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Exchange Effects in Scattering

of

Slow Electrons by Atoms

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ABSTRACT

In this paper, exchange in scattering of electrons by atoms is investigated.

The identity of incident and atomic electrons in the scattering of electrons by atoms requires that the wave function of the system be anti-symmetrized. In the approximation we are using here, this anti-symmetrized wave function gives rise to extra terms in the potential energy of the system: the exchange potential.

So far, discussion of exchange effects has been confined to closed shell atoms and alkali atoms. In one case exchange is negligible because of a tightly bound core and in the other, only exchange between the valence and the incident electron is considered and the problem is similar to that of the Hydrogen atom.

Here, we write a general equation which takes into account the exchange effects in scattering of electrons by any atom. The cross-section for scattering of an electron by an atom can be found using this equation once the orbitals of the atomic electrons are known.

This general equation is then applied to a simple case, Lithium and solved numerically.

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SCATTERING OF ELECTRONS BY ATOMS NEGLECTING EXCHANGE

The time independent Schrödinger equation of the system incident electron plus atom, neglecting spin-orbit interactions is

$$\left(H_a - \frac{\hbar^2}{2m} \nabla_0^2 - \frac{Ze^2}{r_0} + \sum_{k=1}^Z \frac{e^2}{r_{0k}} \right) \Psi(\bar{r}_0, \bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) =$$
(1)

$$E \Psi(\bar{r}_0, \bar{r}_1, \bar{r}_2, \dots, \bar{r}_n)$$

Where H_a is the Hamiltonian of the unperturbed atom; $\bar{r}_0$ is the position of the incident electron and $\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n$ are the coordinates of the atomic electrons.

The wave function of the system can be expanded in terms of a complete set of orthonormal functions ψ_ℓ .

$$\Psi(\bar{r}_0, \bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) = \left(\sum_\ell + \int \right) \psi_\ell(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) F_\ell(\bar{r}_0)$$
(2)

the summation over discrete states $\sum_\ell$ and the integration over continuous states $\int$ are represented by the symbol $\sum_\ell$

$$\Psi(\bar{r}_0, \bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) = \sum_\ell \psi_\ell(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) F_\ell(\bar{r}_0)$$

where F_l is the l^{th} state of the incident electron; ψ_l is the l^{th} state of the atom and satisfies

$$H_a(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) \psi_l(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) = E_l \psi_l(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) \quad (3)$$

If we insert equation (2) into equation (1), multiply on the right by $\psi_k^*(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n)$, the k^{th} state of the atom, and integrate over coordinates $\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n$ we obtain

$$(\nabla_0^2 + k_k^2) F_k(\bar{r}_0) = \frac{2m}{\hbar^2} \int \psi_k^*(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) V_{kl}(\bar{r}_0) F_l(\bar{r}_0) d\bar{r}_1 \dots d\bar{r}_n \quad (4)$$

where

$$k_k^2 = \frac{2m}{\hbar^2} (E - E_k)$$

and

$$V_{kl}(\bar{r}_0) = \int \psi_k^*(\bar{r}_1, \dots, \bar{r}_n) \left\{ \sum_{i=1}^Z \frac{e^2}{r_{0i}} - \frac{Ze^2}{r_0} \right\} \psi_l(\bar{r}_1, \dots, \bar{r}_n) d\bar{r}_1 \dots d\bar{r}_n$$

The ground state of the incident electron, $F_a(\bar{r}_0)$, must represent the sum of an incident and scattered wave; it must have the asymptotic form

$$\lim_{r \rightarrow \infty} F(\vec{r}) \rightarrow e^{i\vec{k}_i \cdot \vec{r}_0} + \frac{1}{r} e^{ik_i r} f_l(\theta, \phi) \quad (5)$$

The l^{th} state of the incident electron, $F_{l \neq 1}(\vec{r}_0)$ must represent scattered waves only and so have the asymptotic form

$$\lim_{r \rightarrow \infty} F_l(\vec{r}) \rightarrow \frac{1}{r} e^{ik_e r} f_l(\theta, \phi) \quad (6)$$

From equation (5) we see that $r^{-2} |f_l(\theta, \phi)|^2$ is the number of electrons per unit volume at a distance r from the atom and in the direction (θ, ϕ) which have excited the state l . The number of particles crossing per unit area per unit time is proportional to $k_l r^{-2} |f_l|^2$ while in the incident beam the number of particles crossing unit area per unit time is proportional to k_1 , hence we have

$$I_l(\theta, \phi) = \frac{k_l}{k_1} |f_l(\theta, \phi)|^2$$

$I_l(\theta, \phi)$ is the differential cross-section for inelastic scattering in which the atom is excited from the ground state to the l^{th} state. The total inelastic differential cross-section is $\sum_{l \neq 1} I_l$. The elastic cross-section is I_1 .

Here, we consider electrons with kinetic energy insufficient to excite the atom from its ground state to the first excited state; there must be no flux from states $F_{l \neq 1}$.

$$I_l = \frac{k_l}{k_1} |f_l(\theta, \phi)|^2 = 0$$

We must have $\lim_{r \rightarrow \infty} r F_l(\vec{r}) = 0$ for $l \neq 1$. The cross-section is purely elastic. To find it, let us solve for $F_1(\vec{r})$ which is a solution of

$$\begin{aligned} (V_0^2 + k_1^2) F_1(\vec{r}_0) &= \frac{2m}{\hbar^2} \sum_l V_{1l}(\vec{r}_0) F_l(\vec{r}_0) \\ &= \frac{2m}{\hbar^2} V_{11}(\vec{r}_0) F_1(\vec{r}_0) + \sum_{l \neq 1} V_{1l}(\vec{r}_0) F_l(\vec{r}_0) \end{aligned} \quad (7)$$

Equation (7) is exact; no approximation has been introduced.

For large r , $\frac{2m}{\hbar^2} \sum_{l \neq 1} V_{1l}(\vec{r}_0) F_l(\vec{r}_0) / F_1(\vec{r}_0)$

is the polarization potential $V_P(\vec{r}_0)$ and can be put in the

form $-\alpha/r^4$. The polarizability α of the atom can be calculated. An electron situated at a distance r from the nucleus of an atom induces a dipole moment in the atom which gives rise to an induced dipole potential $V_p(\bar{r})$. A more detailed discussion of this potential is delayed until later. For the moment we neglect $V_p(\bar{r})$ in equation (7). The equation for $F_1(\bar{r}_0)$ reduces to

$$(\nabla_0^2 + k_1^2) F_1(\bar{r}_0) = \frac{2m}{\hbar^2} V_{11}(\bar{r}_0) F_1(\bar{r}_0) \quad (8)$$

The elastic cross-section from solving equation (7) for the case of the hydrogen atom, does not agree with experimental results of scattering of slow electrons by the hydrogen atom. Obviously, a certain potential that exists in experiments, has not been accounted for in our theory. The origin of this potential, a quantum mechanical effect arising from the identity of particles is the subject of the following section.

IDENTICAL PARTICLES

In this section we shall attempt to show how the exchange potential arises in the scattering of slow electrons by atoms.

In classical mechanics, two electrons are represented by two points and move in sharply defined trajectories; it is then possible to distinguish between them since each of them can be followed during the course of an experiment. In quantum mechanics these same electrons are described by finite wave packets; when these packets overlap it is impossible to tell one electron from the other.

The differential cross-section for two colliding identical particles in classical mechanics is the sum of the cross-sections of the incident and the struck particles. In quantum mechanics, at the moment of collision, one can not distinguish the projectile from the target. To solve the problem quantum mechanically, consider a system of n interacting identical particles. The question is: "What is the effect of the identity of the particles on the wave function of the system?" Two particles are identical if the physical properties of the system of which they are a part remain unchanged when these particles are interchanged.

The Schrodinger equation for n identical particles is

$$i\hbar \frac{\partial}{\partial t} \psi(1,2,\dots,n) = H(1,2,\dots,n) \psi(1,2,\dots,n). \quad (9)$$

Where $H(1,2,\dots,n)$ is the Hamiltonian of the system of electrons; $\psi(1,2,\dots,n)$ is the unsymmetrized wave function of the system and n , for example, represents both spin and spatial coordinates of the n^{th} particle.

Because of the definition of identity just given

$$H(1,2,\dots,n) = H(2,1,\dots,n) = \dots = H(n,1,2,\dots) = \dots \quad (10)$$

The Hamiltonian of the system is symmetric. Permutation of the indices 1 and 2 throughout equation (9) yields

$$i\hbar \frac{\partial}{\partial t} \psi(2,1,\dots,n) = H(2,1,\dots,n) \psi(2,1,\dots,n) \quad (11)$$

this does not change the form of equation (9) since equation (11) corresponds only to a relabeling of particles. Now in equation (11), let us replace $H(2,1,\dots,n)$ by $H(1,2,\dots,n)$

$$i\hbar \frac{\partial}{\partial t} \psi(2,1,\dots,n) = H(1,2,\dots,n) \psi(2,1,\dots,n). \quad (12)$$

Equation (12) is the same as equation (9) for the permuted ψ . In other words $\psi(2,1,\dots,n)$ is also a solution of equation (9). There are $n!$ such solutions to equation (9) corresponding to $n!$ possible permutations of the n indices of ψ . The most general solution of equation (9) then is

$$i\hbar \frac{\partial}{\partial t} \sum_{P_i} P_i \psi(1,2,\dots,n) = H(1,2,\dots,n) \sum_{P_i} P_i \psi(1,2,\dots,n)$$

Where $P_i \psi(1,2,\dots,n)$ is the wave function obtained when the i^{th} permutation P_i is applied to the initial wave function $\psi(1,2,\dots,n)$. P_i is a product of transpositions. A transposition is an interchange of any pair of indices.

A wave function is anti-symmetric if the interchange of any pair of identical particles changes its sign. It is found experimentally that the wave function of a system of n electrons is anti-symmetric and therefore satisfies

$$i\hbar \frac{\partial}{\partial t} \sum_{P_i}^{n!} (-1)^{\sigma_i} P_i \psi(1,2,\dots,n) = H(1,2,\dots,n) \sum_{P_i}^{n!} (-1)^{\sigma_i} P_i \psi(1,2,\dots,n) \quad (13)$$

Where σ^i is the number of transpositions in P_i . We have thus shown that the wave function of a system of n interacting particles is not $\Psi(1,2, \dots, n)$ but

$$\Psi(1,2, \dots, n) + \sum' (-1)^{\sigma^i} P_i \Psi(1,2, \dots, n) .$$

Where the prime means that the summation is over odd permutations. A permutation is odd if it is the product of an odd number of transpositions. It is this summation which, in the course of subsequent calculations, gives rise to new terms in the potential called the exchange terms.

SCATTERING OF ELECTRONS BY ATOMS WITH EXCHANGE

An unpolarized beam of free electrons (i.e. one with as many "spin up" electrons as "spin down" electrons) is incident on a target of neutral atoms. The time independent Schrödinger equation which describes this system is

$$\left\{ \sum_{i=1}^n \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + \sum_{j \neq i} \frac{e^2}{r_{ij}} \right] + \right. \\ \left. \left(-\frac{\hbar^2}{2m} \nabla_0^2 - \frac{Ze^2}{r_0} + \sum_{i=1}^n \frac{e^2}{r_{0i}} \right) \right\} \psi = E \psi \quad (14)$$

where

$$\sum_{i=1}^n \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + \sum_{j \neq i} \frac{e^2}{r_{ij}} \right] = \sum_{i=1}^n H(i) = H_{\text{atom}}$$

and $-\frac{\hbar^2}{2m} \nabla_0^2$ is the kinetic energy of this incident electron; $-\frac{Ze^2}{r_0}$ its interaction potential with the nucleus and $\sum_{j=1}^n e^2/r_{0j}$ its interaction potential with the atomic electrons.

Spin-orbit interactions have been neglected.

Equation (14) cannot be solved exactly. We therefore choose to describe the atom by the exchange, self consistent, Hartree-Fock model. This model assumes that each of the atomic

electrons moves in a spherically symmetric potential that is produced by the nucleus and the spherically averaged potential field of each of the other electrons. The Schrödinger equation is solved for each electron in its own central field; thus the k^{th} electron is described by a normalized wave function that is a solution of the equation.

$$\left[-\frac{\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} + \sum_{i \neq k} \int |u_i(\vec{r}_j)|^2 \frac{e^2}{r_{jk}} d\vec{r}_j \right] u_{i_k}(\vec{r}_k) = E_{i_k} u_{i_k}(\vec{r}_k) \quad (15)$$

In our calculation, we replace the expansion of the total wave function in terms of all atomic states

$$\Psi(0, 1, 2, \dots, n) = \sum \Psi_i(0, 2, \dots, n) F_i(0)$$

by a single term, the ground state

$$\Psi(0, 1, 2, \dots, n) = \Psi_1(0, 2, \dots, n) F_1(0) \quad (16)$$

in doing this, we have assumed that $F_{l \neq 1}$ are small compared to F_1 and can be neglected. By neglecting $F_{l \neq 1}$ in the wave function of the system we, in fact, neglect the polarization potential because, as we have shown in the first section $\sum_{l \neq 1} F_l(0) \psi(1, 2, \dots, n)$ gives rise to the polarization potential.

If we wish to include exchange in equation (16), we must subtract the sum

$$\sum_{l=1}^n F(l) \psi(1, 2, \dots, (l-1), 0, (l+1), \dots, n)$$

from equation (16). The normalized, anti-symmetrized wave function of the system becomes

$$\Psi(0, 1, 2, \dots, n) =$$

$$\frac{1}{\sqrt{n}} \left[F(0) \psi(1, 2, \dots, n) - \sum_{l=1}^n F(l) \psi(1, 2, \dots, 0, \dots, n) \right] \quad (17)$$

Where F is the wave function of the incident electron;
 $\psi(1, 2, \dots, n)$ is the anti-symmetrized, normalized wave function of the unperturbed atom. The summation is over all

atomic electrons and takes into account the possibility of exchange between the incident electron and any atomic electron.

For instance,

$$F(l) \psi(1, 2, \dots, (l-1), 0, (l+1), \dots, n)$$

is the wave function of the system in which the incident electron has changed place with the l^{th} atomic electron.

The wave function of the atom, $\psi(1, 2, \dots, n)$, is taken to be

$$\psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \sum_{i_1 i_2 \dots i_n} \epsilon_{i_1 i_2 \dots i_n} u_{i_1}(1) u_{i_2}(2) \dots u_{i_n}(n) \quad (18)$$

Where

$$\epsilon_{i_1 i_2 \dots i_n} = \begin{cases} 1 & \text{if } i_1, i_2, \dots, i_n \text{ is an even permutation of } 1, 2, \dots, n \\ -1 & \text{if } i_1, i_2, \dots, i_n \text{ is an odd permutation of } 1, 2, \dots, n \\ 0 & \text{if any pair of indices are equal} \end{cases}$$

l_k represents a set of four quantum numbers (n, l, m_l, m_s) .

The symbol n stands for the spatial and spin coordinate of the n^{th} atomic electron. The wave function $\psi_n(n)$ is a solution of equation (15) with eigenvalue E_n .

The Hamiltonian equation of the system is

$$H \left\{ \psi(1, 2, \dots, n) F(0) - \sum_{k=1}^n F(k) \psi(1, 2, \dots, 0, \dots, n) \right\} = \quad (19)$$

$$E \left\{ \psi(1, 2, \dots, n) F(0) - \sum_{k=1}^n F(k) \psi(1, 2, \dots, 0, \dots, n) \right\}$$

Consider the exchange part of equation (19)

$$H \sum_{k=1}^n F(k) \psi(1, 2, \dots, 0, \dots, n) = E \sum_{k=1}^n F(k) \psi(1, 2, \dots, 0, \dots, n) \quad (20)$$

In equation (20), replacing H by

$$\sum_{k=1}^n H(k) + \left(-\frac{\hbar^2}{2m} \nabla_0^2 - \frac{ze^2}{r_0} + \sum_{i=1}^n \frac{e^2}{r_{0i}} \right),$$

we obtain

$$\sum_{k=1}^n \left[H_a(1, 2, \dots, 0, \dots, n) + H(k) - \sum_{j \neq k} V_{jj}(r_0) + \sum_{i=1}^n \frac{e^2}{r_{0i}} \right] F(k) \psi(1, 2, \dots, 0, \dots, n) =$$

(21)

$$E \sum_{k=1}^n F(k) \psi(1, 2, \dots, 0, \dots, n)$$

where

$$H_a(1, 2, \dots, 0, \dots, n) = \sum_{l \neq k}^n \left(-\frac{\hbar^2}{2m} \nabla_l^2 - \frac{ze^2}{r_l} + \sum_{j \neq l}^n \frac{e^2}{r_{lj}} \right) + \left(-\frac{\hbar^2}{2m} \nabla_0^2 - \frac{ze^2}{r_0} + \sum_{j \neq 0}^n \frac{e^2}{r_{0j}} \right)$$

and

$$V_{ij}(\bar{r}_0) = \int |u_{ij}(\bar{r}_j)|^2 \frac{e^2}{r_{0j}} d\tau_j$$

Substituting equation (21) for equation (20) in equation (19); multiplying the resulting equation on the right by $\psi^*(i_2, \dots, i_n)$ expressed as in equation (18) and integrating over $d\tau_1 \dots d\tau_n$ we finally obtain

$$\begin{aligned} & \left(-\frac{\hbar^2}{2m} \nabla_0^2 - \frac{Ze^2}{r_0} + \sum_{i_k} V_{ki}(\bar{r}_0) - \frac{\hbar^2 k^2}{2m} \right) F(0) = \\ & \sum_{i_k} \left[\left(E_{i_k} - \frac{\hbar^2 k^2}{2m} \right) \int u_{i_k}^*(K) F(K) d\tau_K + \int u_{i_k}^*(K) F(K) \times \right. \\ & \left. \frac{e^2}{r_{0K}} d\tau_K - \sum_{i_j \neq i_k} V_{kj}(\bar{r}_0) \int u_{i_j}^*(K) F(K) d\tau_K \right] u_{i_k}(0) \end{aligned} \quad (22)$$

where

$$V_{kj}(\bar{r}_0) = \int u_{i_k}^*(K) u_{i_j}(K) \frac{e^2}{r_{0K}} d\tau_K$$

The letter K represents the spatial and spin of the atomic electron; i_k stands for the set of four quantum numbers (n, l, m_l, m_s) and describes the state of the K^{th} particle.

The left hand side of equation (22) is just equation (8), the equation for F if the total wave function of the system $\Psi(0,1,2,\dots,n)$ were not anti-symmetrized i.e. if there were no exchange. $\left[\frac{Ze^2}{r_0} + \sum_{k \neq n} V_{kk}(r_0)\right]$ is the local potential. The right hand side of equation (22) is the non-local potential multiplied by $F(0)$. It is a result of the anti-symmetrization of the total wave function of the system $\Psi(0,1,2,\dots,n)$. The effects of this non-local potential energy on the phase shifts are the main concern of this paper and will be discussed later.

1. Separation of Spin and Spatial Functions

Equation (22) still contains spin coordinates. We want to obtain an equation dependent on spatial coordinates only. To do this we separate spin and spatial functions. This can be done because spin and spatial coordinates are independent of each other. The wave function of the k^{th} atomic electron, $u_{i_k}(k)$, can be rewritten as $u_{i_k}(\bar{r}_k, s_k) = u_{i_k}(\bar{r}_k) \psi(\frac{1}{2}, m_k)$. $\psi(\frac{1}{2}, m_k)$ is the spin function of the k^{th} electron; $m_k = \pm 1/2$. After separation of spin and spatial coordinates, equation (22) becomes

$$\left(-\frac{\hbar^2}{2m} \nabla_0^2 - \frac{Ze^2}{r_0} + \sum_{i_K} V_{KK}(\bar{r}_0) - \frac{\hbar^2 k^2}{2m}\right) F(\bar{r}_0) =$$

$$\sum_{i_K} \left[\left(E_{i_K} - \frac{\hbar^2 k^2}{2m}\right) \int U_{i_K}^*(\bar{r}) F(\bar{r}) d\bar{r} + \int U_{i_K}^*(\bar{r}') F(\bar{r}') \frac{e^2}{|\bar{r}_0 - \bar{r}'|} d\bar{r}' - \right. \quad (23)$$

$$\left. \sum_{i_j \neq i_K} V_{Kj}(\bar{r}_0) \int U_{i_j}^*(\bar{r}) F(\bar{r}) d\bar{r} \right] U_{i_K}(\bar{r}_0) \delta_{m_K m_F}$$

Experimentally, the incident beam is unpolarized. To realize this theoretically, we first assume an incident beam polarized in the positive $\hat{z}$ direction. We solve the equation for $F^{(+)}(\bar{r}_0)$ which corresponds to this case and obtain the cross-section $\sigma^{(+)}$. Similarly we obtain $\sigma^{(-)}$ corresponding to an incident beam polarized in the negative $\hat{z}$ direction. The cross-section corresponding to the unpolarized beam is then

$$\sigma = \frac{\sigma^{(+)} + \sigma^{(-)}}{2}$$

Two cases arise.

a) If $Z=n$ is even, then $Z/2$ electrons have spin function $\psi(1/2, 1/2)$ and $Z/2$ electrons have spin function $\psi(1/2, -1/2)$. $Z/2$ atomic electrons have spin parallel to the spin of the incident electron. Carrying out the summation over the electronic states i_k in equation (23) we obtain

$$\left[-\frac{\hbar^2}{2m} \nabla_0^2 - \frac{Ze^2}{r_0} + \sum_{i_k} V_{k i_k}(\bar{r}_0) - \frac{\hbar^2 k^2}{2m} \right] F(\bar{r}_0) =$$

$$\frac{1}{2} \sum_{i_k} \left[\left(E_{i_k} - \frac{\hbar^2 k^2}{2m} \right) \int U_{i_k}^*(\bar{r}') F(\bar{r}') d\bar{r}' + \int U_{i_k}^*(\bar{r}') F(\bar{r}') \times \right. \\ \left. \frac{e^2}{|\bar{r}_0 - \bar{r}'|} d\bar{r}' - \sum_{i_j \neq i_k} V_{k i_j}(\bar{r}_0) \int U_{i_j}^*(\bar{r}') F(\bar{r}') d\bar{r}' \right] U_{i_k}(\bar{r}_0). \quad (24)$$

The equations for $F^{(+)}$ and $F^{(-)}$ which correspond to the two oppositely polarized beams are identical and satisfy equation (24). The summation is over states occupied by the n atomic electrons.

b) For odd Z , $F^{(+)}(\vec{r}_0)$ satisfies

$$\left[\frac{\hbar^2}{2m} \nabla_0^2 - \frac{Ze^2}{r_0} + \sum_{iK} V_{KK}(\vec{r}_0) - \frac{\hbar^2 k^2}{2m} \right] F^{(+)}(\vec{r}_0) =$$

$$\frac{1}{2} \sum_{iK \neq i_n} \left[(E_{iK} - \frac{\hbar^2 k^2}{2m}) \int U_{iK}^*(\vec{r}') F^{(+)}(\vec{r}') d\vec{r}' + \int U_{iK}^*(\vec{r}') F^{(+)}(\vec{r}') \times \right. \quad (25)$$

$$\left. \frac{e^2}{|\vec{r}_0 - \vec{r}'|} d\vec{r}' - \sum_{i_j \neq i_K} V_{Kj}(\vec{r}_0) \int U_{i_j}^*(\vec{r}') F^{(+)}(\vec{r}') d\vec{r}' \right] U_{iK}(\vec{r}_0) +$$

$$\left[(E_{i_n} - \frac{\hbar^2 k^2}{2m}) \int U_{i_n}^*(\vec{r}') F^{(+)}(\vec{r}') d\vec{r}' + \int U_{i_n}^*(\vec{r}') F^{(+)}(\vec{r}') \frac{e^2}{|\vec{r}_0 - \vec{r}'|} d\vec{r}' - \right.$$

$$\left. \sum_{i_j \neq i_n} V_{nj}(\vec{r}_0) \int U_{i_j}^*(\vec{r}') F^{(+)}(\vec{r}') d\vec{r}' \right] U_{i_n}(\vec{r}_0).$$

Where i_n denotes the state of the n^{th} atomic electron, assumed to have spin function $\psi(1/2, 1/2)$.

$F^{(-)}(\vec{r}_0)$ satisfies

$$\left(\frac{\hbar^2}{2m} \nabla_0^2 - \frac{Ze^2}{r_0} + \sum_{iK} V_{KK}(\vec{r}_0) - \frac{\hbar^2 k^2}{2m} \right) F^{(-)}(\vec{r}_0) = \quad (26)$$

$$\frac{1}{2} \sum_{iK \neq i_n} \left[(E_{iK} - \frac{\hbar^2 k^2}{2m}) \int U_{iK}^*(\vec{r}') F^{(-)}(\vec{r}') d\vec{r}' + \int U_{iK}^*(\vec{r}') \times \right.$$

$$\left. F^{(-)}(\vec{r}') \frac{e^2}{|\vec{r}_0 - \vec{r}'|} d\vec{r}' - \sum_{i_j \neq i_K} V_{Kj}(\vec{r}_0) \int U_{i_j}^*(\vec{r}') F^{(-)}(\vec{r}') d\vec{r}' \right] U_{iK}(\vec{r}_0)$$

2. The Radial Equation

Equation (22) can be reduced to a radial equation through the use of the partial wave expansions

$$F(\bar{r}) = \sum_{l, m_l} Y_{lm_l}(\Omega) \frac{R_l(r)}{r} \quad (27a)$$

$$U_{nlm_l}(\bar{r}) = \frac{P_{nl}(r)}{r} Y_{lm_l}(\Omega) \quad (27b)$$

Where n is the principal quantum number, l is the angular momentum quantum number and m_l its projection on the z axis.

Equation (22) becomes

$$\sum_{l', m_{l'}} \left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V(r) + \frac{\hbar^2}{2m} \frac{l'(l'+1)}{r^2} - \frac{\hbar^2 k^2}{2m} \right] Y_{l'm_{l'}}(\Omega) f_{l'} \frac{r}{r} - \sum_n \left\{ \sum_{l_n} \left(\frac{\hbar^2 k^2}{2m} - E_n \right) \int_0^\infty P_{nl_n}(r') f_{l_n}(r') dr' \right\} \frac{P_{nl_n}(r)}{r} Y_{l_n m_{l_n}}(\Omega) \quad (28)$$

$$\sum_{n=1} \frac{P_{n0}(r)}{r} \left\{ \sum_{l', m_{l'}} \frac{Y_{l'm_{l'}}(\Omega)}{r^{l'+1}} \int P_{n0}(r') f_{l'}(r') g_{l'}(r, r') dr' \right\} +$$

$$\sum_{n=2} \frac{P_{n1}(r)}{r} \left\{ \frac{3 Y_{10}(\Omega)}{r^{l'+1}} \left(\frac{l'+1}{r^{l'+3}} \int P_{n1}(r') f_{l'}(r') g_{l'+1}(r, r') dr' + \right. \right.$$

$$\frac{\ell'}{2\ell'-1} \left\{ P_{n2}(r') f_{\ell'}(r') g_{\ell'-1}(r, r') dr' \right\} +$$

$$\sum_{n=3} \frac{P_{n2}(r)}{r} \left\{ \sum_{\ell'm_{\ell'}} \frac{5 Y_{\ell'm_{\ell'}}(\Omega)}{2\ell'+1} \left(\frac{3(\ell'+2)(\ell'+1)^2}{(2\ell'+1)(2\ell'+2)(2\ell'+3)} \int P_{n2}(r') f_{\ell'}(r') \times \right. \right.$$

$$g_{\ell'+2}(r, r') dr' - \frac{\ell'(\ell'+1)}{(2\ell'-1)(2\ell'+3)} \int P_{n2}(r') f_{\ell'}(r') g_{\ell'}(r, r') dr' +$$

$$\left. \frac{3\ell'(\ell'-1)^2}{(2\ell'-2)(2\ell'-1)(2\ell'+1)} \int P_{n2}(r') f_{\ell'}(r') g_{\ell'-2}(r, r') dr' \right\} -$$

$$\sum_n \sum_{\ell'm_{\ell}} Y_{\ell'm_{\ell}}(\Omega) \frac{P_{n\ell}(r)}{r} \sum_{n''\ell''m_{\ell}'' \neq n\ell m_{\ell}} \left[\int P_{n''\ell''}(r') f_{\ell''}(r') dr' \right] \times$$

$$\int U_{n\ell m_{\ell}}^*(\vec{r}') \frac{e^2}{|\vec{r}-\vec{r}'|} U_{n''\ell''m_{\ell}''}(\vec{r}') d\vec{r}',$$

Where

$$V(r) = \sum_K V_{KK}(r) - \frac{Ze^2}{r}$$

$$g_{\ell'}(r, r') = \begin{cases} \frac{r^{\ell'}}{r'^{\ell'+1}} & r < r' \\ \frac{r'^{\ell'}}{r^{\ell'+1}} & r > r' \end{cases}$$

The third line of equation (28) is the contribution to the non-local potential due to exchange between $s, (l=0)$, atomic electrons and the incident electron. This is shown by the presence of the factor $P_{n0}(r)$. Similarly the fourth and fifth lines are contributions to the non-local potential due to exchange of $p, (l=1)$, atomic electrons and the incident electron. The sixth, seventh and eighth lines are contributions from exchange with $d, (l=2)$, atomic electrons.

Equation (28) allows for exchange between s, p, d atomic electrons and the incident electron. This is sufficient to take care of exchange effects in most light atoms. Exchange between an $f, (l=3)$, electron and the incident electron would be described by integrals involving $P_{n3}(r)$.

One can neglect the possibility of exchange between the incident electron and the inner shell electrons. The radii of these shells are small and their binding energy large. The slowly incoming electron interacts mainly with the outer atomic electrons which are loosely bound and have large radii. Then equation (28) is greatly simplified.

Consider for example the Aluminum atom

There are 2 electrons in the 1s state, 2 in the 2s state, 6 in the 2p state, 2 in the 3s state and 1 in the 3p state.

The binding energy of each shell is

$$E_{100} = -115.3 \quad \text{Rydbergs}$$

$$E_{200} = -9 \quad \text{Rydbergs}$$

$$E_{211} = E_{210} = E_{21-1} = -5.8 \quad \text{Rydbergs}$$

$$E_{300} = -0.83 \quad \text{Rydbergs}$$

$$E_{311} = E_{310} = E_{31-1} = -0.44 \quad \text{Rydbergs}$$

We follow the argument presented on the previous page, which says that exchange probability of the incident electron with the 1s, 2s, 2p electrons is very small because these atomic electrons are very tightly bound in a small core and only consider exchange between the incident electron and the 3s and 3p atomic electrons. Then equation (28) reduces to

$$\sum_{l'm_l'} \left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V(r) + \frac{\hbar^2 l(l+1)}{2m r^2} - \frac{\hbar^2 k^2}{2m} \right] \chi$$

$$Y_{l'm_l}(\Omega) f_{l'}(r)/r =$$

$$- 2 Y_{00}(\Omega) \frac{P_{30}(r)}{r} \left(\frac{\hbar^2 k^2}{2m} - E_{300} \right) \int_0^\infty P_{30}(r') f_0(r') dr'$$

$$- Y_{10}(\Omega) \frac{P_{31}(r)}{r} \left(\frac{\hbar^2 k^2}{2m} - E_{310} \right) \int_0^\infty P_{31}(r') f_1(r') dr'$$

(29)

$$+ \frac{2 P_{30}(r)}{r} \left\{ \sum_{l'm_l'} \frac{Y_{l'm_l}(\Omega)}{2^{l'+1}} \int_0^\infty P_{30}(r') f_{l'}(r') g_{l'}(r, r') dr' \right\}$$

$$+ \frac{P_{31}(r)}{r} \left\{ \sum_{l'm_l'} \frac{3}{2^{l'+1}} \left[\frac{l'+1}{2l'+3} \int P_{31}(r') f_{l'}(r') g_{l'}(r, r') dr' \right. \right.$$

$$\left. + \frac{l'}{2^{l'-1}} \int P_{31}(r') f_{l'}(r') g_{l'-1}(r, r') dr' \right] Y_{l'm_l}(\Omega) \left. \right\}$$

which is much less formidable than equation (28).

APPLICATION TO LITHIUM

1. The Radial Equation for Lithium

Applied to Lithium, equation (28) becomes

$$\begin{aligned}
 & \sum_{l'm_l'} \left(-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) + V(r) + \frac{\hbar^2 l'(l'+1)}{2m r^2} \right) Y_{l'm_l'}(\Omega) f_{l'}(r)/r = \\
 & - 2 \frac{P_{10}(r)}{r} Y_{00}(\Omega) \left(\frac{\hbar^2 k^2}{2m} - E_{100} \right) \int_0^\infty P_{10}(r') f_0(r') dr' \\
 & - \frac{P_{20}(r)}{r} Y_{00}(\Omega) \left(\frac{\hbar^2 k^2}{2m} - E_{200} \right) \int_0^\infty P_{20}(r') f_0(r') dr' \\
 & + 2 \frac{P_{10}(r)}{r} \sum_{l'm_l'} \frac{Y_{l'm_l'}(\Omega)}{2l'+1} \int_0^\infty P_{10}(r') f_{l'}(r') g_{l'}(r, r') dr' \\
 & + \frac{P_{20}(r)}{r} \sum_{l'm_l'} \frac{Y_{l'm_l'}(\Omega)}{2l'+1} \int_0^\infty P_{20}(r') f_{l'}(r') g_{l'}(r, r') dr' \\
 & - 2 \frac{P_{10}(r)}{r} Y_{00}(\Omega) V_{100,200}(r) \int_0^\infty P_{20}(r') f_0(r') dr' \\
 & - \frac{P_{20}(r)}{r} Y_{00}(\Omega) V_{100,200}(r) \int_0^\infty P_{10}(r') f_0(r') dr'
 \end{aligned} \tag{30}$$

Equation (30) takes into account exchange with all atomic electrons; however, in heavier atoms, only electrons in the last shell need be considered.

Applying equation (25) to the case of a "spin up" incident electron and odd $Z, (Z=3)$, we find that the radial wave function $f_{l'}^{(+)}$ satisfies the equation.

$$\begin{aligned}
 & f_{l'}^{(+)}'' + (k^2 - V(r) - l'(l'+1)/r^2) f_{l'}^{(+)}(r) = \\
 & P_{10}(r) \delta_{l'0} (k^2 - E_{100}) \int_0^\infty P_{10}(r') f_0^{(+)}(r') dr' + \\
 & P_{20}(r) \delta_{l'0} (k^2 - E_{200}) \int_0^\infty P_{20}(r') f_0^{(+)}(r') dr' - \\
 & \frac{2 P_{10}(r)}{2l'+1} \int_0^\infty P_{10}(r') f_{l'}^{(+)}(r') g_{l'}(rr') dr' - \frac{2 P_{20}(r)}{2l'+1} \int_0^\infty P_{20}(r') f_{l'}^{(+)}(r') g_{l'}(rr') dr' + \\
 & V_{100,200}(r) P_{10}(r) \int_0^\infty P_{20}(r') f_0(r') dr' \delta_{l'0} + V_{100,200}(r) P_{20}(r) \times \\
 & \int_0^\infty P_{10}(r') f_0(r') dr' \delta_{l'0}
 \end{aligned} \tag{31}$$

and $f_{l'}^{(-)}(r)$, the radial wave function of a "spin down" incident electron is a solution of

$$\begin{aligned}
 f_{l'}^{(-)}(r)'' + (k^2 - V(r) - \frac{l'(l'+1)}{r^2}) f_{l'}^{(-)}(r) = & P_{l0}(r) \delta_{l0} (k^2 - E_{100}) \int_0^\infty P_{l0}(r') f_0^{(-)}(r') dr' \\
 - \frac{2 P_{l0}(r)}{2l'+1} \int_0^\infty P_{l0}(r') f_{l'}^{(-)}(r') g_{l'}(rr') dr' + & V_{100,200}(r) P_{l0}(r) \times \\
 \int_0^\infty P_{20}(r') f_0^{(-)}(r') dr' \delta_{l0} ; &
 \end{aligned} \quad (32)$$

equations (31) and (32) have been written in atomic units¹

where the unit of length is the Bohr radius

$$a_0 = \frac{\hbar^2 4\pi \epsilon_0}{4\pi^2 m e^2}$$

the unit of energy is the Rydberg = $\frac{2\pi^2 m e^4}{(4\pi \epsilon_0)^2 \hbar^2} = 13.6 \text{ eV.}$

and cross-sections are measured in units of πa_0^2

2. Method of Solution

Let us, to illustrate, solve for $f_0^{(+)}$. With $g_{l'}(r, r')$ replaced by its explicit value given in equation (28),

$$\int_0^\infty f(r') dr' \quad \text{written as} \quad \int_0^\infty f(r') dr' - \int_0^r f(r') dr' \quad \text{and}$$

$l' = 0$, equation (31) becomes

$$f_0^{(+)}(r) + (k^2 - V(r)) f_0^{(+)}(r) =$$

$$P_{10}(r) \{k^2 - E_{100}\} \int_0^\infty P_{10}(r') f_0^{(+)}(r') dr' +$$

$$P_{20}(r) \{k^2 - E_{200}\} \int_0^\infty P_{20}(r') f_0^{(+)}(r') dr' - \quad (33)$$

$$= P_{10}(r) \left[\int_0^r P_{10}(r') f_0^{(+)}(r') \left\{ \frac{1}{r} - \frac{1}{r'} \right\} dr' + \int_0^\infty P_{10}(r') f_0^{(+)}(r') / r' dr' \right] -$$

$$= P_{20}(r) \left[\int_0^r P_{20}(r') f_0^{(+)}(r') \left\{ \frac{1}{r} - \frac{1}{r'} \right\} dr' + \int_0^\infty P_{20}(r') f_0^{(+)}(r') / r' dr' \right] +$$

$$P_{10}(r) V_{100,200}(r) \int_0^\infty P_{20}(r') f_0^{(+)}(r') dr' +$$

$$P_{20}(r) V_{100,200}(r) \int_0^\infty P_{10}(r') f_0^{(+)}(r') dr' ;$$

rearranging, we obtain

$$f_0^{(+)}(r) + \{k^2 - V(r)\} f_0^{(+)}(r) =$$

$$[(k^2 - E_{200}) P_{20}(r) + P_{10}(r) V_{100,200}(r)] \int_0^\infty P_{20}(r') f_0^{(+)}(r') dr' +$$

$$[(k^2 - E_{100}) P_{10}(r) + P_{20}(r) V_{100,200}(r)] \int_0^\infty P_{10}(r') f_0^{(+)}(r') dr' -$$

(34)

$$2 \int_0^\infty P_{10}(r') \frac{f_0^{(+)}(r')}{r'} dr' \times P_{10}(r) - 2 P_{20}(r) \int_0^\infty P_{20}(r') \frac{f_0^{(+)}(r')}{r'} dr'$$

$$- 2 \int_0^r P_{10}(r') f_0^{(+)}(r') \left\{ \frac{1}{r} - \frac{1}{r'} \right\} dr' \times P_{10}(r)$$

$$- 2 \int_0^r P_{20}(r') f_0^{(+)}(r') \left\{ \frac{1}{r} - \frac{1}{r'} \right\} dr' \times P_{20}(r) .$$

Equation (34) is of the form

$$\begin{aligned}
 u''(r) + \phi(r) u(r) = & \psi_1(r, u) + \psi_2(r) \int_0^\infty g_2(r') u(r') dr' \\
 & + \psi_3(r) \int_0^\infty g_3(r') u(r') dr' + \psi_4(r) \int_0^\infty g_4(r') u(r') dr' + \\
 & \psi_5(r) \int_0^\infty g_5(r') u(r') dr',
 \end{aligned} \tag{35}$$

where ϕ_i and g_i are known functions of r

Let

$$u(r) = w_1(r) + A w_2(r) + B w_3(r) + C w_4(r) + D w_5(r) \tag{36}$$

If

$$\begin{aligned}
 \phi_1(r, u) = & \phi_1(r, w_1 + A w_2 + B w_3 + C w_4 + D w_5) \\
 = & \phi_1(r, w_1) + A \phi_1(r, w_2) + B \phi_1(r, w_3) + \\
 & C \phi_1(r, w_4) + D \phi_1(r, w_5),
 \end{aligned} \tag{37}$$

which is the case in our problem, since from equation (34)

$$\begin{aligned}\psi_1(r, u) &= \int_0^r u(r') q(r') dr' = \int_0^r (W_1 + A W_2 + B W_3 + C W_4 + D W_5) \times \\ & q(r') dr' = \int_0^r W_1 q dr' + A \int_0^r W_2 q dr' + B \int_0^r W_3 q dr' + C \int_0^r W_4 q dr' + \\ & D \int_0^r W_5 q dr'\end{aligned}$$

where

$$u(r') = f_0^{(t)}(r')$$

and

$$q(r') = -2R_0(r') \left\{ \frac{1}{r} - \frac{1}{r'} \right\}.$$

Then W_1, W_2, W_3, W_4 and W_5 satisfy the following equations

$$W_1''(r) + \psi(r) W_1(r) = \psi_1(r, W_1) \quad (38)$$

$$W_2''(r) + \psi(r) W_2(r) = \psi_1(r, W_2) + \psi_2(r) \quad (39)$$

$$W_3''(r) + \psi(r) W_3(r) = \psi_1(r, W_3) + \psi_3(r) \quad (40)$$

$$W_4''(r) + \psi(r) W_4(r) = \psi_1(r, W_4) + \psi_4(r) \quad (41)$$

$$W_5''(r) + \psi(r) W_5(r) = \psi_1(r, W_5) + \psi_5(r) \quad (42)$$

A, B, C, and D satisfy the following simultaneous equations

$$-\int_0^{\infty} g_2 w_1 dr = A \left[\int_0^{\infty} g_2 w_2 dr - 1 \right] + B \int_0^{\infty} g_2 w_3 dr + C \int_0^{\infty} g_2 w_4 dr + D \int_0^{\infty} g_2 w_5 dr \quad (43)$$

$$-\int_0^{\infty} g_3 w_1 dr = A \int_0^{\infty} g_3 w_2 dr + B \left[\int_0^{\infty} g_3 w_3 dr - 1 \right] + C \int_0^{\infty} g_3 w_4 dr + D \int_0^{\infty} g_3 w_5 dr \quad (44)$$

$$-\int_0^{\infty} g_4 w_1 dr = A \int_0^{\infty} g_4 w_2 dr + B \int_0^{\infty} g_4 w_3 dr + C \left[\int_0^{\infty} g_4 w_4 dr - 1 \right] + D \int_0^{\infty} g_4 w_5 dr \quad (45)$$

$$-\int_0^{\infty} g_5 w_1 dr = A \int_0^{\infty} g_5 w_2 dr + B \int_0^{\infty} g_5 w_3 dr + C \int_0^{\infty} g_5 w_4 dr + D \left[\int_0^{\infty} g_5 w_5 dr - 1 \right]. \quad (46)$$

The problem reduces to solving for the five uncoupled second order differential equations. Having w_1, w_2, w_3, w_4 and w_5 , we then evaluate the matrix elements $\int_0^{\infty} g_i w_j dr$ and solve for A, B, C and D using the matrix inversion method. And finally

$$f_0^{(+)} = w_1 + A w_2 + B w_3 + C w_4 + D w_5.$$

A. The Runge-Kutta Method of Solving Second Order Differential Equation²

We have an equation of the form $y''(x) = f(x, y)$; f is a known function. The R-K method allows us to obtain the value of $y(x_r + h)$ once $y(x_r)$, $y'(x_r)$ and $f(x_r, y_r)$ are known. To find $y(x_r + h)$ and $y'(x_r + h)$, we first evaluate the quantities

$$K_1 = \frac{h^2}{2} f(x_r, y_r) \quad (47)$$

$$K_2 = \frac{h^2}{2} f\left(x_{r+\frac{1}{2}}, y_r + \frac{h}{2} y'_r + \frac{1}{4} K_1\right) \quad (48)$$

$$K_3 = \frac{h^2}{2} f(x_{r+1}, y_r + h y'_r + K_2) \quad (49)$$

where h is the interval of integration. The five uncoupled equations, equations (38), (39), (40), and (41) can be put into this form

$$y''(x) = f(x, y) \quad (50)$$

namely

$$W_4''(r) + \psi(r)W_4(r) = \psi_1(r, W_4) \quad (51)$$

becomes

$$W_1'' = -\psi(r)W_1(r) + \psi_1(r)W_1(r). \quad (52)$$

We choose as starting values $W_1(0) = 0$; this is required by the boundary condition at the origin; and $W_1'(0) = 1$. The phase shift is independent of the magnitude of the slope at the origin. It is, however, convenient to choose the value +1 because in the calculation of phase shifts, at least for zero angular momentum, we compare W_1 with a sine wave whose slope at the origin is +1.

The phase shift at r is

$$\delta_l^{(+)} = \arctan \left[- \frac{L(r)j_l(kR) - j_l'(kR)}{L(r)\eta_l(kR) - \eta_l'(kR)} \right] \quad (53)$$

where

$$L(r) = \frac{j_l^{(+)}(r)}{j_l^{(+)}(r)}$$

and

$$j_l(kR) = kR J_l(kR)$$

$$\eta_l(kR) = -kR N_l(kR).$$

$\delta_l^{(+)}$ is evaluated at values of r larger than the range of the potential. The correctness of the method of calculation is checked by turning off all potentials. The wave function obtained

is then a sine wave, as expected and the phase shift is zero.

The orthogonal orbitals of the 1s and 2s electrons in Lithium are given by V. Fock and M.J. Petrashen³. The non-exchange radial wave function, f_l (non-exchange) is calculated with the right hand side of equation (30) and equation (31) turned off.

3. Discussion of Results

We are now in a position to discuss the magnitude and sign of the exchange potential, and its effect on the phase shifts.

Most of the exchange effects come from the interaction between the 2s valence electron and the incident electron. The exchange effects coming from the interaction between the 1s core electron and the incident electron are neglected. Equation (34) then reduces to

$$f_0^{(+)}(r) + \left([k^2 - V(r)] - \left[(k^2 - E_{200}) \frac{P_{20}(r)}{f_0^{(+)}(r)} + \frac{P_{10}(r)}{f_0^{(+)}(r)} V_{100,200}(r) \right] \int_0^\infty P_{20}(r') f_0^{(+)}(r') dr' - \frac{2P_{20}(r)}{f_0^{(+)}(r)} \int_0^\infty P_{20}(r') x \right. \\ \left. f_0^{(+)}(r') dr' - \frac{2P_{20}(r)}{f_0^{(+)}(r)} \int_0^h P_{20}(r') f_0^{(+)}(r') \left\{ \frac{1}{r} - \frac{1}{r'} \right\} dr' \right] f_0^{(+)}(r) = 0 \quad (54)$$

where $V(r)$ is the local potential. The non-local potential is contained in the second set of square brackets. The sign of the non-local potential depends on the relative signs of $f_0^{(+)}(r)$ and $P_{20}(r)$. At this point let us note that $V(r)$ is attractive ($V(r) < 0$) and that the scattering is elastic ($k^2 < (E_{200} - E_{100})$).

Consider Fig. (1). At $k = 0.4$ and for $0 < r < 6$, $P_{20}(r)$, $f_0^{(+)}(r)$ and $P_{10}(r)$ have the same sign. Therefore, the first three terms in the non-local potential in equation (54) are negative in this range and out-weigh the fourth term which is positive. $0 < r < 6$ is the range in which $P_{20}(r)$, $f_0^{(+)}(r)$ and $P_{10}(r)$ are large and contribute appreciably to the non-local potential. The non-local potential is attractive; so that $(V_{\text{local}} + V_{\text{non-local}} < V_{\text{local}})$. The more negative a potential, the larger the phase shift⁴; thus we expect that $\delta_0^{(+)}(\text{exchange}) > \delta_0(\text{non exchange})$. This is indeed the case; $\delta_0^{(+)}$ is found to be larger than $\delta_0(\text{non exchange})$ at $k = 0.4$.

Fig. 3 shows that the main contribution to exchange effects comes from the p state, ($l = 1$). That there can be exchange between the Lithium electrons which are all in the s state, ($l = 0$) and a p state is due to the presence in the non-local potential of integrals of the form $\int u_{nlm}^*(\bar{r}') f(\bar{r}') \frac{e^2}{|\bar{r} - \bar{r}'|} d\bar{r}'$

which, when expanded in partial wave functions give non-vanishing terms in $Y_{1m_1}(\Omega)$.

The contribution to the phase shift from the angular momentum state $l=1$ is such that $\delta_1^{(+)}(\text{exchange}) \gg \delta_1(\text{non exchange})$, therefore, from the discussion above, we deduce that the non-local potential corresponding to $l=1$ is attractive and is very large compared to the local potential.

The only experimental cross-sections for scattering of electrons by Lithium are those of Perel et al.⁵ Let σ_t be the cross-section calculated in this paper and σ_E be Perel's cross-section. We note from Fig. 5 that for $k^2 > 1.3 \text{ eV}$, the threshold energy, $\sigma_E > \sigma_t$; this is because σ_E is the total cross-section while σ_t is only the elastic part of the total cross-section (in the calculation of σ_t , the kinetic energy is kept below the threshold energy). The peak in the σ_E curve at $k^2 = 1.3 \text{ eV} = (E_{210} - E_{200})$ is due to the $2p \rightarrow 2s$ excitation cross-section which has its maximum at this energy.

There is no adequate experimental data for $0 < k^2 < 1.3 \text{ eV}$ which is the region of elastic scattering. Comparison with the cross-section for Cesium given by Reitz and Stone⁶ in this range of energy shows a striking resemblance between the two cross-

section curves; in particular we note that the minimum and maximum of the two curves occur at the same incident electron energy (see Fig. 5). The resemblance of the two cross-section curves coupled with the fact that both Cesium and Lithium are alkali atoms, leads us to believe that the approximation made for the wave function of the system is valid.

A. Exchange Effects for Closed-Shell Electrons and Valence Electrons

The cross-section $\sigma^{(+)}$ corresponds to the physical situation shown in Fig. 6a. The incident electron is identical with atomic electrons a and c; all three have parallel spins. $\sigma^{(+)}$ is the cross-section which takes into account the possibility of exchange between the incident electron and the 2s valence electron and one 1s electron. The cross-section $\sigma^{(-)}$ corresponds to the physical situation shown in Fig. 6b. The incident electron is identical with electron b. $\sigma^{(-)}$ takes into account the possibility of exchange between the incident electron and one 1s atomic electron.

Fig. 4 shows that $\sigma^{(-)}$ is very nearly equal to σ (non exchange); this is because the b electron is sharply distinguishable from the incident electron and therefore the possibility of exchange is small. b is tightly bound in a small core; its wave packet hardly overlaps with the incident

wave packet. Thus, exchange effects between incident and core electrons are negligible.

For large $\hbar^2 k^2 / 2m$, both cross-sections, exchange and non-exchange, converge towards the same value, this is because in the equation for $F(r)$ the kinetic energy of the incident electron completely dominates the potential energy $V(\bar{r}) + \frac{l(l+1)}{r^2}$ and even more so the non-local term.

B. Polarization of the Atom by The Incident Electron

For clarity and because it is small compared to exchange effects the polarization of the atomic target by the incident electron has been neglected. We shall discuss polarization effects briefly here and show that the polarization potential, $V_p(\bar{r})$, can be calculated and added to the exchange potential.

The Hamiltonian of the system electron plus atom can be written as

$$H = H_a(\bar{r}_a) + H_e(\bar{r}) + V(\bar{r}, \bar{r}_a). \quad (55)$$

$\bar{r}$ is the position of the incident electron and $\bar{r}_a$ the position of the atom. H_a is the Hamiltonian of the unperturbed atom. H_e is the kinetic energy of the incident electron.

$V(\bar{r}, \bar{r}_a)$ is the interaction potential between the electron and the atom. $V(\bar{r}, \bar{r}_a)$ is the perturbation potential of the

atom. Because of the presence of an external electron, the atom wave function is perturbed and can be written as

$$\psi(\bar{r}_a) = \psi_0(\bar{r}_a) + \sum_{n \neq 0} \beta_n(\bar{r}) \psi_n(\bar{r}_a). \quad (56)$$

From first order perturbation theory,

$$\beta_n(\bar{r}) = \frac{V_{n0}(\bar{r})}{E_n - E_0} \quad (56a)$$

where

$$V_{n0}(\bar{r}) = \langle \psi_n(\bar{r}_a) | V(\bar{r}, \bar{r}_a) | \psi_0(\bar{r}_a) \rangle$$

and E_n is such that

$$H_a \psi_n(\bar{r}_a) = E_n \psi_n(\bar{r}_a).$$

Equation (56) can be rewritten as

$$\psi(\bar{r}_a) = \psi_0(\bar{r}_a) + \sum_{n \neq 0} \frac{V_{n0}(\bar{r})}{E_n - E_0} \psi_n(\bar{r}_a) \quad (57)$$

The charge density $\rho(\bar{r}_a)$ of the perturbed atom, neglecting terms of order V_{n0}^2 is thus

$$\rho(\bar{r}_a) = e |\psi_0|^2 + e \sum_{n \neq 0} \left\{ \frac{V_{n0}(\bar{r})}{E_n - E_0} \psi_n(\bar{r}_a) \psi_0^*(\bar{r}_a) + \text{conjugate} \right\}. \quad (58)$$

The second term, in general, is not spherically symmetrical and gives rise to a dipole moment.

The total wave function of the system is

$$\Psi(\vec{r}, \vec{r}_a) = \Psi(\vec{r}_a) F(\vec{r}) = \left\{ \psi_0(\vec{r}_a) + \sum_{n \neq 0} \beta_n(\vec{r}) \psi_n(\vec{r}_a) \right\} F(\vec{r}) \quad (59)$$

where $F(\vec{r})$ is the wave function of the incident electron.

Now, consider the time independent Schrödinger equation

$$H\Psi = E\Psi.$$

Replacing H by its value in equation (55) and Ψ by its value in equation (59) we obtain

$$\begin{aligned} & \left\{ H_a(\vec{r}_a) + H_e(\vec{r}) + V(\vec{r}, \vec{r}_a) \right\} \left[\left\{ \psi_0(\vec{r}_a) + \sum_{n \neq 0} \beta_n(\vec{r}) \psi_n(\vec{r}_a) \right\} F(\vec{r}) \right] = \\ & (E_a + \frac{\hbar^2 k^2}{2m}) \left[\left\{ \psi_0(\vec{r}_a) + \sum_{n \neq 0} \beta_n(\vec{r}) \psi_n(\vec{r}_a) \right\} F(\vec{r}) \right]. \end{aligned} \quad (60)$$

Multiplying equation (60) on the left by $\psi_0^*(\vec{r}_a)$ and integrating over $\vec{r}_a$ we get

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \frac{\hbar^2 k^2}{2m} + V_{00}(\vec{r}) + V_p(\vec{r}) \right] F(\vec{r}) = 0 \quad (61)$$

where

$$\begin{aligned} V_p(\vec{r}) &= \sum_{n \neq 0} \beta_n(\vec{r}) \langle \psi_0(\vec{r}_a) | V(\vec{r}, \vec{r}_a) | \psi_n(\vec{r}_a) \rangle \\ &= \sum_{n \neq 0} \beta_n(\vec{r}) V_{0n}(\vec{r}) \end{aligned}$$

and

$$V_{00}(\bar{r}) = \langle \psi_0(\bar{r}_a) | V(\bar{r}, \bar{r}_a) | \psi_0(\bar{r}_a) \rangle$$

and using equation (56a), we obtain

$$V_p(\bar{r}) = - \sum_{n \neq 0} \frac{|V_{0n}(\bar{r})|^2}{E_n - E_0} \quad (62)$$

$V_p(\bar{r})$ is the potential of the atomic dipole moment, Castillejo, Percival, and Seaton⁷ have shown that it is of the form $V_p(\bar{r}) = -\alpha/r^4$ for large r . This potential is attractive and therefore increases the phase shift of $\tau(\bar{r})$.

Let us look at $V_{0n}(\bar{r})$ in more detail. The potential $V(\bar{r}, \bar{r}_a)$ is the electron-atom interaction.

$$V(\bar{r}, \bar{r}_a) = - \frac{Ze^2}{r} + \sum_{i=1}^n \frac{e^2}{|\bar{r} - \bar{r}_i|}$$

therefore

$$\begin{aligned} V_{0n}(\bar{r}, \bar{r}_a) &= \int \psi^*(\bar{r}_a) \sum_{i=1}^n \frac{e^2}{|\bar{r} - \bar{r}_i|} \psi_n(\bar{r}_a) d\bar{r}_a \\ &= e^2 \sum_{i=1}^n \int \psi_0^*(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) \frac{1}{|\bar{r} - \bar{r}_i|} \psi_n(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) d\bar{r}_1 \dots d\bar{r}_n \end{aligned}$$

$V_{0n}(\bar{r}, \bar{r}_a)$ is readily evaluated when $\psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n)$ is written as

$$\psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_n) = \sum_{i_1 i_2 \dots i_n} \epsilon_{i_1 i_2 \dots i_n} u_{i_1}(\bar{r}_1) u_{i_2}(\bar{r}_2) \dots u_{i_n}(\bar{r}_n)$$

and $1/|\vec{r}-\vec{r}_i|$ is expanded in spherical harmonics. A good approximation for V_p is obtained if only the first excited state ($n=1$) is considered in the summation in equation (62).

Castillejo, Percival and Seaton⁸ have shown that for Hydrogen the first excited state contributes 65.8% to the polarization potential and Stone and Reitz⁹ showed that in Cesium the first excited state contributes 92% to the polarization potential.

We have thus shown in this section that polarization potential can be calculated independently and added to the exchange potential.

CONCLUSION

An equation for the radial wave function of the incident electron in scattering of slow electrons by atoms is approximated and solved numerically. The results obtained agree with predictions; that is: the exchange potential which arises from the indistinguishability of interacting particles is an attractive potential and therefore increases the phase shift of the incident wave function; it is large compared to the local-potential for values of incident energy below the threshold energy and must be included in elastic scatterings. The contribution to exchange comes from the atomic electrons of the last shell. Closed-shell electrons do not contribute appreciably to the exchange potential.

Thus, it seems that the approximations made in arriving at the radial equation are reasonable and this equation can be used to calculate cross-section for scattering of slow electrons by atoms.

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TABLE I. PHASE SHIFT FOR $\ell = 0$

k ($10^{-2} \times 1/a_0$)	PHASE SHIFT	FOR $\ell = 0$	IN RADIAN
	WITH SPIN UP INC- IDENT ELECTRON	EXCHANGE SPIN DOWN INCI- IDENT ELECTRON	WITH OUT EXCHANGE
2	3.07	3.25	3.27
4	3.01	3.35	3.39
6	2.94	3.44	3.49
8	2.88	3.50	3.56
10	2.81	3.55	3.61
12	2.75	3.59	3.64
14	2.70	3.62	3.66
16	2.64	3.63	3.66
18	2.59	3.64	3.65
20	2.54	3.64	3.64
22	2.51	3.63	3.62
24	2.49	3.62	3.60
26	2.49	3.61	3.58
28	2.51	3.60	3.55
30	2.57	3.58	3.52
32	2.69	3.56	3.49
34	2.89	3.54	3.47
36	3.16	3.52	3.44
38	3.43	3.50	3.41
40	3.65	3.48	3.38

TABLE II. PHASE SHIFT FOR $\ell = 1$

k ($10^{-2} \times 1/a_0$)	PHASE SHIFT FOR $\ell = 1$ IN RADIAN		
	WITH SPIN UP INCI- DENT ELECTRON	EXCHANGE SPIN DOWN INCI- DENT ELECTRON	WITH OUT EXCHANGE
2	8.10×10^{-4}	1.14×10^{-4}	1.12×10^{-4}
4	6.60×10^{-3}	9.14×10^{-4}	8.90×10^{-4}
6	2.35×10^{-2}	3.07×10^{-3}	3.00×10^{-3}
8	5.90×10^{-2}	7.25×10^{-3}	2.10×10^{-3}
10	1.24×10^{-1}	1.40×10^{-2}	1.37×10^{-2}
12	2.34×10^{-1}	2.40×10^{-2}	7.34×10^{-2}
14	4.04×10^{-1}	3.77×10^{-2}	3.67×10^{-2}
16	6.38×10^{-1}	5.54×10^{-2}	5.38×10^{-2}
18	8.99×10^{-1}	7.73×10^{-2}	7.50×10^{-2}
20	1.13×10^0	1.034×10^{-1}	1.00×10^{-1}
22	1.29×10^0	1.336×10^{-1}	1.29×10^{-1}
24	1.40×10^0	1.675×10^{-1}	1.62×10^{-1}
26	1.46×10^0	2.044×10^{-1}	1.97×10^{-1}
28	1.49×10^0	2.435×10^{-1}	2.36×10^{-1}
30	1.50×10^0	2.84×10^{-1}	2.72×10^{-1}
32	1.496×10^0	3.25×10^{-1}	3.11×10^{-1}
34	1.48×10^0	3.66×10^{-1}	3.49×10^{-1}

TABLE II - (continued)

k ($10^{-2} \times 1/a_0$)	PHASE SHIFT FOR $l = 1$		IN RADIAN
	WITH SPIN UP INCI- DENT ELECTRON	EXCHANGE SPIN DOWN INCI- DENT ELECTRON	WITH OUT EXCHANGE
36	1.46×10^0	4.05×10^{-1}	3.86×10^{-1}
38	1.44×10^0	4.40×10^{-1}	4.22×10^{-1}
40	1.415×10^0	4.80×10^{-1}	4.55×10^{-1}

TABLE III. CROSS-SECTION WITH AND WITHOUT
EXCHANGE FOR SCATTERING OF
ELECTRONS BY LITHIUM

k^2 (RYDBERGS)	$\sigma(\text{EX})$ (πa_0^2)	$\sigma(\text{NE})$ (πa_0^2)
4.00 x 10^{-4}	77.74	175.80
16.00 x 10^{-4}	74.15	156.60
36.00 x 10^{-4}	70.675	130.00
64.00 x 10^{-4}	63.65	104.80
1.00 x 10^{-2}	61.90	82.48
1.44 x 10^{-2}	68.55	64.55
1.96 x 10^{-2}	87.70	50.00
2.56 x 10^{-2}	119.14	38.70
3.24 x 10^{-2}	145.38	32.00
4.00 x 10^{-2}	151.13	26.24
4.84 x 10^{-2}	140.40	22.10
5.76 x 10^{-2}	127.35	19.30
6.76 x 10^{-2}	108.35	17.50
7.84 x 10^{-2}	94.40	16.56
9.00 x 10^{-2}	62.05	16.10
10.24 x 10^{-2}	71.30	16.20
11.56 x 10^{-2}	61.95	16.36

TABLE III. - (continued)

k^2 (RYDBERGS)	$\sigma(\text{EX})$ (πa_0^2)	$\sigma(\text{NE})$ (πa_0^2)
12.96 x 10^{-2}	55.88	16.68
14.46 x 10^{-2}	52.45	17.00
16.00 x 10^{-2}	50.30	17.31

Figure 1. Radial orbitals of the 1s and 2s electrons P_{10} , P_{20} and radial wave function of the incident electron

Figure 2. Phase shift for $l=0$ in electron scattering by Lithium, including and neglecting exchange

Figure 3. Phase shift for $l=4$ in electron scattering by Lithium, with and without exchange.

Figure 4. Cross-section for Scattering of Electrons
By Lithium Including and Neglecting Exchange

Figure 5. Cross-Section for Scattering of Electrons
by
Cesium and Lithium

Figure 6. Scattering of "spin up", (a) and "spin down", (b) electrons by the Lithium atom