19}$$

Here $\mathcal{P}$ is a general permutation of the x's, and $\epsilon_{\mathcal{P}}$, as usual, is (±1) depending upon whether the number of interchanges is even or odd. The g's are single-particle Hartree orbital states, and the index n refers to the set $(\nu_1 \ldots \nu_z)$.

An operator that projects onto the Hartree orbital states may be introduced:

$$\begin{aligned}(p' \mid \Lambda_\nu^{(0)} \mid p) &\equiv (\lambda_{p'}(x_0), [g_\nu(x_0) g_\nu^*(x_0)]\, \lambda_p(x_0)\,) \\ &= \langle\, \lambda_{p'} \mid g_\nu \rangle \langle\, g_\nu \mid \lambda_p \,\rangle \quad .\end{aligned} \tag{2.20}$$

Then, in an obvious notation, we obtain

$$\sum_p (p' \mid \Lambda_\nu^{(0)} \mid p)\, \psi(p\, n) = 0 \; , \tag{2.21}$$

if the Hartree orbital state ν is contained in the set n . The operator

$$\Lambda^{(0)} = \sum_{\nu=\nu_1}^{\nu_z} \Lambda_\nu^{(0)} \tag{2.22}$$

is a projection operator on the set of orbital states in n . In Eq. (2.21), $\Lambda_\nu^{(0)}$ and ψ may be regarded as operators in the space of functions n .

In this sense, Eq. (2.21) is equivalent to the operator equation,

$$\Lambda^{(0)} \psi = 0 \quad . \tag{2.23}$$

The wave function

$$\langle p\, n \mid \Psi \rangle \equiv \sqrt{z+1}\ \delta_{\ell\ \ell} \langle p\, n \mid \Psi \rangle$$

has recently been used, by Coester and Kümmel,[7] in a context similar to ours. These authors, however, did not discuss means of actually satisfying the symmetry conditions (2.18 A, B, and C).

III. DERIVATION OF THE SCATTERING EQUATION

We shall now follow the argument of Takeda and Watson[6] to devise a formally correct integral equation for the scattering problem. This is easily done--the major task confronting us is to show how this equation may be used.

Let us first introduce several quantities:

$$a \equiv E + i\eta - H$$

$$a_\ell \equiv a + \overline{V}_\ell = E + i\eta - H_\ell \quad . \tag{3.1}$$

Next, a set of wave functions Ψ_ℓ is defined by

$$\Psi_\ell = \mid p_0\, n_0 \rangle_\ell + \frac{1}{a_\ell}\, \overline{V}_\ell\, \Psi_\ell \quad . \tag{3.2}$$

The wavefunction Ψ_ℓ represents the scattering of the ℓth electron by an atom containing the remaining electrons. Clearly, in Ψ_ℓ the ℓth electron is treated as distinguishable from the others. Thus Ψ_ℓ has the symmetry properties of the $[\, Q\, \emptyset\,]$ used in Eq. (2.15). It follows then that the

correctly antisymmetrized wave function Ψ for the problem is

$$\Psi = \sum_{\ell} \delta_{\ell} \Psi_{\ell} \quad . \tag{3.3}$$

Having once obtained the Ψ_{ℓ} , the correct wavefunction is easily constructed. The scattering cross section is then obtained by the use of the arguments associated with Eqs. (2.16) and (2.17).

It is of interest, however, to obtain a single integral equation for Ψ itself. To do this, we first write Eq. (3.2) in the form

$$a \Psi_{\ell} = a_{\ell} \mid p_0 \, n_0 \rangle_{\ell} \quad . \tag{3.4}$$

We then multiply by δ_{ℓ} and sum over all ℓ to get:

$$a \Psi = \sum_{\ell} \delta_{\ell} \, a_{\ell} \mid p_0 \, n_0 \rangle_{\ell} \; , \tag{3.5}$$

or

$$\Psi = e_0 + \frac{1}{a_0} \bar{V}_0 \Psi \quad . \tag{3.6}$$

Here we have

$$\begin{aligned} e_0 &= \sum_{\ell} \delta_{\ell} \frac{1}{a_0} a_{\ell} \mid p_0 \, n_0 \rangle_{\ell} \\ &= \mid p_0 \, n_0 \rangle_0 - \sum_{\ell} \frac{i \eta}{a_0} \mid p_0 \, n_0 \rangle_{\ell} \; , \end{aligned} \tag{3.7}$$

because

$$a_{\ell} \mid p_0 \, n_0 \rangle_{\ell} = i \eta \mid p_0 \, n_0 \rangle_{\ell} \quad .$$

From this derivation, one sees that Eq. (3.6) is actually independent of the choice of 0 as the subscript, and that any other choice, ℓ , would lead to an equation of identical form.

Equation (3.6) may be rewritten in the representation of Eq. (2.18):

$$\psi(p\ n) = {}_0\langle\ p\ n\ |\ e_0\rangle + \frac{1}{a_0(p\ n)}\ {}_0\langle\ p\ n\ |\ \bar{V}_0\ \Psi\ \rangle\ . \tag{3.8}$$

Here we have

$$a_0(p\ n) \equiv E + i\,\eta - W_n - \frac{p^2}{2m}\ , \tag{3.9}$$

which is, of course, independent of the subscript 0 .

One may readily verify that the integral equation (3.6) [or the equivalent Eq. (3.8)] generates, by iteration, the properly antisymmetrized Ψ . Also, the advantage of employing $(1/a_0)$ as the propagator is apparent, since this is <u>diagonal</u> in the representation Eq. (3.8). This advantage was obtained at a considerable price, however, because now neither e_0 nor $(1/a_0)\ \bar{V}_0\ \Psi$ is individually antisymmetrized. (This may be easily seen, for instance, by observing the form (2.18C) for the antisymmetry condition.) Equation (3.6) also has a singular behavior when the limit $\eta \to \infty$ is taken.

An immediate simplification of Eq. (3.8) is possible in the approximation that the atomic nucleus has a mass very large compared to m:

$${}_0\langle\ p\ n\ |\ v_N(x_0)\ \Psi\ \rangle = \sum_{p'} (p\ |\ v_N\ |\ p')\ \psi(p'\ n)\ , \tag{3.10}$$

where

$$(p\ |\ v_N\ |\ p') = (\lambda_p\ (x_0),\ v_N(x_0)\ \lambda_{p'}(x_0)\ )\ .$$

The sum over all values of (p, n) in intermediate states counts each <u>antisymmetric</u> state (z + 1) times, as is well known. (Alternatively, we may say that a physical state (p n) may be obtained by putting any one of the (z + 1) particles in the state p , the remaining being in the atom.) This

complicates sums over virtual states unless one uses considerable care.

Now, the potential V_0 in Eq. (3.8) may be multiplied on the right by any projection operator onto the antisymmetrized sub-space for the $(z + 1)$ electrons. It will prove convenient to replace V_0 by

$$U_0 = \sum_j v_{0j} \frac{(1 - \mathcal{P}_{0j})}{2} , \tag{3.11}$$

where we define $\mathcal{P}_{00}$ to be the unit operator. Clearly, we have

$$\frac{1}{2}(1 - \mathcal{P}_{0j}) \Psi = \Psi ,$$

so Eq. (3.8) is unchanged on replacing V_0 by U_0. We may now drop the factor of $1/2$ above if we restrict intermediate state sums so that the states of the pair $(0, j)$ are not counted twice. With this understanding we replace Eq. (3.11) by

$$U_0 = \sum_j v_{0j} (1 - \mathcal{P}_{0j}) . \tag{3.12}$$

We emphasize that Eqs. (3.11) and (3.12) are entirely equivalent. Equation (3.12) is more convenient, however, since we do not wish to distinguish between the states of a scattered pair of electrons $(0, j)$.

Now we may write Eq. (3.8) as

$$\Psi = e_0 + \frac{1}{a_0} [U_0 + v_N(x_0)] \Psi . \tag{3.13}$$

In matrix form this is

$$\psi(p\ n) = {}_0\langle p\ n \mid e_0\rangle + \sum_{p'n'} \frac{1}{a_0(p\ n)} [{}_0\langle p\ n \mid U_0 \mid p'\ n'\rangle_0 + \langle p \mid v_N \mid p'\rangle \delta_{nn'}] \psi(p'\ n') . \tag{3.14}$$

The convention for carrying out intermediate-state sums that was introduced in connection with Eq. (3.12) must be kept in mind.

To proceed, we follow the method of I. Equation (3.13) may be written as

$$\Psi = F \Psi_C \quad , \tag{3.15}$$

where

$$\Psi_e = e_0 + \frac{1}{a_0} \mathcal{V}^{(0)} \Psi_C \quad , \tag{3.16}$$

$$F = 1 + \frac{1}{d_0} [U_0 + v_N(x_0) - \mathcal{V}^{(0)}] F \quad , \tag{3.17}$$

and

$$d_0 \equiv a_0 - \mathcal{V}^{(0)} \quad .$$

As was shown in I, the function (3.15) satisfies Eq. (3.13) for an arbitrary $\mathcal{V}^{(0)}$. Again, as in I, we shall impose on the "potential" $\mathcal{V}^{(0)}$ the condition that it be diagonal in the states n of the atom. The actual form chosen for $\mathcal{V}^{(0)}$ will be given presently.

To simplify Ψ_C, we rewrite Eq. (3.16) as

$$\begin{aligned} \Psi_C &= \frac{1}{d_0} a_0 e_0 \\ &= \frac{1}{d_0} \sum_\ell \delta_\ell a_\ell \mid p_0 n_0 \rangle_\ell \\ &= \frac{1}{d_0} \sum_\ell \delta_\ell d_\ell \Psi_C^{(\ell)} \quad ; \end{aligned} \tag{3.18}$$

where

$$d_\ell = \mathcal{P}_{0\ell} d_0 \mathcal{P}_{0\ell} \tag{3.19}$$

and

$$\Psi_C^{(\ell)} = \frac{1}{d_\ell} \; a_\ell \; | p_0 \, n_0 \rangle_\ell$$

$$= | p_0 \, n_0 \rangle_\ell + \frac{1}{a_\ell} \; \mathcal{V}^{(\ell)} \, \Psi_C^{(\ell)} \quad . \tag{3.20}$$

Because $\mathcal{V}^{(\ell)}$ is diagonal in the appropriate set of states n, we conclude that

$$\Psi_C^{(\ell)} = \mathcal{P}_{0_\ell} \, \chi_{p_0}(x_0) \, \phi_{n_0}(x_1 \ldots x_s) \quad , \tag{3.21}$$

where

$$[K_0 + \mathcal{V}_0^{(0)}] \, \chi_{p_0}(x_0) = \epsilon_0 \, \chi_{p_0}(x_0) \quad . \tag{3.22}$$

Here $\mathcal{V}_0^{(0)}$ is the matrix element of $\mathcal{V}^{(0)}$ associated with the atomic state n_0, and χ_{p_0} is that solution of Eq. (3.22) which has outgoing scattered waves: i.e.,

$$\chi_{p_0}(x_0) = \lambda_{p_0}(x_0) + (\text{outgoing scattered waves}) \; . \tag{3.23}$$

Physically therefore, $\chi_{p_0}(x_0)$ describes the scattering of particle 0 by the equivalent single-particle potential $\mathcal{V}_0^{(0)}$.

Returning to Eq. (3.18), we introduce the quantity

$$\Delta_\ell \equiv d_\ell - d_0 = (\overline{V}_\ell - \mathcal{V}^{(\ell)}) - (\overline{V}_0 - \mathcal{V}^{(0)}) \quad . \tag{3.24}$$

Substituting for d_ℓ into Eq. (3.18), we obtain

$$\Psi_C = \sum_\ell \delta_\ell \, \Psi_C^{(\ell)} + \sum_\ell \delta_\ell \, \frac{1}{d_0} \, \Delta_\ell \, \Psi_C^{(\ell)} \quad . \tag{3.25}$$

With a convenient choice for the potential $\mathcal{V}^{(0)}$, we now have a definite perturbation prescription for evaluating Ψ. We may anticipate that Δ_ℓ, which arises only because of the Pauli principle, will often be small.

IV. SIMPLIFICATION WHEN ATOMIC STATES ARE DESCRIBED BY HARTREE WAVE FUNCTIONS

For many scattering problems, such as we are considering, the properties of the scattering medium may be specified with much less accuracy than is required for the wave function of the scattered particle. The reason for this is that frequently only the state of the scattered particle is observed in any detail. For example, Hartree states often may be used for the scattering medium, even when such an approximation for the scattered particle would be very inaccurate. (We note that, in practice, Hartree wave functions are usually the best available!)

In this section, we shall therefore assume a Hartree model for the atom in order to simplify the scattering equations of Section III. We may, if desired, use any model of the atom for the final equations that we shall derive. This is reasonable, because the Hartree assumption is used only to derive exclusion-principle corrections to the theory of I.

We shall first note that it is desirable to choose $\mathcal{V}^{(0)}$ so that χ_{p_0} represents the actual elastic scattering of the electron by the atom. When x_0 is large, we have

$$\lim_{x_0 \to \infty} \chi_p(x_0) = e^{i\underset{\sim}{p}_0 \cdot \underset{\sim}{x}_0} + \frac{e^{ip_0 x_0}}{x_0} f_C ,$$

so the differential cross section for elastic scattering by the atom is

$$\left(\frac{d\sigma}{d\Omega}\right)_{el} = |f_C|^2 . \tag{4.1}$$

To achieve this we extend the definition of the χ_p to include the bound Hartree orbital states g_ν. Let

$$[K_\ell + v_N(x_\ell) + B^{(\ell)}]g_\nu(x_\ell) = b_\nu g_\nu(x_\ell) \tag{4.2}$$

determine the g's where $B^{(\ell)}$ is the Hartree potential. Let us next impose on $\mathcal{V}^{(0)}$ the condition that it have the form[8]

$$\mathcal{V}^{(0)} = (1 - \Lambda^{(0)})\mathcal{V}^{(0)} + \Lambda^{(0)}[B^{(0)} + v_N(x_0)] , \tag{4.3}$$

where $\Lambda^{(0)}$ is defined by Eq. (2.22). Equation (4.3) ensures the orthogonality of the χ_p and the g_ν:

$$\begin{aligned}\big(g_\nu(x_0), [K_0 + (1 - \Lambda^0)\mathcal{V}^{(0)} + \Lambda^{(0)}(B^{(0)} + v_N(x_0))]\chi_p(x_0)\big) \\ = b_\nu(g_\nu, \chi_p) = \epsilon_p(g_\nu, \chi_p) .\end{aligned} \tag{4.4}$$

Since we have $b_\nu < 0$ and $\epsilon_p > 0$, the orthogonality follows.[9]

We shall now <u>define</u> our Hartree approximation. We suppose the $\mathcal{V}^{(\ell)}$, as defined by Eq. (4.3) etc. are the Hartree potentials. This means that we must replace $\overline{V}_\ell$ by $\mathcal{V}^{(\ell)}$ for all values of ℓ. When this is done, the expression (3.24) evidently vanishes, as does the second term in Eq. (3.25). Now, we have

$$(1 - \Lambda^{(0)})\Psi_C = \Psi_C , \tag{4.5}$$

since Ψ_C is antisymmetric in the Hartree approximation. Also, we saw in Eq. (2.23) that

$$(1 - \Lambda^{(0)})\Psi = \Psi \quad .$$

Since $\Lambda^{(0)}$ commutes with d_0, this means that we can replace Eq. (3.17) for F by

$$F = 1 + \frac{1}{d_0}(1 - \Lambda^{(0)})\,[U_0 + v_N(x_0) - \mathcal{V}^{(0)}]F \quad . \tag{4.6}$$

At this point we can follow the steps of I precisely and write, first,

$$F = 1 + \frac{1}{d_0}\, P(1 - \Lambda^{(0)})U_0 \; F \quad , \tag{4.7}$$

and then

$$\mathcal{V}^{(0)} = v_N(x_0) + \Lambda^{(0)} B^{(0)} + (n \mid (1 - \Lambda^{(0)})U_0 \, F \mid n) \quad . \tag{4.8}$$

Here P is an instruction operator which forbids repetition of states n of the atom when we expand Eq. (4.7) in powers of U_0. (A word of caution is necessary here. We do not distinguish between the states of two particles which have just scattered. This means that <u>neither</u> of them must go into a state forbidden by P.)

To continue, we write

$$F = 1 + \frac{1}{d_0}\, P\, U_0\, F \quad ,$$

where the $(1 - \Lambda^{(0)})$ has been momentarily dropped to simplify notation. Now, the exact Ψ is

$$\Psi = \Psi_C + F \frac{1}{d_0} P U_0 \sum_\ell \delta_\ell [1 + \frac{1}{d_0} \Delta_\ell] \psi_C^{(\ell)} , \tag{4.9}$$

if we keep the Δ_ℓ terms. After a little algebra, we obtain

$$\Psi = \sum_\ell \delta_\ell \Psi_C^{(\ell)} + 2(F - 1)\Psi_C^{(0)} + \delta \Psi , \tag{4.10}$$

where

$$\delta \Psi = \sum_\ell \delta_\ell \frac{1}{d_0} \Delta_\ell \Psi_C^{(\ell)} - F \frac{1}{d_0} \left(\sum_{\ell \neq 0} \right) \Big\{ (1 - P) [- \sum_{j \neq 0, \ell} v_{0j} + \mathcal{V}^{(0)}]$$

$$+ [\sum_{s \neq 0, \ell} v_{\ell s} - \mathcal{V}^{(\ell)}] \Big\} \Psi_C^{(\ell)} . \tag{4.11}$$

We see that $\delta \Psi$ vanishes in our "Hartree" approximation. In this approximation, then, we have

$$\Psi = \Psi_C^{(0)} + 2(F - 1)\Psi_C^{(0)} \tag{4.12}$$

if we calculate the flux of scattered 0 particles only. Here $\Psi_C^{(0)}$ gives the elastic and

$$2(F - 1)\Psi_C^{(0)}$$

the inelastic scattering. (The factor of 2 arises because we have dropped an exchange term for the first scattering. The operator $(1 - \mathcal{P}_{0j})$ makes this exchange term redundant.)

V. THE SCATTERING POTENTIAL

We now illustrate the considerations of the last section by calculating the potential $\mathcal{V}^{(0)}$ to second order. Aside from the v_N and $B^{(0)}$ terms, to first order we have

$$\mathcal{V}_1^{(0)} = (1 - \Lambda^{(0)}) \langle 0 | \sum_j v_{0j} (1 - \mathcal{P}_{0j}) | 0 \rangle . \tag{5.1}$$

The nonexchange part is

$$\int v(x - y) \rho(y) d^3y ,$$

where

$$\rho(y) = \sum_\gamma g_\gamma (y) g_\gamma (y) . \tag{5.2}$$

The exchange part is, approximately,

$$\int v(x - y) [\sum_\gamma{}' g_\gamma{}^* (y) g_\gamma(x)] d^3y$$

where Σ' is restricted to spins parallel to that of the incident electron. Now we use the approximation,

$$\sum_\gamma{}' g_\gamma(y) g_0{}^*(x) \approx \rho(y) \eta(x - y) , \tag{5.3}$$

where

$$\begin{aligned} \eta(r) &= \frac{1}{2} \quad \text{for} \quad r \ll \frac{\hbar}{P_f} \\ &= 0 \quad \text{for} \quad r \ll \frac{\hbar}{P_f} , \end{aligned} \tag{5.4}$$

and P_f is the Fermi-momentum within the atom.

Thus we obtain

$$\mathcal{V}_1^{(0)} \approx \int d^3y\, \rho(\underset{\sim}{y})\, v(\underset{\sim}{x} - \underset{\sim}{y})\, [\, 1 - \eta(\underset{\sim}{x} - \underset{\sim}{y})] \quad . \tag{5.5}$$

This form of the potential has been obtained by Slater[2] using the Hartree-Fock method. The significance of the η term is that the charge density of those electrons whose spin is parallel to that of the scattered electron should vanish near the point $\underset{\sim}{x}$.

The second-order potential is

$$\mathcal{V}_2^{(0)} = (1 - \Lambda^{(0)})(0 \mid V_0 \frac{(1 - \Lambda^{(0)})}{a_0} V_0 \mid 0) \quad , \tag{5.6}$$

where, to this order of accuracy, $d_0 \sim a_0$. Now, the excited states n differ from 0 by the substitution of γ' for one of the gammas in 0 . Hence, if we consider all such substitutions, the matrix elements of U_0 between the state 0 and an excited state n have the form,

$$(q, n \mid U_0 \mid p, 0) = \sum_{\gamma} [(q\,\gamma' \mid v \mid p\,\gamma) - (q\,\gamma' \mid v \mid \gamma\, p)] \, , \tag{5.7}$$

where the sum on γ runs over the orbital states of 0 , and γ' is the excited orbital state ($\gamma' \neq$ any γ). Also we have

$$(q\ \gamma' \mid v \mid p\,\gamma) = \int \chi_q^{\,*}(x)\, \chi_{\gamma'}^{\,*}(y)\, v(x - y)\, \chi_p(x)\, \chi_\gamma(y) d^3x\, d^3y \, , \tag{5.8}$$

etc. Then we obtain

$$(p' \,|\, \mathcal{V}_2^{(0)} \,|\, p) = \sum_{\gamma} \sum_{q > \gamma'} (1 - \Lambda^{(0)}) \, [(p\,\gamma \,|\, v \,|\, q\,\gamma')$$

$$- (p\,\gamma \,|\, v \,|\, \gamma'\, q)] \, \frac{(1 - \Lambda^{(0)})}{a_0(q, \gamma')}$$

$$\times [(q\,\gamma' \,|\, v \,|\, p\,\gamma) - (q\,\gamma' \,|\, v \,|\, \gamma\, p)]$$

$$= \sum_{\gamma} \sum_{q} \sum_{\gamma'} (1 - \Lambda^{(0)}) \left\{ (p\,\gamma \,|\, v \,|\, q\,\gamma') \, \frac{(1 - \Lambda^{(0)})}{a_0(q\,\gamma')} \, (q\,\gamma' \,|\, v \,|\, p\,\gamma) \right.$$

$$\left. - (p\,\gamma \,|\, v \,|\, q\,\gamma') \, \frac{(1 - \Lambda^{(0)})}{a_0(q\,\gamma')} \, (\gamma'\, q \,|\, v \,|\, p\,\gamma) \right\} \quad . \tag{5.9}$$

The first term represents the usual potential induced by the polarizability of the atom. When transformed into coordinate space, and at large distances from the atom, it has the form[1]

$$\mathcal{V}_{2\,\mathrm{dir}} \approx P/x^4 \tag{5.10}$$

where P is a constant. The exchange term falls off exponentially with distance from the atom, so it is important only at points within the electronic orbits.

FOOTNOTES

1. M. H. Mittleman and K. M. Watson, Phys. Rev. 113, 198 (1959). This paper will be referred to as I.
2. John C. Slater, Phys. Rev. 81, 385 (1951).
3. Aaron Temkin, Phys. Rev. 107, 1004 (1957).
4. Hammerling, Shine, and Kivel, J. Appl. Phys. 28, 760 (1957).
5. The discussion that follows may be generalized to include spin interactions by merely including the appropriate terms in the v_{ij} and v_N.
6. G. Takeda and K. Watson, Phys. Rev. 97, 1336 (1955).
7. F. Coester and H. Kummel, Nuclear Physics 9, 225 (1958).
8. Such a form has been suggested by Frantz, Mills, Newton, and Sessler, Phys. Rev. Lett. 1, 340 (1958).
9. The states χ_p do not in general form a complete set, since $\mathcal{V}^{(0)}$ may not be Hermitean. In a strict sense, therefore, one cannot use these as the basis for expanding F. Instead, some complete orthonormal set including the g_γ should be introduced. In most practical applications it seems likely that this is not an important distinction, however.

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