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ELECTRON SCATTERING BY THE RARE GASES

A Thesis submitted to the  
Faculty of Science  
for the Degree of  
Doctor of Philosophy

in

University of London

by

Margaret Knowles, B.Sc. (London)

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ABSTRACT

In the first part of this thesis an optical potential approach is applied to the problem of elastic electron-helium scattering at low energies. First the deficiencies in the second order calculation of Pu and Chang are removed and then third order corrections to the phaseshifts are considered. In Chapter I a short review of Brueckner-Goldstone perturbation theory is presented and explicit expressions for the second order phase shifts are derived. The methods of computing these expressions are considered in Chapter II. Various other theoretical models are discussed in Chapter III where also our second order results for the s, p and d-wave phase shifts are given. Chapter IV comprises our calculation of the polarisability of helium, using a Brueckner-Goldstone approach. In Chapter V a method of determining all the distinct Feynmann diagrams of any order is given, and third order corrections to the d-wave phase shift are discussed.

The aim of the work described in Part II of this thesis has been to test for electron-neon scattering the dispersion relation conjectured by Gerjuoy and Krall. An introduction to the dispersion relation and the technique of phase shift analysis is given in Chapter VI and previous work on electron-helium scattering is reviewed. In Chapter VII the various quantities which have to be calculated in order to test the validity of the dispersion relation for electron-neon scattering are discussed. In particular, the analysis involved is the calculation of the Born exchange scattering amplitude,  $g_B(0, k^2)$  is given. A more accurate evaluation of this amplitude for zero energy, using a configuration interaction ground state wave function, is described in

Chapters VIII and IX. Preliminary results for  $g_B(0, 0)$  are given in Chapter X.

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CHAPTER I

THE OPTICAL POTENTIAL MODEL

1.1. Introduction

Considerable advances have been made recently in understanding the elastic scattering of slow electrons by helium atoms. Theoretical studies by Callaway and his collaborators (La Bahn and Callaway 1966, Callaway et al. 1968) and by Duxler et al. (1971), using variants of the polarised orbital approach, have led to values of the s and p wave phase shifts in good agreement with those derived directly from elastic scattering experiments (Andrick and Bitsch 1972). They also agree with the results of a phase shift analysis of experimental data (Bransden and McDowell 1969, McDowell 1971a, Bransden et al. 1973) and with those of several other recent theoretical calculations. These are the optical potential approach of Pu and Chang (1966), the Green's function method of Yarlagadda et al. (1973) and the variational calculation of Sinfailam and Nesbet (1972).

However, the d wave ( $l = 2$ ) results obtained in these various theoretical calculations differ considerably and disagree with the values proposed by McDowell (1971a) on the basis of a phase shift analysis of experimental data.

Kelly (1967) has pointed out that the optical potential calculation of Pu and Chang (1966) is incomplete, certain second order terms being omitted. Pu and Chang restricted their work to second order in perturbation theory (omitting terms discussed below), considered the s and p wave phase shifts only and allowed only s, p and d intermediate states. In the first part of this thesis we extend their work to remove



these deficiencies, presenting what we believe to be a complete second order calculation. We also discuss the third order terms in some detail.

Many-body perturbation theory as developed by Brueckner (1955) and Goldstone (1957) has proved very useful in the study of many-particle systems. The theory was initially used principally to investigate nuclear structure (Brueckner and Gammel 1958) and the electron gas (Gell-Man and Brueckner 1957). Kelly successfully applied the method to a calculation of correlation energies in the neutral beryllium atom (1963) and later in 1964 he obtained very good values for many atomic properties including polarisabilities and oscillator strengths.

Bell and Squires (1959) used a diagrammatic approach similar to the Brueckner-Goldstone perturbation theory to set on a more rigorous basis the optical potential approach which was being used by Mittleman and Watson (1959) and others. The optical potential is a one-body potential representing the effect of the target atom on the scattering particle.

This optical potential method was modified slightly by Pu and Chang (1966) and applied to the elastic scattering of slow electrons from the helium atom. Conventionally, having obtained the formal optical potential expression, the scattering wave function was calculated by solving the one-body Schrödinger equation with the appropriate optical potential. However, because the operators for the scattering electrons are contained in the optical potential, the latter is extremely difficult to evaluate and one is forced to make several approximations, including the adiabatic approximation. Pu and Chang point out that the validity of the adiabatic condition for low-energy electron-atom scattering is rather dubious and to avoid this difficulty they use the optical

potential directly in a variational expression for the scattering phase shifts.

As we have mentioned earlier, the calculation of Pu and Chang is incomplete and we will now describe how we have extended it. First we give a review of the relevant results of Brueckner-Goldstone theory and obtain explicit expressions for all the second order corrections to the phase shifts.

### 1.2. Brueckner-Goldstone Perturbation Theory

The problem considered is that of the scattering of a slow electron by a neutral atom with  $N$  atomic electrons which interact through two-body potentials. The total Hamiltonian for such a system is

$$H = \sum_{i=1}^{N+1} T_i + \sum_{i < j}^{N+1} v_{ij} \quad (1.1)$$

where  $v_{ij}$  is the mutual Coulomb interaction between the  $i$ th and  $j$ th electrons and  $T_i$  is the sum of the kinetic energy of the  $i$ th particle and all the one-body potentials acting on it.

Schrödinger's equation for the system is

$$H \psi^{(N+1)} = E \psi^{(N+1)} \quad (1.2)$$

where  $E$  is the total energy and  $\psi^{(N+1)}$  the exact wave function of the system. This equation cannot be solved exactly, because of the two body terms, and so we approximate the effect of the interacting particles by a single-particle potential  $V_i$ . The true state of the system is then approximated by an unperturbed state function  $\psi_0^{(N+1)}$  and Hamiltonian  $H_0$

$$H_0 = \sum_{i=1}^{N+1} (V_i + T_i) = \sum_{i=1}^{N+1} H_{0i} \quad (1.3)$$

with

$$H_0 \psi_0^{(N+1)} = E_0 \psi_0^{(N+1)} \quad (1.4)$$

where  $E_0$  is the approximation to the correct energy  $E$ . If  $H'$  denotes the difference between the total and unperturbed Hamiltonians, then

$$H' = H - H_0 = \sum_{i < j}^{N+1} v_{ij} - \sum_{i=1}^{N+1} V_i \quad (1.5)$$

At this point,  $V_i$  is an arbitrary one-body potential, but it is taken to be Hermitian, so that the single-particle wave functions  $\phi_n$ , the solutions of

$$H_{oi} \phi_n = (T_i + V_i) \phi_n = \epsilon_n \phi_n \quad (1.6)$$

form a complete set. The unperturbed ground state of the target atom,  $\phi_0^{(N)}$ , is the Slater determinant formed from the  $N$  lowest energy solutions of (1.6) (allowing for spin and angular momenta). The corresponding unperturbed function for the total system,  $\psi_0^{(N+1)}$  is formed by adding a suitable solution of (1.6) to describe the free electron. We refer to those states  $\phi_m$  which are occupied in  $\phi_0^{(N)}$  as unexcited states and to all other  $\phi_n$ 's as excited states. An unoccupied unexcited state is called a hole and an occupied excited state is called a particle. The complete set of  $\phi_n$ 's is used as a basis for a perturbational expansion for the solution  $\psi^{(N+1)}$  of (1.2).

Before we can proceed, two concepts need to be introduced, namely, the interaction picture and adiabatic switching. There are three ways of describing the time development of the system, either in the operators (the Heisenberg picture), or in the wavefunctions (the Schrödinger picture)

or in both. It is the last which we use and this is called the interaction picture. The total Hamiltonian is split up as in (1.5) and then the time development of the observable depends only on  $H_0$  and that of the wave functions only on  $H'$ . We have

$$H'(t) = e^{\frac{iH_0 t}{\hbar}} H' e^{-\frac{iH_0 t}{\hbar}} \quad (1.7)$$

where  $H_0$  and  $H'$  are in the Schrödinger picture. A time development operator in the interaction picture,  $U(t, t_0)$ , is introduced where

$$\psi(t) = U(t, t_0)\psi(t_0),$$

and the Schrödinger equation becomes

$$\frac{\hbar}{i} \frac{\partial}{\partial t} U(t, t_0) + H'(t)U(t, t_0) = 0 \quad (1.8)$$

with the initial condition  $U(t_0, t_0) = 1$ . Integrating (1.8) by a method of successive approximations gives

$$U(t, t_0) = \sum_{n=0}^{\infty} U_n(t, t_0)$$

where

$$U_n(t, t_0) = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t \int_{t_0}^{t_1} \dots \int_{t_0}^{t_{n-1}} H'(t_1) \dots H'(t_n) dt_1 \dots dt_n \quad (1.9)$$

with  $t \geq t_1 \geq \dots \geq t_n \geq t_0$ .

Secondly, we deal with adiabatic switching. The scattering process is usually treated as a perturbation of the initial free state caused by a time-dependent interaction which is switched on at a time  $t = 0$  and off again at some later time  $t = r$ . The question arises as to whether this abrupt switching on and off is a permissible idealisation. The problem

is solved by introducing a factor  $e^{-\alpha|t|}$  where  $\alpha$  is small, so that equation (1.7) becomes

$$H'(t) = e^{iH_0 t} H' e^{-iH_0 t} e^{-\alpha|t|} \quad (1.10)$$

Eventually the limit  $\alpha \rightarrow 0$  is taken.

With these ideas, Goldstone (1957) has shown that the true ground state of the atom,  $\phi^{(N)}$  is given by

$$\phi^{(N)} = \lim_{\alpha \rightarrow 0} \frac{U_\alpha(0)\phi_0^{(N)}}{\langle \phi_0^{(N)} | U_\alpha(0) | \phi_0^{(N)} \rangle} \quad (1.11)$$

where  $U_\alpha(0)$  is the time development operator in the interaction picture, defined above, evaluated at time  $t = 0$ . That is

$$U_\alpha(0) = U_\alpha(0, t_0) = \sum_{n=0}^{\infty} (-i)^n \int_{t_0}^t \dots \int_{t_0}^{t_{n-1}} H'(t_1) \dots H'(t_n) dt_1 \dots dt_n \quad (1.12)$$

with  $0 > t_1 > \dots > t_n$ , where we have used atomic units ( $\hbar = 1$ ).

Equation (1.11) is Goldstone's Theorem which effectively says that the true wave function  $\phi^{(N)}$  is formed from the approximate wave function  $\phi_0^{(N)}$  by gradually switching on the perturbation  $H'$ . The factor in the denominator is for normalisation.

At this point, a second quantisation approach is useful; the creation and annihilation operators for single particle states satisfy the Fermi-Dirac anti-commutation relations, so that the Pauli Exclusion Principle is satisfied. In this formalism equations (1.3) and (1.5) become

$$H_0 = \sum_n \epsilon_n \eta_n^* \eta_n \quad (1.13)$$

$$H' = \sum_{p,q,m,n} \langle pq|v|mn \rangle \eta_p^* \eta_q^* \eta_m \eta_n - \sum_{p,m} \langle p|V|m \rangle \eta_p^* \eta_m \quad (1.14)$$

$\eta_n^*$ ,  $\eta_n$  are the usual creation and annihilation operators for the state  $\phi_n$  and the matrix elements are given explicitly by

$$\langle pq|v|mn \rangle = \iint \phi_p^*(\underline{r}) \frac{\phi_q^*(\underline{r}') e^2}{|\underline{r}-\underline{r}'|} \phi_m(\underline{r}) \phi_n(\underline{r}') d\underline{r} d\underline{r}'$$

$$\langle p|V|m \rangle = \int \phi_p^*(\underline{r}) V(\underline{r}) \phi_m(\underline{r}) d\underline{r} .$$

The summation is over distinct matrix elements only.

Using the results (1.13) and (1.14) in the expression for  $H'(t)$ , equation (1.10),  $U_\alpha(0)$  becomes a sum of products of  $v$  and  $V$  matrix elements,  $e^{iEt}$  and  $e^{\alpha t}$  factors and  $\eta^*$  and  $\eta$  operators.

By use of Wick's Theorem,  $\phi^{(N)}$  can be represented by a sum of distinct Feynmann diagrams in which a 'particle' is represented by a line directed upwards and a 'hole' by a line directed downwards. Interactions are represented by horizontal dotted lines, and diagrams corresponding to a  $V$  matrix element have an extra minus sign (see equation (1.14)). Also, each diagram must be multiplied by a factor  $(-1)^{h+\ell}$  where  $h$  is the number of internal hole lines and  $\ell$  the number of closed loops.

Goldstone's Factorization Theorem shows that the numerator,  $U_\alpha(0)\phi_0^{(N)}$ , of the expression for  $\phi^{(N)}$ , factorizes into the produce of two terms, one the sum of all linked diagrams, the other the sum of all unlinked diagrams, the denominator also being equal to this second factor. By a linked diagram we mean one which has no parts totally disconnected from the rest of the diagram.

Using these results and carrying out the line integrations in (1.12) in the limits  $t_0 \rightarrow -\infty$ ,  $\alpha \rightarrow 0$ , we find that

$$\phi^{(N)} = \sum_{n=0}^{\infty} \left( \frac{1}{E_0 - H_0} H' \right)^n \phi_0^{(N)} \quad (1.15)$$

where  $E_0' = E_0 - \frac{1}{2}k_0^2$ , the sum being over linked diagrams only.

Similarly, the true solution for the entire scattering system is

$$\psi^{(N+1)} = \sum_{n=0}^{\infty} \left( \frac{1}{E_0 - H_0 + i\epsilon} H' \right)^n \psi_0^{(N+1)} \quad (1.16)$$

It was first shown by Bell and Squires (1959) that by projecting  $\psi^{(N+1)}$  onto  $\phi_0^{(N)}$  one obtains the true scattering wave function  $\chi(k_0)$  for the incident electron.

$$\begin{aligned} \chi(k_0) &= \langle \phi_0^{(N)} | \psi^{(N+1)} \rangle \\ &= \sum_{n=0}^{\infty} \left( \frac{1}{E_0 - H_0 + i\epsilon} H' \right)^n \phi_{k_0} \end{aligned} \quad (1.17)$$

that is,  $\chi$  is the sum of all linked diagrams having one particle line  $k_0$  at the bottom and one particle line at the top.

In this method the effect of the target atom on the scattering particle is represented by an equivalent one-body potential,  $\omega_{op}$ . Then the true scattering wave function  $\chi(k_0)$  satisfies the one-particle Schrödinger equation

$$(T_{k_0} + V_{k_0} + \omega_{op})\chi(k_0) = \epsilon_{k_0} \chi(k_0) \quad (1.18)$$

where  $V_{k_0}$  is the potential  $V_i$  acting on the particle with momentum  $k_0$ . The optical potential, as first derived by Bell and Squires (1959) is

$$\omega_{op} = \sum_{n=0}^{\infty} \Pi' \left( \frac{1}{E_0 - H_0 + i\epsilon} H' \right)^n \quad (1.19)$$

where the summation is over linked and proper diagrams only. By 'proper' we mean those linked diagrams which are not connected by a single particle line at any intermediate stage. As Goldstone points out, this is to be expected physically, since such a single-particle line would mean that the atom was in its ground state at that intermediate stage.

### 1.3. The Single-Particle States

Before we can make use of this Brueckner-Goldstone theory, it is first necessary to obtain a complete set of single-particle states, solutions of equation (1.6), and they are determined by the potential  $V_i$ . It is shown by Goldstone (1957) that if  $V_i$  is chosen to be the Hartree-Fock potential  $V_i^{HF}$ , defined by its matrix elements

$$\langle i | V_i^{HF} | j \rangle = \sum_{n=1}^N \{ \langle i n | v | j n \rangle - \langle i n | v | n j \rangle \}, \quad (1.20)$$

the summation being over all orbitals of the ground state atom, then the first order optical potential diagrams cancel exactly (see Figure 1.1).

Thus, with this choice of  $V_i$ , the leading terms in the expansion for the optical potential, (1.19), are second order.

Choosing  $V_i$  to be the Hartree-Fock potential we can write the single-particle eigenvalue equation (1.6) in the more explicit form

$$\left\{ -\frac{2}{k^{2m}} \nabla^2 - \frac{Ne^2}{r} + \sum_{i=1}^N \int \phi_i^*(\underline{r}') \frac{e^2}{|\underline{r}-\underline{r}'|} \phi_i(\underline{r}') d\underline{r}' \right\} \phi_n(\underline{r}) - \sum_{i=1}^N \delta(m_{s_n}, m_{s_i}) \int d\underline{r}' \frac{\phi_i^*(\underline{r}') e^2}{|\underline{r}-\underline{r}'|} \phi_n(\underline{r}') \phi_i(\underline{r}) = \epsilon_n \phi_n(\underline{r}) \quad (1.21)$$



where  $m_{s_n}$  is the spin of the electron in the state  $\phi_n$ . The Hartree-Fock orbitals for the ground state,  $\phi_0^{(N)}$  are generated by (1.21).

For  $n \in (i = 1, \dots, N)$  one of the direct terms cancels with one of the exchange terms, so that the electron in state  $n$  sees a potential due to the nucleus and  $(N-1)$  other orbital electrons. For excited states  $\phi_n$ , ( $n > N$ ), however, no such cancellation occurs and so the potential contains  $N$  direct terms; thus an excited state  $\phi_n$  sees the field of the nucleus and  $N$  orbital electrons. The  $N$  states which determine this potential are fixed and are independent of the excited state.

Calculations by Hylleraas (1930) show that this undisturbed potential for the neutral hydrogen atom is too weak for a bound excited state of hydrogen to exist. Kelly (1963) conjectured that for many other neutral atoms all excited states would lie in the continuum and he proved this to be so for beryllium and later for oxygen (Kelly 1966). Kelly stressed, however, that when calculations are made on a particular atom there still should be a search for bound excited states. Pu and Chang (1966) invoked Levinson's theorem and looked for bound excited states of helium, but none were found, and so we expect all excited states for the two-electron atom to lie in the continuum.

The continuum states  $\phi(k_n, \ell; m, m_s)$  are determined from equation (1.21) by letting  $\epsilon_n = k_n^2/2m$ . Spherical symmetry is assumed so that

$$\phi(k, \ell; m, m_s) = \frac{R(k\ell, r)}{r} Y_{\ell m}(\theta, \phi) X_s(m_s) \quad (1.22)$$

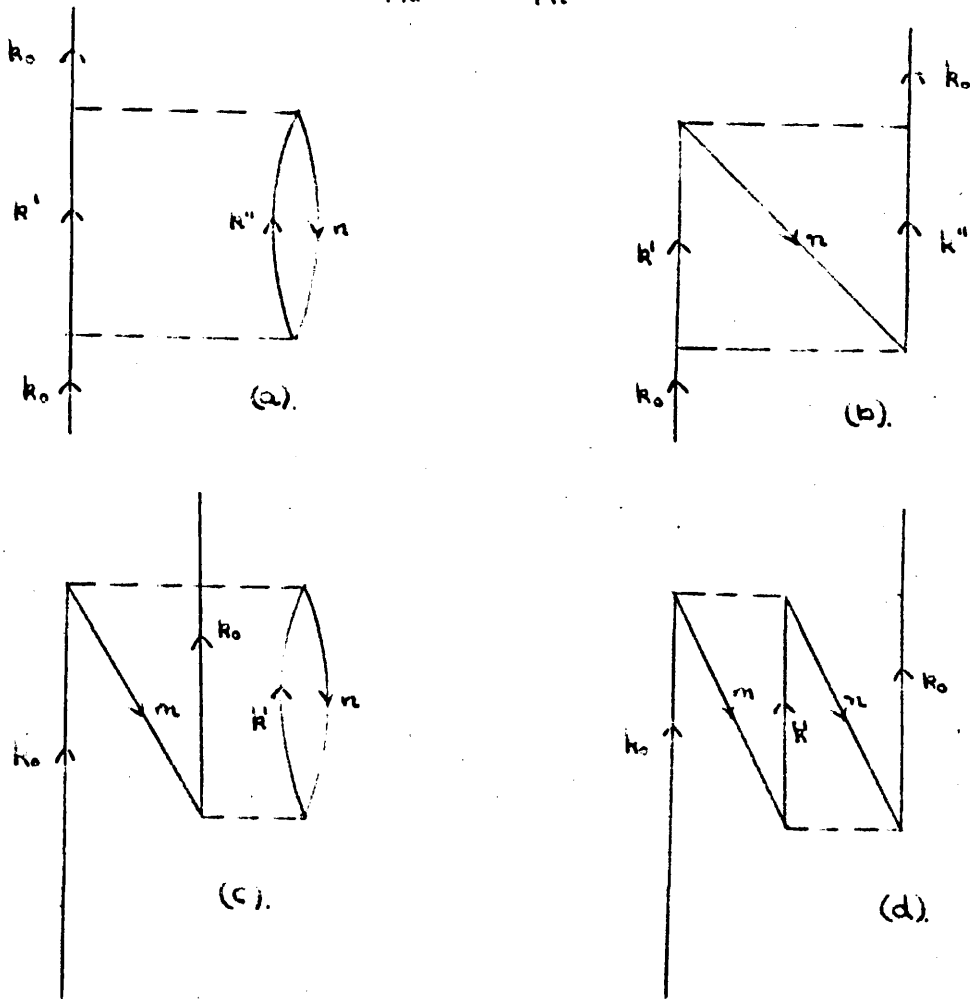
is the usual notation. The  $Y_{\ell m}$  are the spherical harmonics and  $X_s(m_s)$  the spin eigenfunctions. The radial function  $R(k\ell, r)$  satisfies the integro-differential equation

Figure 1.1 The first order diagrams.

$$\sum_n \left[ \begin{array}{c} \text{Diagram 1: } \begin{array}{c} \text{Line } r \text{ and } m \text{ meet at a vertex, with a dashed line to a circle labeled } n. \end{array} + \begin{array}{c} \text{Diagram 2: } \begin{array}{c} \text{Line } m \text{ and } n \text{ meet at a vertex, with a dashed line to a vertex where } n \text{ and } p \text{ meet.} \end{array} \end{array} \right] + \begin{array}{c} \text{Diagram 3: } \begin{array}{c} \text{Line } r \text{ and } m \text{ meet at a vertex, with a dashed line to an 'X'.} \end{array} \end{array} \equiv 0$$

$$\sum_n \left\{ (-1)^2 \langle pn|v|mn \rangle + (-1) \langle pn|v|nm \rangle \right\} - \langle p|V^i|m \rangle \equiv 0$$

Figure 1.2 The four second order diagrams which represent correlations between an incoming electron in state  $\phi_{k_0}$  and atomic electrons in states  $\phi_m$  and  $\phi_n$ .



$$\left(-\frac{d^2}{dr^2} + \frac{2m}{\hbar^2} \left(\frac{z}{r} + V^{\text{HF}}\right) + \frac{\ell(\ell+1)}{r^2}\right) R(k\ell, r) = k^2 R(k\ell, r) \quad (1.23)$$

where  $V^{\text{HF}}$  is the Hartree-Fock potential, defined in terms of its matrix elements in equation (1.20).

We now follow the method of Kelly (1963) and show how the summation over intermediate states  $\phi_k$  can be replaced by an integration over  $k$  with a factor  $2/\pi$ . Consider the atom to be enclosed in a large spherical volume of radius  $R_0$  which tends to infinity. At large distances from the atom the potential is effectively zero and the  $R$  functions are linear combinations of  $j_\ell(kr)$  and  $n_\ell(kr)$ , the spherical Bessel and spherical Neumann functions respectively. As  $r \rightarrow \infty$ ,

$$R(k\ell, r) \sim kr \left[ \cos[\delta_0(k, \ell)] j_\ell(kr) - \sin[\delta_0(k, \ell)] n_\ell(kr) \right]$$

$$\underset{kr \rightarrow \infty}{\sim} \cos(kr + \delta_0(k, \ell) - \frac{1}{2}(\ell+1)\pi)$$

where  $\delta_0(k, \ell)$  is the zero order scattering phase shift.

Since  $\int_0^\infty dr r^2 R^2(k\ell, r) = 1$ , the normalisation constant required is  $(2/R_0)^{\frac{1}{2}}$  and

$$R(k\ell, r) \underset{r \rightarrow \infty}{\sim} \left(\frac{2}{R_0}\right)^{\frac{1}{2}} \cos(kr + \delta_0(k, \ell) - \frac{1}{2}(\ell+1)\pi).$$

Now the wavefunction must vanish on the boundary  $R_0$ , and so

$$kR_0 + \delta_0(k, \ell) - (\ell+1)\frac{\pi}{2} = (n+\frac{1}{2})\pi$$

where  $n$  is an integer. For a fixed value of  $\ell$  the number of eigenstates  $\Delta n$  in the interval  $\Delta k$  is determined by

$$(\Delta k)R_0 + \Delta\delta_0(k, \ell) = (\Delta n)\pi \quad .$$

Since  $\Delta\delta_0(k, \ell)/R_0 \rightarrow 0$  as  $R_0 \rightarrow \infty$ ,

$$\Delta n = \left(\frac{R_0}{\pi}\right) \Delta k \quad ,$$

and 
$$\sum_k = \frac{R_0}{\pi} \int_0^\infty dk \quad .$$

The normalisation factor  $(2/R_0)^{\frac{1}{2}}$  may then be omitted and the summation over continuum states changed to an integration:

$$\sum_k = \frac{2}{\pi} \int_0^\infty dk \quad . \quad (1.24)$$

Summations over  $\ell$ ,  $m$ , and  $m_s$  remain to be carried out.

#### 1.4. Expressions for the second order corrections to the phase shifts

As we have mentioned before, Pu and Chang (1966) have pointed out that it is impracticable to solve the Schrödinger equation of the scattering electron without making an adiabatic approximation to the optical potential  $\omega_{op}$ . The validity of such an approximation is dubious and so, to avoid the dilemma, Pu and Chang obtain expressions for the phase shifts by using a variational approach. We now give an outline of this approach; a fuller account of the method is available in Wu and Ohmura (1962).

If we define the operator L by

$$L = -\frac{d^2}{dr^2} - k_0^2 + \frac{\ell(\ell+1)}{r^2} + \frac{2m}{\hbar^2} \left( V^{HF} + \frac{z}{r} + \omega_{op} \right)$$

then by comparing with equation (1.18) we see that the exact scattering wavefunction,  $\chi(k_0)$ , satisfies the equation  $L\chi(k_0) = 0$ .

We now define the function  $I_t(\phi)$  by

$$I_t(\phi) = \int_0^{\infty} \phi_t^*(r) L\phi_t(r) dr$$

where  $\phi_t$  is a trial wavefunction which satisfies the usual boundary conditions; that is, it vanishes at the origin and has the asymptotic form

$$\phi_t(r) \underset{r \rightarrow \infty}{\sim} \sin(k_0 r - \frac{\ell\pi}{2} + \eta_\ell) ,$$

where  $\eta_\ell$  is the trial phase shift. We consider a small variation  $\delta\phi_t$  in the function  $\phi_t$ . Then

$$\begin{aligned} \delta I_t &= I_t(\phi + \delta\phi) - I_t(\phi) \\ &= \int_0^{\infty} \phi_t^* L(\delta\phi_t) ds + \int_0^{\infty} (\delta\phi_t^*) L\phi_t dr + O(\delta\phi)^2 . \end{aligned}$$

The first term can be integrated by parts, giving

$$\delta I_t = - \phi_t^* \frac{d}{dr}(\delta\phi_t) - \frac{d\phi_t^*}{dr} \delta\phi_t \Big|_0^{\infty} + 2 \int_0^{\infty} \delta\phi_t^* L\phi_t dr + O(\delta\phi)^2 .$$

Now, using the boundary conditions satisfied by  $\phi_t$  and noting that

$$\delta\phi_t(0) = 0 \text{ and } \delta\phi_t(r) \underset{r \rightarrow \infty}{\sim} \cos(k_0 r - \frac{\ell\pi}{2} + \eta_\ell) \delta\eta_\ell ,$$

we obtain

$$\delta I_t = k_0 \delta\eta_\ell + 2 \int_0^{\infty} \delta\phi_t^* L\phi_t dr + O(\delta\phi)^2 .$$

Thus, for  $\phi_t$  to be an exact solution of the equation  $L\phi_t = 0$ , we require, to first order in  $\delta\phi$ ,

$$\delta(I_t - k\eta_\ell) = 0 .$$

That is,  $I_t - k\eta_\ell$  is a constant. If  $\delta_{\text{corr}}$  is the corrected phase shift corresponding to the exact wave function then

$$\delta_{\text{corr}}(k_o, \ell) = \eta_\ell - \frac{1}{k_o} \int_0^\infty \phi_t^* L \phi_t dr + O(\delta\phi)^2 .$$

We take as our trial function the radial wave function  $R(k_o \ell, r)$  which satisfies equation (1.23) and so

$$\delta_{\text{corr}}(k_o, \ell) = \delta_o(k_o, \ell) - \frac{1}{k_o} \int_0^\infty R^*(k_o \ell, r) LR(k_o \ell, r) dr ,$$

where  $\delta_o(k_o, \ell)$  is the zero order phase shift and where

$$\begin{aligned} LR(k_o, \ell, r) &= \left( -\frac{d^2}{dr^2} - k^2 + \frac{\ell(\ell+1)}{r^2} + \frac{2m}{\hbar^2} \left( \frac{z}{r} + V^{\text{HF}} + \omega_{\text{op}} \right) \right) R(k_o, \ell, r) \\ &= \left( \frac{2m}{\hbar^2} \omega_{\text{op}} \right) R(k_o \ell, r) . \end{aligned}$$

Therefore the correction to the zero order phase shift is

$$\begin{aligned} \Delta\delta(k_o, \ell) &= \delta_{\text{corr}}(k_o, \ell) - \delta_o(k_o, \ell) \\ &= -\frac{2m}{\hbar^2 k_o} \int_0^\infty R^*(k_o \ell, r) \omega_{\text{op}} R(k_o \ell, r) dr . \end{aligned} \quad (1.25)$$

We have seen that the lowest order contributions to  $\langle k_o | \omega_{\text{op}} | k_o \rangle$  come from second order terms. A point to note is that this means that the zero order results for the phase shifts,  $\delta_o(k_o, \ell)$ , are themselves quite accurate. There are four second order terms and the

corresponding diagrams are shown in Figure 1.2. These diagrams represent correlations between an incoming electron in state  $\phi_{k_0}$  and atomic electrons in states  $\phi_m$  and  $\phi_n$ . The first of these diagrams, Figure 1.2a is a simple extension of Figure 1.1a and represents direct scattering by an atomic electron in state  $\phi_n$ . At the first interaction the incident electron in state  $\phi_{k_0}$  is scattered in state  $k'$  while the atomic electron is excited into state  $k''$ . At some later time the two electrons interact again and return to their initial states. Figure 1.2b represents exchange scattering in which the incident electron and one of the atomic electrons exchange places. The remaining two diagrams, Figures 1.2c and 1.2d, are exclusion-principle-violating (EPV) diagrams which arise from the linked-cluster factorisation. In each of these, at a time between the two interactions there are two electrons in the state  $\phi_{k_0}$ . This is a violation of the Pauli Exclusion Principle which states that no two electrons can occupy the same state simultaneously. However, Goldstone (1957) stresses that in order for the Factorisation Theorem to hold, all diagrams must be included whether or not they violate the Exclusion Principle. These EPV diagrams were omitted in the calculations of Pu and Chang (1966) but should be considered in any problem with two or more atomic electrons.

Using equations (1.19) and 1.25) we can write down the contributions of each of the diagrams of Figure 1.2 to the second order correction to the zero order phase shift. From Figure 1.2a we have

$$\Delta\delta_{(a)}(k_0, l) = -\frac{2}{k_0} \langle \phi_0^{(N)} | \eta_{k_0} \cdot \frac{v}{E_0 - H_0} \Sigma | n k'' l'' k' l' \rangle \times$$

$$\langle n k'' l'' k' l' | v | \eta_{k_0} * \phi_0^{(N)} \rangle$$

where the summation is over all states  $|n k'' \ell'' k' \ell'\rangle$  of the system, excluding the groundstate. We can replace the summation by an integration by means of equation (1.24) and thus we obtain

$$\Delta\delta_{(a)}(k_o, \ell) = -\frac{4}{k_o} \left(\frac{2}{\pi}\right)^2 \sum_{n=1}^N \int_0^\infty dk' \int_0^\infty dk'' \frac{|\langle k_o n | v | k' k'' \rangle|^2}{2\varepsilon_n + k_o^2 - k'^2 - k''^2} \quad (1.26)$$

where only unexcited states are included in the summation over  $n$  and where we have suppressed angular momentum indices. Similarly, the contributions from Figures 1.2b, 1.2c and 1.2d are as follows:

$$\Delta\delta_{(b)}(k_o, \ell) = +\frac{4}{k_o} \left(\frac{2}{\pi}\right)^2 \sum_{n=1}^N \int_0^\infty dk' \int_0^\infty dk'' \delta(m_{s_n}, m_{s_{k_o}}) \frac{\langle k_o n | v | k' k'' \rangle \langle k'' k' | v | k_o n \rangle}{2\varepsilon_n + k_o^2 - k'^2 - k''^2} \quad (1.27)$$

$$\Delta\delta_{(c)}(k_o, \ell) = \frac{4}{k_o} \left(\frac{2}{\pi}\right)^2 \int_0^\infty dk' \sum_{m,n} \delta(m_{s_n}, m_{s_{k_o}}) \frac{|\langle mn | v | k_o k' \rangle|^2}{\varepsilon_m + \varepsilon_n - k_o^2 - k'^2} \quad (1.28)$$

$$\Delta\delta_{(d)}(k_o, \ell) = -\frac{4}{k_o} \left(\frac{2}{\pi}\right)^2 \int_0^\infty dk' \sum_{m,n} \delta(m_{s_n}, m_{s_m}) \frac{\langle mn | v | k_o k' \rangle \langle k' k_o | v | mn \rangle}{\varepsilon_m + \varepsilon_n - k_o^2 - k'^2} \quad (1.29)$$

The summations over  $m$  and  $n$  include only unexcited states. Also, in equations (1.26) - (1.29) the angular momentum of the  $k_o$ ,  $k'$  and  $k''$  states have been suppressed; we still have summations over  $\ell'$ ,  $\ell''$ ,  $m'$  and  $m''$ .

For the helium atom the states  $m$  and  $n$  are both  $1s$  states. Both orbitals contribute to the direct part (1.26), whilst only the electron with the same spin as the incident electron contributes to the exchange term (1.27) and the EPV direct term (1.28). There is no contribution from



the EPV exchange term (1.29) since the two atomic electrons necessarily have opposite spins.

CHAPTER II

THE EVALUATION OF THE SECOND ORDER PHASE SHIFTS

In this chapter we give details as to how the radial wavefunctions, and hence the zero-order phase shifts were evaluated. Also, the matrix elements needed in the expressions for the second-order corrections to the phase shifts, equations (1.26) to (1.29) are examined, and the expressions themselves are written in a form suitable for computation.

2.1. The radial wavefunctions and the zero order phase shifts

In this calculation the ground state helium wavefunction was assumed to have the Clementi (1965) analytic form.

The continuum states satisfy the integro-differential equation (1.21) where as in equation (1.22)

$$\begin{aligned} \phi_k &= \phi(k, \ell, m, m_s) = \frac{R(k, \ell, r)}{r} Y_{\ell m}(\theta, \phi) X_s(m_s) \\ &\equiv P(k, \ell, r) Y_{\ell m}(\theta, \phi) X_s(m_s) . \end{aligned}$$

The angular integrations involved in equation (1.21) were carried out by using the usual expansion for  $\frac{1}{|r_1 - r_2|}$ , namely,

$$\frac{1}{|r_1 - r_2|} = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi}{2\lambda+1} \gamma_{\lambda}(r_1, r_2) Y_{\lambda\mu}(\hat{r}_1) Y_{\lambda\mu}^*(\hat{r}_2) \quad (2.1)$$

where the  $Y_{\lambda\mu}$  are spherical harmonics and  $\gamma_{\lambda}(r_1, r_2) = r_{<}^{\lambda} / r_{>}^{\lambda+1}$ , with  $r_{<}$  being the minimum and  $r_{>}$  the maximum of  $r_1$  and  $r_2$ . We obtain the radial equation

$$\left[ \frac{d^2}{dr^2} + \frac{2z}{r} + k^2 - \frac{\ell(\ell+1)}{r^2} - 4v(r) \right] P(k\ell, r) \quad (2.2)$$

$$= - \frac{2}{2\ell+1} \int_0^\infty P(1s, r') P(k\ell, r') \gamma_\ell(r, r') dr' P(1s, r)$$

where

$$v(r) = \int \frac{\phi_{1s}^*(r') \phi_{1s}(r') dr'}{|r - r'|} = \int_0^\infty \frac{P(1s, r') dr'}{r >}$$

We now follow a method proposed by Percival and used by Marriott (1958) to solve equation (2.2).

We write  $L_\ell = \frac{d^2}{dr^2} + \frac{2z}{r} + k^2 - \frac{\ell(\ell+1)}{r^2} - 4v(r)$ , then we have

$$L_\ell P(k\ell, r) = - \frac{2}{2\ell+1} P(1s, r) \quad (2.3)$$

$$\frac{1}{r^{\ell+1}} \int_0^r s^\ell P(1s, s) P(k\ell, s) ds + r^\ell \int_r^\infty \frac{1}{s^{\ell+1}} P(1s, s) P(k\ell, s) ds$$

$$= g(P, r) \alpha(r) - h(P, r) \beta(r) + \beta(r) h(P, \infty)$$

where

$$g(P, r) = \int_0^r P(1s, s) P(k\ell, s) s^\ell ds \quad (2.4)$$

$$h(P, r) = \int_0^r \frac{P(1s, s) P(k\ell, s) ds}{s^{\ell+1}},$$

$$\alpha(r) = - \frac{2 P(1s, r)}{(2\ell+1)r^{\ell+1}} \quad \text{and} \quad \beta(r) = - \frac{2r^\ell P(1s, r)}{2\ell+1}$$

This equation can be reduced to two simpler equations by letting  $P(k\ell, r) = U(k\ell, r) + \gamma V(k\ell, r)$ , for a constant  $\gamma$ . We then obtain

$$L_{\ell}U = g(U, r)\alpha(r) - h(U, r)\beta(r)$$

and 
$$L_{\ell}V = g(V, r)\alpha(r) - h(V, r)\beta(r) + \beta(r)$$

with 
$$\gamma = \frac{h(U, \infty)}{1-h(V, \infty)}$$

These equations were solved by a non-iterative procedure, using a Newton-Cotes open 5-point form for the integrals for  $g$  and  $h$  and a Numerov method for the functions  $U$  and  $V$ . The cycle was started by assuming power series expansions for the first three values of each of the functions  $g$ ,  $h$ ,  $U$  and  $V$ . The mesh size for  $r$  was  $0.01 a_0$  and the procedure ceased at  $r = 25 a_0$ , by which point the asymptotic forms had been reached.

The Newton-Cotes routine was checked by putting  $P(l_s, r) = e^{-r}$  and  $U(r) = r^2 \sin kr$ , functions which give analytic results for the  $g(U, r)$  and  $h(U, r)$  integrals. The Numerov routine was checked by putting the differential operator  $L_{\ell}$  equal to  $\frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell+1)}{r^2}$  and the functions  $g$  and  $h$  equal to zero. The equation (2.3) then reduces to the spherical Bessel equation which has tabulated solutions.

The constant  $\gamma$  can now be evaluated easily, and hence the radial function  $P(k\ell, r)$ . The normalisation constant and the zero order phase shifts were extracted by fitting the wavefunction  $P(k\ell, r)$  asymptotically to a linear combination of spherical Bessel and spherical Neumann functions ( $j_{\ell}(kr)$  and  $n_{\ell}(kr)$  respectively). We have

$$P(k\ell, r_1) = A kr_1 [j_{\ell}(kr_1) - \tan \delta_0(k, \ell) n_{\ell}(kr_1)]$$

where  $r_1$  is a point in the asymptotic region. If  $r_2$  is another such point

$$P(k\ell, r_2) = Akr_2 [j_{\ell}(kr_2) - \tan \delta_0(k, \ell) n_{\ell}(kr_2)]$$

Hence, solving these equations for A and  $\tan \delta_o(k, \ell)$ , we obtain

$$A = \frac{P(k\ell, r_i) \sec(\delta_o(k, \ell))}{kr_i [j_\ell(kr_i) - \tan(\delta_o(k, \ell)) \cdot n_\ell(kr_i)]}, \quad i = 1, 2,$$

$$\tan(\delta_o(k, \ell)) = \frac{P(k\ell, r_2) r_1 j_\ell(kr_1) - P(k\ell, r_1) r_2 j_\ell(kr_2)}{P(k\ell, r_2) r_1 n_\ell(kr_1) - P(k\ell, r_1) r_2 n_\ell(kr_2)}.$$

The starting value of  $r_1$  was chosen to be  $20.60 a_o$  and  $r_1$  and  $r_2$  were increased in successive steps of  $0.02 a_o$  until the results for A and  $\delta_o(k, \ell)$  had converged, with an accuracy of  $10^{-8}$ .

## 2.2. The matrix elements $\langle k_o \ell 1s | v | k' \ell' k'' \ell'' \rangle$

These matrix elements occur in the expressions for the second-order corrections to the phase shifts arising from the direct and exchange diagrams, Figures 1.2a and 1.2b. We have

$$\langle k_o \ell 1s | v | k' \ell' k'' \ell'' \rangle = \iint \frac{\phi_{1s_o}^*(\underline{r}_1) \phi_{k_o \ell}^*(\underline{r}_2) \cdot \phi_{k' \ell' m'}(\underline{r}_2) \phi_{k'' \ell'' m''}(\underline{r}_1)}{|\underline{r}_1 - \underline{r}_2|} d\underline{r}_1 d\underline{r}_2$$

Using equation (2.1) and carrying out the angular integration over  $\underline{r}_1$  we obtain

$$\langle k_o \ell 1s | v | k' \ell' k'' \ell'' \rangle = \frac{\sqrt{4\pi}}{2^{\ell''+1}} I_{\ell''}(1s, k_o \ell; k'' \ell'', k' \ell') \cdot \int Y_{\ell_o}^*(\hat{r}_2) Y_{\ell' m'}(\hat{r}_2) Y_{\ell'' m''}(\hat{r}_2) d\hat{r}_2 \quad (2.5)$$

where

$$I_{\ell''}(1s, k_o \ell; k'' \ell'', k' \ell') = \int_0^\infty dr_1 \int_0^\infty dr_2 P(1s, r_1) P(k_o \ell, r_2) P(k' \ell', r_2) \cdot P(k'' \ell'', r_1) \gamma_{\ell''}(r_1, r_2)$$

and where we have assumed without loss of generality that the incident electron has zero magnetic quantum number. The triple spherical harmonic integral can be written in terms of Wigner 3-j coefficients as

$$\int Y_{\ell_1 m_1}(\hat{r}_1) Y_{\ell_2 m_2}(\hat{r}_1) Y_{\ell_3 m_3}(\hat{r}_1) d\hat{r}_1 = \left[ \frac{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)}{4\pi} \right]^{\frac{1}{2}} \cdot \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

and values of these coefficients are tabulated in Edmonds (1957).

Values of the triple integral for selected values of  $\ell$ ,  $\ell'$  and  $\ell''$  are given in Tables 2.1 and 2.2.

We can re-write the function  $I_{\ell''}$  as

$$I_{\ell''}(1s, k_0 \ell; k'' \ell'', k' \ell') = \int_0^{\infty} dr_2 P(k_0 \ell, r_2) P(k' \ell', r_2) f(k'' \ell'', r_2) \quad (2.6)$$

where

$$f(k'' \ell'', r_2) = \frac{1}{r_2^{\ell''+1}} \int_0^{r_2} r_1^{\ell''} P(1s, r_1) P(k'' \ell'', r_1) dr_1 + r_2^{\ell''} \int_{r_2}^{\infty} \frac{P(1s, r_1) P(k'' \ell'', r_1)}{r_1^{\ell''+1}} dr_1 \quad (2.7)$$

Now these integrals are precisely g and h integrals (see equation (2.4))

and so we can write

$$f(k'' \ell'', r_2) = \frac{1}{r_2^{\ell''+1}} g(P, r_2) + r_2^{\ell''} h(P, \infty) - r_2^{\ell''} h(P, r_2)$$

The f functions were therefore evaluated in the same routine as the radial wavefunctions. The integration the right-hand-side of equation (2.6)

was then evaluated by a 475-point Simpson's rule, using mesh sizes of  $0.02 a_0$  for  $r \in [0, 6]$ ,  $0.04 a_0$  for  $r \in (6, 10]$  and  $0.2 a_0$  for  $r \in (10, 25]$ . A mesh of  $0.01 a_0$  throughout was used initially, but it was found that the above scheme whilst reducing the computing time considerably did not lead to any loss of accuracy.

### 2.3. Second order corrections from the direct and exchange diagrams

From equation (1.26) the second order correction to the zero order phase shift from the direct diagram, Figure 1.2a is given by

$$\Delta\delta_{(a)}(k_0, \ell) = -\frac{32}{\pi^2 k_0} \int_0^\infty dk' \int_0^\infty dk'' \frac{A'(k'', k')}{2\epsilon_{1s} + k_0^2 - k'^2 - k''^2} \quad (2.8)$$

where

$$A'(k'', k') = \sum_{\ell', \ell''} \sum_{m', m''} |\langle 1s k_0 \ell | v | k'' \ell'' k' \ell' \rangle|^2,$$

the matrix elements being given by equation (2.5). We consider  $A'(k'', k')$  for incident s-, p- and d-waves, in turn. For the s- and p-wave cases we allow intermediate angular momenta  $\ell', \ell'' = 0, 1, 2, 3$  and for the d-wave also  $\ell', \ell'' = 4$ .

#### (i) s-wave ( $\ell = 0$ )

$$\text{Since } \int Y_{00}^*(\hat{r}_2) Y_{\ell'm'}(\hat{r}_2) Y_{\ell''m''}(\hat{r}_2) d\hat{r}_2 = \frac{(-1)^{m''}}{\sqrt{4\pi}} \delta_{\ell''\ell'} \delta_{m'', -m'}$$

it follows that

$$\begin{aligned}
 A'(k'', k')_{\ell=0} &= \sum_{\ell''=0}^3 \sum_{m''=-\ell''}^{\ell''} \left( \frac{I_{\ell''}(\ell'', \ell')}{2\ell''+1} \right)^2 \\
 &= (I_0(0,0))^2 + \frac{(I_1(1,1))^2}{3} + \frac{(I_2(2,2))^2}{5} + \frac{(I_3(3,3))^2}{7}
 \end{aligned} \tag{2.9}$$

where  $I_{\ell''}(\ell'', \ell') = I_{\ell''}(\ell_s, k_0 \ell; k'' \ell'', k' \ell')$  and is given by equation (2.6).

(ii) p-wave ( $\ell = 1$ )

There are six combinations of allowed values of  $\ell'$  and  $\ell''$  which give non-zero values of the angular integral occurring in equation (2.5). These are shown in Table 2.1; in each case  $m' = -m''$ . It is easily shown that

$$\begin{aligned}
 A'(k'', k')_{\ell=1} &= (I_0(0,1))^2 + \left( \frac{I_1(1,0)}{3} \right)^2 + 2 \left( \frac{I_1(1,2)}{3} \right)^2 \\
 &\quad + 2 \left( \frac{I_2(2,1)}{5} \right)^2 + 3 \left( \frac{I_2(2,3)}{5} \right)^2 + 3 \left( \frac{I_3(3,2)}{7} \right)^2.
 \end{aligned} \tag{2.10}$$

(iii) d-wave ( $\ell = 2$ )

In the case of an incident d-wave electron there are ten combinations of the allowed values of  $\ell'$  and  $\ell''$  which give non-zero values of the triple spherical harmonic integral, and these are shown in Table 2.2; again,  $m' = -m''$ , and it follows that

$$\begin{aligned}
 A'(k'', k')_{\ell=2} &= (I_0(0,2))^2 + \frac{6}{5} \left( \frac{I_1(1,1)}{3} \right)^2 + \frac{9}{5} \left( \frac{I_1(1,3)}{3} \right)^2 \\
 &\quad + \left( \frac{I_2(2,0)}{5} \right)^2 + \frac{10}{7} \left( \frac{I_2(2,2)}{5} \right)^2 + \frac{18}{7} \left( \frac{I_2(2,4)}{5} \right)^2 + \frac{9}{5} \left( \frac{I_3(3,1)}{7} \right)^2 \\
 &\quad + \frac{28}{15} \left( \frac{I_3(3,3)}{7} \right)^2 + \frac{18}{7} \left( \frac{I_4(4,2)}{9} \right)^2 + \frac{180}{77} \left( \frac{I_4(4,4)}{9} \right)^2.
 \end{aligned}$$



The functions  $A'(k'', k')$  were evaluated numerically using the methods of §2.2. The  $k'$  and  $k''$  integrations in equation (2.8) were then carried out using a 42-point Simpson's rule and assuming an upper limit of  $k', k'' = 10$ , since negligible contributions were obtained from the higher  $k', k''$  region. Hence the correction  $\Delta\delta_{(a)}(k_0, \ell)$  to the phase shift was found.

The second order correction to the phase shift due to the exchange diagram, given by equation (1.27) was evaluated similarly.

Table 2.1

Values of  $\sqrt{4\pi} \int Y_{10}^*(\hat{r}) Y_{\ell' m'}(\hat{r}) Y_{\ell'' m''}(\hat{r}) d\hat{r}$

		$\ell' = 0$	$\ell' = 1$	$\ell' = 2$	$\ell' = 3$
$\ell'' = 0$	$m'' = 0$	0	1	0	0
$\ell'' = 1$	$m'' = 0$	1	0	$\sqrt{4/5}$	0
	$m'' = \pm 1$	0	0	$-\sqrt{3/5}$	0
$\ell'' = 2$	$m'' = 0$	0	$\sqrt{4/5}$	0	$\sqrt{27/35}$
	$m'' = \pm 1$	0	$-\sqrt{3/5}$	0	$-\sqrt{24/35}$
	$m'' = \pm 2$	0	0	0	$\sqrt{15/35}$
$\ell'' = 3$	$m'' = 0$	0	0	$\sqrt{27/35}$	0
	$m'' = \pm 1$	0	0	$-\sqrt{24/35}$	0
	$m'' = \pm 2$	0	0	$\sqrt{15/35}$	0
	$m'' = \pm 3$	0	0	0	0

Table 2.2

Values of  $\sqrt{4\pi} \int Y_{20}^*(\hat{r}_2) Y_{\ell'm'}(\hat{r}_2) Y_{\ell''m''}(\hat{r}_2) d\hat{r}_2$

		$\ell'=0$	$\ell'=1$	$\ell'=2$	$\ell'=3$	$\ell'=4$
$\ell''=0$	$m''=0$	0	0	1	0	0
$\ell''=1$	$m''=0$	0	$\sqrt{4/5}$	0	$\sqrt{27/35}$	0
	$m''=\pm 1$	0	$\sqrt{1/5}$	0	$-\sqrt{18/35}$	0
$\ell''=2$	$m''=0$	1	0	$\sqrt{20/49}$	0	$\sqrt{36/49}$
	$m''=\pm 1$	0	0	$-\sqrt{5/49}$	0	$\sqrt{30/49}$
	$m''=\pm 2$	0	0	$\sqrt{20/49}$	0	$\sqrt{15/49}$
$\ell''=3$	$m''=0$	0	$\sqrt{27/35}$	0	$\sqrt{16/45}$	0
	$m''=\pm 1$	0	$-\sqrt{18/35}$	0	$-\sqrt{9/45}$	0
	$m''=\pm 2$	0	0	0	0	0
	$m''=\pm 3$	0	0	0	$\sqrt{25/35}$	0
$\ell''=4$	$m''=0$	0	0	$\sqrt{36/49}$	0	$\sqrt{\frac{2000}{5929}}$
	$m''=\pm 1$	0	0	$\sqrt{30/49}$	0	$\sqrt{\frac{1445}{5929}}$
	$m''=\pm 2$	0	0	$\sqrt{15/49}$	0	$-\sqrt{\frac{320}{5929}}$
	$m''=\pm 3$	0	0	0	0	$\sqrt{5/121}$
	$m''=\pm 4$	0	0	0	0	$\sqrt{80/121}$

#### 2.4. The second order EPV diagram

The contribution to the second order phase shift of the EPV diagram, Figure 1.2c is given, as in equation (1.28) by

$$\Delta\delta_{(c)}(k_o, \ell) = \frac{16}{k_o \pi^2} \int_0^\infty dk' \sum_{\ell', m'} \frac{|\langle 1s \ 1s | v | k_o \ell \ k' \ell' \rangle|^2}{2\epsilon_{1s} - k_o^2 - k'^2} \quad (2.12)$$

$$\begin{aligned} \text{Now } \langle 1s \ 1s | v | k_o \ell \ k' \ell' \rangle &= \iiint d\underline{r}_1 d\underline{r}_2 \phi_{1s o}^*(\underline{r}_1) \phi_{1s o}^*(\underline{r}_2) \\ &\times \frac{1}{|\underline{r}_1 - \underline{r}_2|} \phi_{k_o \ell o}(\underline{r}_1) \phi_{k' \ell' m'}(\underline{r}_2). \end{aligned}$$

Using the expansion for  $\frac{1}{|\underline{r}_1 - \underline{r}_2|}$  given in equation (2.1) and carrying out the angular integrations one obtains

$$\langle 1s \ 1s | v | k_o \ell \ k' \ell' \rangle = I_\ell(1s, 1s; k_o \ell, k' \ell') \frac{\delta_{\ell \ell'} \delta_{m' o}}{2\ell + 1}.$$

That is

$$\Delta\delta_{(c)}(k_o, \ell) = \frac{16}{\pi^2 k_o} \int_0^\infty \frac{dk'}{2\epsilon_{1s} - k_o^2 - k'^2} \left( \frac{I_\ell(1s, 1s; k_o \ell, k' \ell)}{2\ell + 1} \right)^2$$

where  $I_\ell(1s, 1s; k_o \ell, k' \ell) = \int_0^\infty dr P(1s, r) P(k' \ell, r) f(k_o \ell, r)$  with  $f(k_o \ell, r)$  defined by equation (2.7). As before, the integration over  $r$  was carried out by using a 475-point Simpson's rule and the integration over  $k'$  by using a 42-point Simpson's rule.

CHAPTER III

RESULTS OF THE COMPLETE SECOND ORDER OPTICAL  
POTENTIAL CALCULATION

3.1. Other Theoretical Models

Our analysis to this point is identical with that of Pu and Chang (1966) except that

- (i) we include EPV diagrams 1.2c and 1.2d,
- (ii) intermediate angular momenta  $\ell'$ ,  $\ell''=0, 1, 2, 3, 4$  are included, whereas Pu and Chang considered only  $\ell'$ ,  $\ell'' = 0, 1, 2$ ,
- (iii) we evaluate the second order correction to the d-wave phase shift ( $\ell = 2$ ).

In section 3.2 we give our results, which represent a complete second-order calculation, and we compare with the results of four other recent calculations, in addition to that of Pu and Chang. In this section we give a brief summary of each of these four methods.

(a) The Polarised Orbital Method (POM)

The polarised orbital method is discussed in detail by Drachman and Temkin (1971) and so we present only a brief description here. The method attempts to incorporate the essential physics of the problem in the form of the wave function. The scattering problem is divided into two parts to be treated sequentially: the calculation of the distorted target wavefunction and the calculation of the scattering phase shifts.

The wave function for the whole system,  $\psi^{(N+1)}$ , satisfies the Schrödinger equation

$$(H - E)\psi^{(N+1)} = 0 \quad (3.1)$$

where  $H$  is the sum of the Hamiltonian for the atom, the kinetic energy operator for the incident electron and the potential energy  $V_{N+1,A}$  due to the Coulomb interaction of the incident electron with the atomic system. In the POM we use a trial solution of equation (3.1),  $\psi_t^{(N+1)}$ , given by

$$\psi_t^{(N+1)} = A \{ \phi_o^{(N)} + \phi_{p\Omega}^{(N+1)} \phi_{N+1} \} .$$

That is,  $\psi_t^{(N+1)}$  is the antisymmetrized product of  $\phi_{N+1}$ , the electron wavefunction describing the scattering process and

$$\phi_o^{(N+1)} = \phi_o^{(N)} + \phi_{p\Omega}^{(N+1)} ,$$

the distorted (polarised) atomic wavefunction consisting of the ground state atomic wavefunction  $\phi_o^{(N)}$  and a correction factor  $\phi_{p\Omega}^{(N+1)}$  due to the polarisation of the atomic orbitals caused by the presence of the incident electron.

It is assumed that the unperturbed ground state of the atom which is described by a single Slater determinant of one electron wavefunctions is perturbed adiabatically by the incoming electron. Also the perturbation, which is in fact the electrostatic repulsion between the scattering and atomic electrons, is dipole approximated and assumed to be zero when the incident particle is 'inside' the atom. That is

$$V_{N+1,A} \cong \sum_{j=1}^N \frac{2r_j}{r_{N+1}^2} P_1(\cos \theta_{j,N+1}) \epsilon(r_j, r_{N+1})$$

where

$$\begin{aligned} \epsilon(r_j, r_{N+1}) &= 1 & \text{if } r_j < r_{N+1} \\ &= 0 & \text{if } r_j > r_{N+1} \end{aligned}$$

To the first order we can write the distorted atomic wavefunction  $\phi^{(N+1)}$  as

$$\phi^{(N+1)} = \phi_0 + \sum_{j=1}^N \frac{\phi_j'}{r_{N+1}^2}$$

where  $r_{N+1}$  is fixed because of the adiabatic approximation and where

$$\phi_j' = \frac{1}{\sqrt{N!}} \det(\phi_1, \dots, \phi_{j-1}, \phi_j', \phi_{j+1}, \dots, \phi_N)$$

The distorted functions  $\phi_j'$  satisfy a coupled set of integro-differential equations. Temkin (1957) reduces these to an uncoupled set of ordinary differential equations by invoking Sternheimer's approximation, first used by Sternheimer (1954) to calculate polarizabilities of various closed shell ions and atoms. Temkin shows this to be a good approximation in the problem which we are considering. He then obtained the subsidiary equations

$$\phi_{\ell', m'}' = \sum_{\ell, m} \frac{U_{n\ell \rightarrow \ell'}(r)}{r} C_{n\ell \rightarrow \ell'}^{(m \rightarrow m')} Y_{\ell', m'}(\Omega) Y_{\ell m}(\Omega_{N+1}) \chi(\frac{1}{2})$$

where the constants  $C_{n\ell \rightarrow \ell'}^{m \rightarrow m'}$  are given by

$$C_{n\ell \rightarrow \ell'}^{m \rightarrow m'} = (-1)^{m-m'+1} \frac{16\pi(2\ell+1)}{3(2\ell'+1)^{\frac{1}{2}}} (1\ell 00 | \ell' 0) (1\ell m' -m m | \ell' m')$$

The latter two brackets in this expression are Clebsch-Gordon coefficients in the usual notation.) The radial functions  $U_{n\ell \rightarrow \ell'}(r)$  satisfy the equations

$$\left[ -\frac{d^2}{dr^2} + V_{nl \rightarrow l'}(r) \right] U_{nl \rightarrow l'}(r) = r U_{nl}(r)$$

where

$$V_{nl \rightarrow l'}(r) = \frac{1}{U_{nl}(r)} \left\{ \frac{d^2}{dr^2} (U_{nl}(r)) \right\} + \frac{l'(l'+1) - l(l+1)}{r^2}$$

From the properties of the Clebsch-Gordon coefficient  $(1\ell 00 | \ell' 0)$  it follows that  $l' = l + 1$ .

Thus we see that each determinant in the original wavefunction is replaced by a sum of determinants in which each orbital is replaced by a subsum over all its polarised orbitals.

The equation of motion of the scattering electron's wavefunction  $\phi_{\underline{N+1}}(r)$  is obtained by projecting onto equation (3.1) by the unperturbed atomic wavefunction  $\phi_0^{(N)}$  and integrating over the coordinates:

$$\int_{\underline{1}}^{d\underline{r}} - \int_{\underline{N}}^{d\underline{r}} \phi_0^{*(N)} (H - E) \psi_t^{(N+1)} = 0$$

In this equation there are four terms in the effective potential. They are the static, static-exchange, polarization and polarization-exchange potentials, and all must be included in a full polarised orbital calculation. The scattering phase shifts are then found from the wave function of the scattered electron.

The POM method as outlined above is applied in a straightforward manner to electron-helium scattering by Duxler et al. (1971). The radial wavefunction for the scattered electron satisfies a rather lengthy equation involving all the various potentials and the function  $U_{1s \rightarrow p}(r)$ . This dipole distortion function,  $U_{1s \rightarrow p}(r)$ , satisfies the Sternheimer equation

$$\left(-\frac{d^2}{dr^2} + \frac{U_{1s}''(r)}{U_{1s}(r)} + \frac{2}{r^2}\right) U_{1s-p}(r) = rU_{1s}(r),$$

and the 1s radial function,  $U_{1s}$ , is taken to be the Hartree-Fock helium wavefunction of Roothaan Sachs and Weiss (1960).

Duxler et al. carry out a full polarised orbital method calculation, making no deletions in either the equation satisfied by the radial wavefunctions for the scattered electron or in equation (3.2).

(b) A Green's Function Method

Yarlagadda et al. (1973) apply the generalised random-phase approximation (GRPA) suggested by Schneider et al. (1970) to the scattering and bound-state properties of the helium atom.

In the case of scattering of a slow electron from an atom exchange and distortion effects play important roles, the distortions being due basically to the polarisation of the atomic charge cloud by the incident electron. One can think of the incident electron as moving in the potential of the polarised target, and as a result of this motion the target electrons are perturbed. Thus the external electron probes the interaction between target electrons as well as reacting to the distortions of the target density due to its own presence. In the GRPA there are two basic equations; the first is the equation for the linear response function of the target, which represents the distortion of the atomic charge cloud by the moving incident electron. The second is the equation for the one-particle Green's function. This second equation depends upon a knowledge of the linear response function which appears in the optical potential that governs the equation of motion for the Green's function. This optical potential, which is the true non-local energy-dependent potential seen by a particle moving in the field of the ground-state target is in fact identical



with the optical potential occurring in the Brueckner-Goldstone theory of Chapter I.

Only a very brief summary of the work of Yarlagadda et al. is given, since the derivations of the equations are unnecessary here. The Green's function in the notation of the GRPA is written as

$$G(\underline{r}_1, \underline{r}', z) = \sum_{\alpha=1}^N \frac{\phi_{\alpha}(\underline{r}_1)\phi_{\alpha}^*(\underline{r}')}{z-E_{\alpha}-i\epsilon} + \sum_j \frac{\phi_j(\underline{r}_1)\phi_j^*(\underline{r}')}{z-E_j+i\epsilon} \quad (3.3)$$

where  $E_j$  is the orbital energy of the electron ion state  $\phi_j$ . The  $\phi_{\alpha}$  and  $\phi_j$  are the Dyson amplitudes,  $\alpha$  being an occupied orbital and  $j$  being an unoccupied orbital, and they satisfy the Dyson equation

$$h_1(\underline{r}_1)\phi_n(\underline{r}_1) + \int d\underline{r}_1' \Sigma(\underline{r}_1, \underline{r}_1', E_n)\phi_n(\underline{r}_1') = E_n\phi_n(\underline{r}_1) \quad (3.4)$$

where  $h_1$  is the kinetic energy plus the nuclear attraction and  $\Sigma$  is the optical potential (c.f. equation (1.18)).  $\Sigma$  is expanded as

$$\Sigma(\underline{r}, \underline{r}_1', z) = \Sigma_{\text{HF}}(\underline{r}_1, \underline{r}_1') + \Sigma^{\leftarrow}(\underline{r}_1, \underline{r}_1', z) + \Sigma^{\rightarrow}(\underline{r}_1, \underline{r}_1', z) \quad (3.5)$$

The first order term in the optical potential,  $\Sigma_{\text{HF}}$ , is precisely the Hartree-Fock potential which we have called the zero-order term. The second order terms,  $\Sigma^{\leftarrow}$  and  $\Sigma^{\rightarrow}$  correspond to the two parts of the Green's function of equation (3.3) and are equivalent to the second order optical potential in our work in a first iteration of this method with the  $\phi_{\alpha}$ ,  $\phi_j$  taken to be Hartree-Fock orbitals. They involve the Bethe-Salpeter amplitudes,  $X^n$ , given by

$$X^n(\underline{r}_1, \underline{r}_1') = \sum_{a,c} X_{ac}^n \phi_a^*(\underline{r}_1) \phi_c(\underline{r}_1')$$

where the coefficients  $X_{ac}^n$  satisfy

$$(E_c - E_a - W_n) X_{ac}^n = (N_c - N_a) \sum_{b,d} (V_{ac}^{db} - V_{dc}^{ab}) X_{bd}^n \quad (3.6)$$

where  $N_a = 1$  if  $a \in G^c$  and 0 otherwise. Also

$$V_{ac}^{db} = \langle ad | \frac{1}{r_{12}} | cb \rangle$$

where  $a, b, c$  and  $d$  represent both occupied and unoccupied orbitals and  $W_n$  is the excitation energy from the ground state to excited states of the system.

The linear response function is given by

$$R(\underline{r}_1 \underline{r}_2 \underline{r}_1' \underline{r}_2', z) = \sum_n \frac{\text{sign}(W_n) X^n(\underline{r}_1 \underline{r}_1') X^{n*}(\underline{r}_2 \underline{r}_2')}{W_n - z - i\epsilon \text{sign}(W_n)}$$

The procedure for extracting the phase shifts is to solve the Hartree-Fock equation for helium to obtain a basis set of orbitals which then give the Hartree-Fock Green's function. Secondly, this Green's function is used to solve the RPA eigenvalue equation (3.6). The eigenvalues are the excitation energies of helium. The eigenvalues and eigenfunctions are then used to construct the optical potential of equation (3.5). Finally the Dyson equation (3.4) is solved to give the partial wave phase shifts.

Although this work seems on the surface to be very different from ours we can see that it is in fact a parallel method to our second order calculation and we could expect comparable results. The main interest in the paper of Yarlagadda et al. is however to demonstrate the way in which many scattering and bound-state properties can be calculated simultaneously, using the Green's function technique. For this reason they have decided to work with a limited basis set of thirty-six orbitals (12s-type, 12 p-type

and 12 d-type), thus keeping the computation at a low level. We include also f orbitals (and in the case of the d wave, g orbitals) and we show that they give significant contributions to the phase shifts. We also include more orbitals of each  $\ell$  value.

(c) A variational Method

Sinfailam and Nesbet (1972) have made calculations on the elastic scattering of slow electrons by helium using a variational procedure.

Consider first the general case of the scattering of an electron by an N-electron atom. A complete orthonormal set of one electron orbitals is assumed, of which the first N, denoted by  $\phi_i$  ( $i = 1, \dots, N$ ) are occupied in  $\phi_0$ , the Slater determinant which is the ground state of the atom. A total trial wave function describing the system can be written in the form

$$\Psi = \sum_p A_p \theta_p \psi_p + \sum_{\mu} \phi_{\mu} c_{\mu} \quad (3.7)$$

where  $\theta_p$  is a normalised N-electron wavefunction for the target atom which can be expressed as

$$\theta_p = \sum_{\sigma} \phi_{\sigma} c_{\sigma}^p \quad (3.8)$$

where each  $\phi_{\sigma}$  is a normalised N-electron Slater determinant constructed from the orbital functions  $\phi_j$ . The coefficients  $c_{\sigma}^p$  are elements of an eigenvector of the N-electron configuration interaction matrix  $H_{\sigma\sigma}$ , corresponding to the energy eigenvalue  $E_p$ .

$\psi_p$  is the one electron wave function for an open channel with angular momentum  $\ell_p$  and kinetic energy  $\frac{1}{2}k_p^2$  a.u.. It is of the form

$$\psi_p = f_p(r) Y_{\ell_p m_{\ell_p}}(\theta, \phi) X(m_{s_p})$$

where  $f_p$  satisfies the usual boundary condition at  $r = 0$ , is orthogonal to all radial functions for the orbitals  $\phi_j$  having the same angular and spin quantum numbers, and has the asymptotic form

$$f_p(r) \sim k_p^{-\frac{1}{2}} r^{-1} \sin(k_p r - \frac{1}{2} \ell_p \pi + \delta_p) .$$

That is

$$f_p(r) = \alpha_{op} S_p + \alpha_{lp} C_p \tag{3.9}$$

where

$$S_p \sim k_p^{-\frac{1}{2}} r^{-1} \sin(k_p r - \frac{1}{2} \ell_p \pi)$$

$$C_p \sim k_p^{-\frac{1}{2}} r^{-1} \cos(k_p r - \frac{1}{2} \ell_p \pi) .$$

The operator  $A$  occurring in equation (3.7) antisymmetrizes  $\theta_p \psi_p$  and includes the factor  $(N+1)^{-\frac{1}{2}}$  which is required to give this function the same relative normalization as an  $(N+1)$ -electron Slater determinant.

The  $\phi_\mu$  appearing in the last term of equation (3.7) is one of an assumed orthonormal set of  $(N+1)$  particle Slater determinants. This basic set of determinants is defined in terms of virtual excitations of the ground state  $\phi_0$ , in which orbitals  $\phi_a$  ( $a > N$ ) replace the occupied orbitals of  $\phi_0$ .

The basis functions are exemplified by

$$\begin{aligned} \phi^a &= \det\{\phi_1(1) - \phi_i(i) - \phi_j(j) - \phi_N(N) \phi_a(N+1)\} \\ \psi_i^{ab} &= \det\{\phi_1(1) - \phi_a(i) - \phi_j(j) - \phi_N(N) \phi_b(N+1)\} \\ \phi_{cj}^{abc} &= \det\{\phi_1(1) - \phi_a(i) - \phi_b(j) - \phi_N(N) \phi_c(N+1)\} \end{aligned} \tag{3.10}$$

Using equations (3.8) and (3.9) and noting that the Schrödinger equation is linear we can express equation (3.7) in the form

$$\Psi = \sum_{I=0,1} \sum_p \alpha_{Ip} \left( \sum_{\rho} \phi_{\rho}^{Ip} c_{\rho}^p + \sum_{\mu} \phi_{\mu} c_{\mu}^{Ip} \right) \quad (3.11)$$

The coefficients  $c_{\mu}$  of equation (3.7), which are to be determined by the variational calculation, have been expanded as

$$c_{\mu} = \sum_p \left( \alpha_{op} c_{\mu}^{op} + \alpha_{lp} c_{\mu}^{lp} \right),$$

and the  $(N+1)$ -electron Slater determinants  $\phi_{\rho}^{Ip}$  are defined by

$$\phi_{\sigma}^{op} = A \phi_{\sigma} S_p, \quad \phi_{\sigma}^{lp} = A \phi_{\sigma} c_p.$$

With these definitions, Sinfailam and Nesbet proceed to use a modified version of the multichannel Kohn variational method, which is described in detail by Nesbet and Oberoi (1972), and calculate the coefficients  $c_{\mu}^{Ip}$  occurring in equation (3.11).

In the case of the d-wave elastic scattering of electrons by helium, basis states of the form (3.10) which include the virtual excitation of one electron from the ground state are used. In addition to the usual channel  $(1s)^2 \tilde{d}$ , where  $\tilde{d}$  denotes the continuum function, other channels are included:

$$1s2p \tilde{p}, \quad 1s2p \tilde{f}, \quad 1s \bar{p} \tilde{p}, \quad 1s \bar{p} \tilde{f}, \quad 1s \bar{d} \tilde{s}, \quad \dots \quad \text{etc.},$$

where the bar denotes a pseudostate. In this way polarization and correlation can be taken into account.

There is no rigorous way of choosing the set of basis functions used for the linear expansion of the trial wavefunction; care must be taken that

they form a complete set. Sinfailam and Nesbet (1972) have used one electron orbitals of the form

$$N r^n e^{-\alpha r} Y_{\ell m}(\hat{r})$$

where the values of  $n$  and  $\alpha$  have been chosen in a systematic way to ensure completeness and also to give good convergence of the results for the phase shifts.

#### (d) Phase Shift Analysis of Experimental Data

A detailed description of this method is given in Part II of this thesis. The case of electron-helium scattering is considered in two papers (Bransden and McDowell 1969, McDowell 1971a) but we use the results of a more recent revision using new experimental measurements (Bransden et al. 1973).

#### 3.2. The Results of our Second Order Calculation

We consider each phase shift in turn. We show in Table 3.1 our results for the  $s$  wave ( $\ell = 0$ ) phase shift. We give the zero order result (the central field exchange approximation), the second order correction from the direct and exchange non-EPV diagrams, Figures 1.2a and 1.2b, the EPV correction from Figure 1.2c, and the results of Pu and Chang (1966). The EPV correction is very small, but is numerically greater than the extra contribution from intermediate angular momenta  $\ell'$ ,  $\ell'' = 3$ . For this reason, our results are slightly lower than those of Pu and Chang.

Table 3.1. s-wave phaseshifts including all second order contributions

$k_o$ (a.u.)	Zero order	Correction from Figs. 1.2a and 1.2b	EPV contri- bution	Our total	Pu and Chang
0.3	2.7045	0.0343	- 0.0049	2.7339	2.7391
0.6	2.3111	0.0450	- 0.0081	2.3480	2.3555
1.0	1.8900	0.0520	- 0.0090	1.9330	1.9412

In Table 3.2 we compare our results with those of the full polarised orbital treatment of Duxler et al. (1971), the Green's function method of Yarlagadda et al. (1973) and the variational calculation of Sinfailam and Nesbet (1972).

Table 3.2. Comparison of s-wave phase shifts of various theoretical models

$k_o$ (a.u.)	This work	Duxler et al.	Yarlagadda et al.	Sinfailam and Nesbet
0.3	2.7339	2.7546	-	2.7459
0.6	2.3480	2.3719	-	2.3638
1.0	1.9330	1.9530	1.9372	1.9550

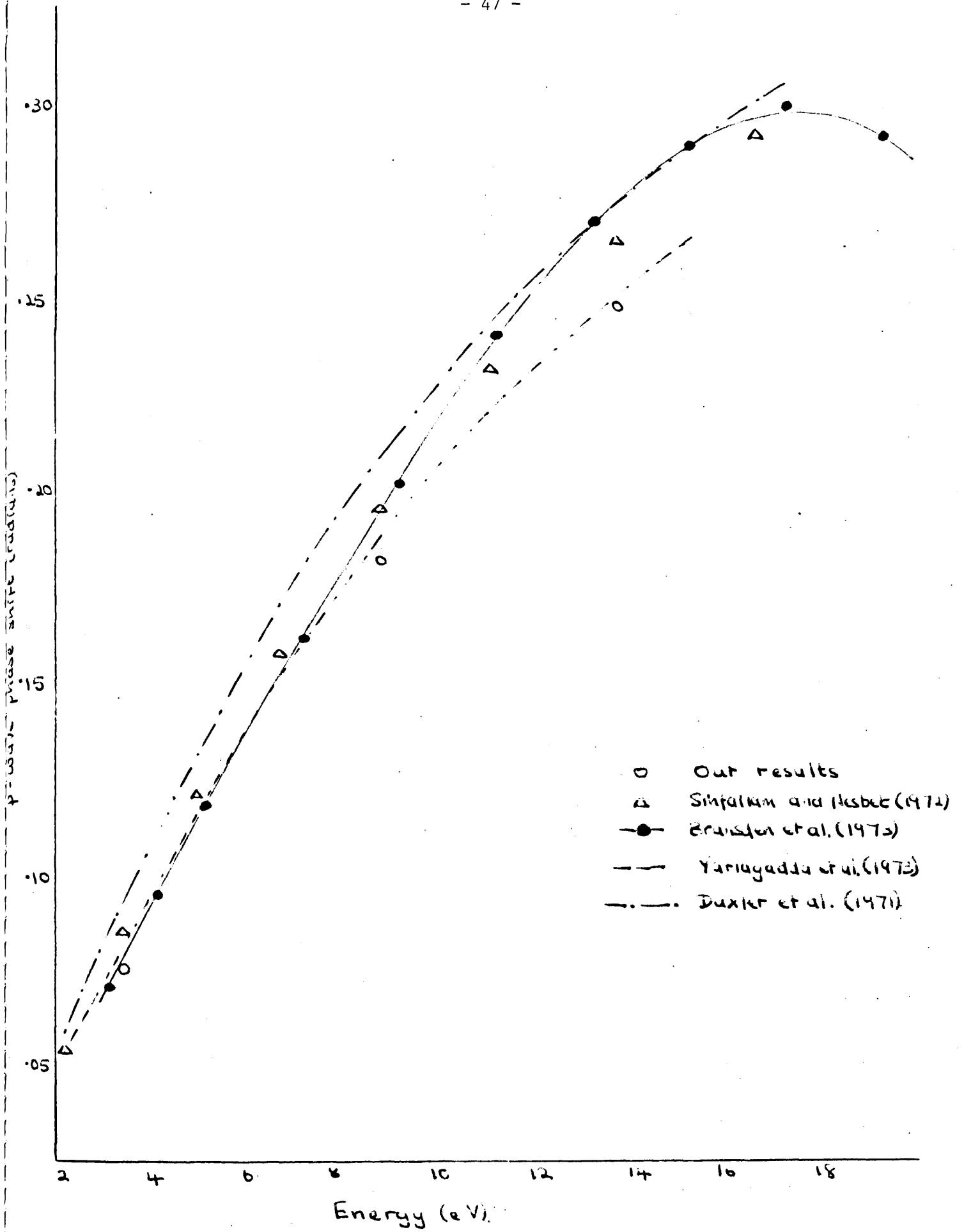


Figure 3.2 p-wave phase shifts from various theoretical models.



In Figure 3.1 we give a visual comparison of the results, including also the phase shift analysis results of Bransden et al. (1973). Our results are in very good agreement with those of Yarlagadda et al., as we would expect since the two calculations are exactly parallel for the s-wave; the extra contribution we have included from intermediate f-waves ( $\ell'' = 3, \ell' = 3$ ) is negligible. The results of Duxler et al. and of Sinfailam and Nesbet lie close to each other and just above ours, and all are lower than the results of the phase shift analysis calculation.

Our p-wave ( $\ell = 1$ ) results are given in Table 3.3. We give also the non-exchange central field approximation results and the Born approximation results using (a) the Hartree-Fock central potential and (b) a polarisation potential of the simple form

$$V(r) = -\frac{\alpha}{r^4} \quad (\text{Ryd}) \quad (3.12)$$

for which the Born phase shift is given analytically by

$$\eta_{\ell}(k^2) = \frac{\pi\alpha k^2}{(2\ell-1)(2\ell+1)(2\ell+3)}, \quad \ell \neq 0 \quad (3.13)$$

The polarisability  $\alpha$  is taken to be  $1.385 a_0^3$ , the value given by Dalgarno and Kingston (1960). For a potential  $U(r)$  the Born phase shift,  $\eta_{\ell}$ , is given by

$$\tan \eta_{\ell}(k^2) = -k \int_0^{\infty} U(r) r^2 j_{\ell}(kr)^2 dr$$

where  $j_{\ell}(kr)$  is the spherical Bessel function of order  $\ell$ . The integral, with  $U(r)$  as the Hartree-Fock potential, was evaluated numerically using a 2500-point Simpson's rule, with a mesh size of  $0.01 a_0$ . The routine was checked by taking  $U(r)$  to be the polarisation potential of equation

(3.12) and comparing the computed results with those obtained analytically from equation (3.13).

Table 3.3 shows that there is reasonable agreement between the Born phases for the Hartree-Fock potential and those obtained from equation (1.21) neglecting exchange. This indicates that our phase shift extraction routine is satisfactory. As expected, exchange is very important, increasing the zero order phase shift by a factor of between three and four in this energy range. To second order the effects of polarisation are represented by diagram 1.2a and of exchange polarisation by 1.2b. These are significant and give a further large increase in the p-wave phase shift at low energies. Again the EPV diagrams give a small (<1%) correction in this order. Our trial results are once more in close agreement with those of Pu and Chang, and also depart very little from the Born results with potential (3.12).

Table 3.3. p-wave phase shifts, including a comparison of the relative importance of exchange and polarisation

$k_0$ (a.u.)	Zero order no ex- change	1st Born with Hartree- Fock potential	1st Born with polaris- ation potential	Zero order with exchange	Our total (no EPV)	Our total + EPV	Pu and Chang
0.5	0.0103	0.0091	0.0725	0.0423	0.0757	0.0750	0.0732
0.8	0.0360	0.0311	0.1856	0.1244	0.1830	0.1810	0.1778
1.0	0.0606	0.0517	0.2901	0.1830	0.2505	0.2477	0.2749

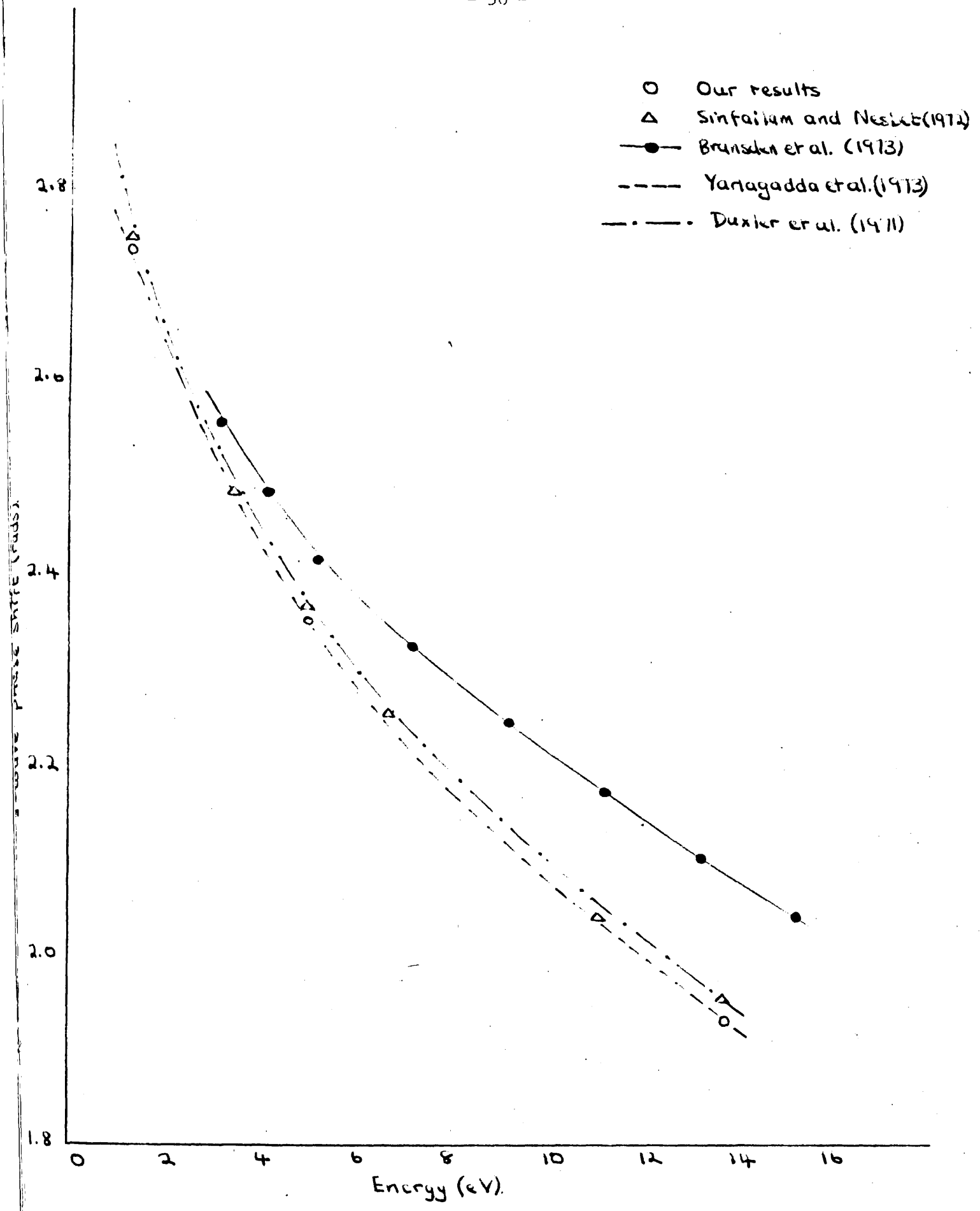


Figure 3.1 s wave phase shifts from various theoretical models.

Table 3.4. Comparison of p-wave phase shifts with those of other theoretical models

$k_0$ (a.u.)	This work	Duxler et al.	Yarlagadda et al.	Sinfailam and Nesbet
0.5	0.0750	0.0926	0.0806	0.0847
0.8	0.1810	-	0.2081	0.1947
1.0	0.2477	0.2749	0.2510	0.2646

Table 3.4 compares our p-wave phase shifts with those of other theoretical models, and Figure 3.2 gives a visual comparison. Again there is close agreement between our results and those of Yarlagadda et al. The variational calculations of Sinfailam and Nesbet lie intermediate between these results and the polarised orbital results of Duxler et al.

The main interest of our second order work was in obtaining values of the d-wave phase shift, since the POM results of Duxler et al. (1971) disagree strongly with those obtained from a phase shift analysis of experimental data (Bransden et al. 1973). Our results (Table 3.5 below) follow the same pattern as for the p-wave and again agree reasonably with those obtained in the Born approximation with the potential given in equation (3.12). The EPV contributions are small, but both exchange and polarisation are important. The contribution from intermediate angular momenta  $\ell'' = 1$ ,  $\ell' = 3$  was found to be comparable with that from  $\ell'' = 1$ ,  $\ell' = 1$ , but the additional contributions obtained by allowing  $\ell'$  and  $\ell''$  to take the value four were negligible.

In Table 3.6 we compare our results with other theoretical results, and Figure 3.3 provides a visual comparison.

Table 3.5. d wave phase shifts comparing the relative importance of different second order contributions

$k_o$ (a.u.)	Zero order no exchange	1st. Born with Hartree-Fock potential	1st. Born with polarisation potential	Zero order with exchange	Our total (No EPV)	Our total + EPV
0.5	0.00006	0.00006	0.0104	0.00061	0.00745	0.00745
0.6	0.00043	0.00042	0.0149	0.00176	0.01149	0.01149
0.7	0.00106	0.00103	0.0203	0.00353	0.01600	0.01600
0.8	0.00200	0.00195	0.0265	0.00609	0.02167	0.02166
0.9	0.00333	0.00323	0.0336	0.00939	0.02779	0.02780
1.0	0.00512	0.00485	0.0414	0.01347	0.03519	0.03516
1.1	0.00728	0.00704	0.050	0.01824	0.04256	0.04260

Table 3.6. Comparison of d wave phaseshifts with those of other theoretical models

$k_o$ (a.u.)	This work	Yarlagadda et al.	Duxler et al.	Sinfailam and Nesbet
0.5	0.00745	0.00533	0.0115	0.0097
0.6	0.01149	-	0.0167	0.0141
0.7	0.01600	-	0.0228	0.0197
0.8	0.02166	-	0.0298	0.0258
0.9	0.02779	-	-	0.0322
1.0	0.03516	0.02819	0.0458	0.0393
1.1	0.04256	-	0.0544	0.0473

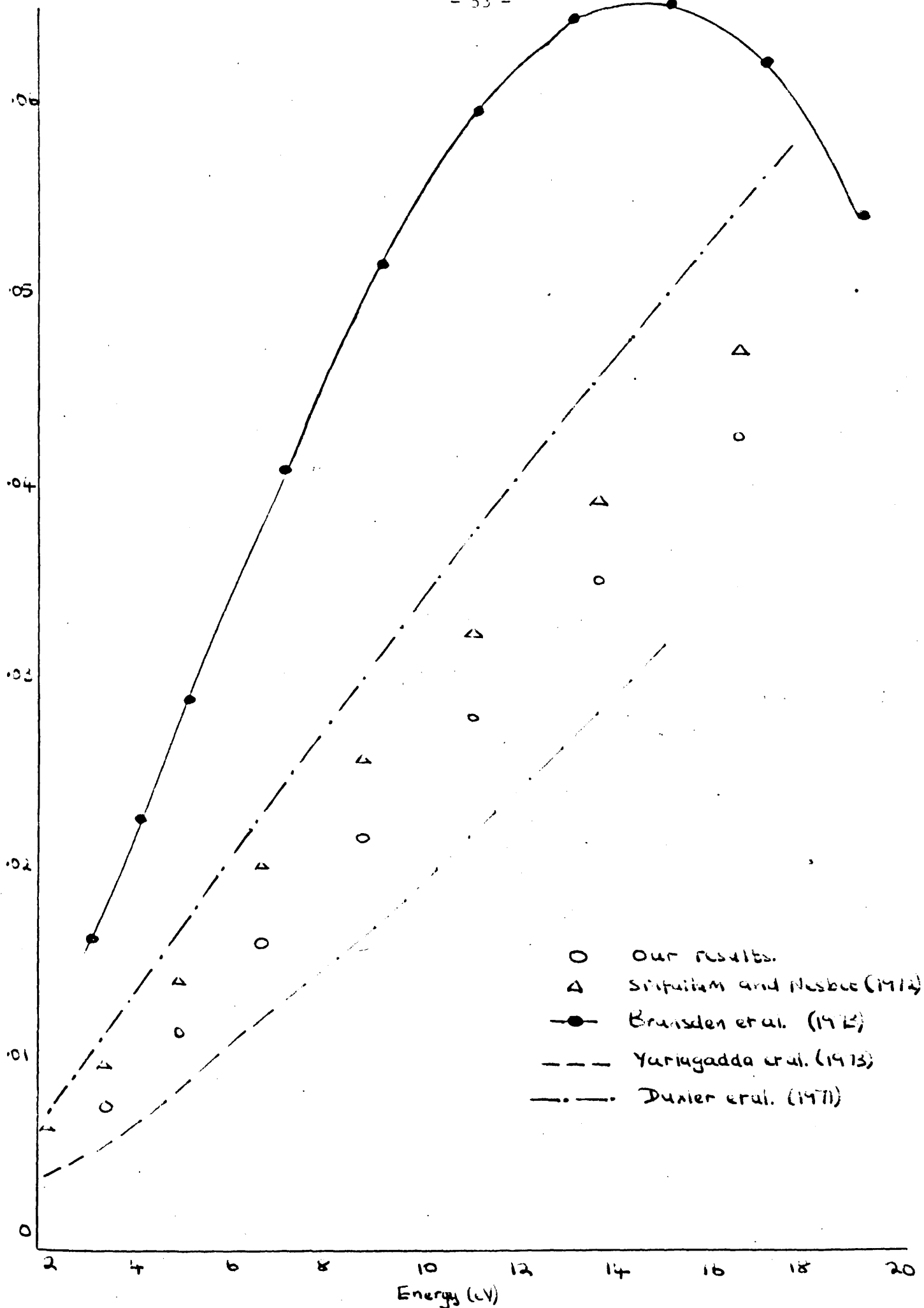


Figure 3.3 d wave phase shifts of various theoretical models.

For the d-wave phase shifts our results differ somewhat from those of the Green's function method of Yarlagadda et al. (1973). This is to be expected as in the latter calculation only s, p and d orbitals are included in the basis set. We have shown that f orbitals give a significant contribution. Our results lie below those of the polarised orbital method of Duxler et al. (1971) and of the variational calculation of Sinfailam and Nesbet (1972), but the results of all the theoretical models are inconsistent with those of the phase shift analysis of experimental data by Bransden et al. (1973). It may well be that the d-wave phase shift is not well determined by the available experimental data. Nevertheless in view of the discord between the theoretical models for the case of d-wave ( $\ell = 2$ ) scattering, and their accord for the  $\ell = 0$  and  $\ell = 1$  cases, it is of interest to attempt to estimate the higher order corrections in our optical potential model.

CHAPTER IV

THE POLARIZABILITY OF HELIUM

From Tables 3.3 and 3.5 we see, choosing  $k_0 = 1.0$  a.u. for convenience, that the polarization correction to the p-wave phase shift (arising from diagrams 1.2a and 1.2b) is approximately 37% of the zero-order exchange result, whereas for the d-wave phase shift it is nearly 250% of the zero-order exchange phase shift. We show below that substantial contributions to the polarizability of helium arise from the third-order bubble diagram, and this suggests that the third order contribution to the phase shift (in particular to the d-wave phase shift) might also be non-negligible. Consequently our p-wave phase shifts may also be uncertain, but by a relatively small amount.

We now give an account of our calculation of the polarizability of helium, using the Brueckner-Goldstone theory, and including all second and third-order terms.

When an atom is placed in the field of an external charge  $Z'$  it is polarised and the resulting distribution of charge can be characterised by a series of induced electric multipole moments, each of which is proportional to  $Z'$ , provided  $Z'$  is small. In particular, the induced dipole moment is related to the electric field of the charge through the atomic dipole polarizability  $\alpha_d$ .

Suppose the unperturbed atom has  $N$  electrons and nuclear charge  $Z$ . The unperturbed Hamiltonian is given by

$$H = - \sum_{i=1}^N \left( \nabla_i^2 + \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}} \quad (4.1)$$

and the corresponding wave function,  $\Psi_0$ , satisfies



$$(\mathbb{H} - E_0') \Psi_0 = 0 \quad , \quad (4.2)$$

$E_0'$  being the energy eigenvalue. The interaction potential between the external charge  $Z'$  located at  $\underline{r}'$  and the atom is given by

$$V_{\text{ext}} = -Z' \sum_{i=1}^N \sum_{k=1}^{\infty} \frac{r_i^k}{r_i'^{k+1}} P_k(\cos \theta_i) \quad (4.3)$$

where the polar axis has been chosen to be in the direction of  $\underline{r}'$  and the constant, spherically symmetric part of  $V_{\text{ext}}$  has been omitted.

$P_k(\cos \theta_i)$  is the Legendre polynomial of order  $k$ . The unperturbed wave function can be written as

$$\Psi = \Psi_0 + Z' \sum_{k=1}^{\infty} \frac{\Psi_1^{(k)}}{r_i'^{k+1}} + O(Z'^2) \quad . \quad (4.4)$$

The dipole polarisability,  $\alpha_d$ , is then given by

$$\alpha_d = 2 \langle \Psi_0 | \sum_{i=1}^N r_i P_1(\cos \theta_i) \Psi_1^{(1)} \rangle / \langle \Psi_0 | \Psi_0 \rangle \quad (4.5)$$

where  $Z'$  is assumed to be small. The wave function  $\Psi_1^{(1)}$  is the function  $\Psi_0$  perturbed once by the term  $U_1$  where

$$U_k = \sum_{i=1}^N r_i^k P_k(\cos \theta_i) \quad , \quad (4.6)$$

that is

$$V_{\text{ext}} = -Z' \sum_{k=1}^{\infty} \frac{U_k}{r_i'^{k+1}} \quad .$$

Since we do not know the function  $\Psi_0$ , we start from the Hartree-Fock wave function,  $\Phi_0$ , and use Brueckner-Goldstone theory to calculate  $\Psi$ . The perturbation to the Hartree-Fock potential  $V^{\text{HF}}$ , defined by equation (1.20), is

$$H' = \sum_{i,j}^N v_{ij} - \sum_{i=1}^N v_i^{HF} - Z \sum_{k=1}^{\infty} \frac{U_k}{r^{k+1}} \quad (4.7)$$

As in Chapter I, we can derive an expansion for the wavefunction  $\Psi$ , namely,

$$\Psi = \Sigma^L \left( \frac{1}{E_0 - H_0} H' \right)^n \phi_0 \quad (4.8)$$

where again,  $\Sigma^L$  indicates that the sum is over linked diagrams only.

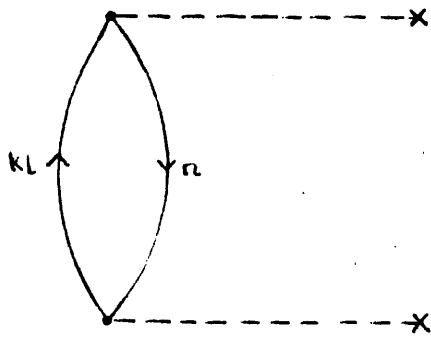
The function  $\psi_0$  is given by the sum of all terms in  $\Psi$  in which there are no interactions involving  $U_k$ . The term  $\psi_1^{(1)}$  is the sum of all terms in  $\Psi$  in which  $-U_1$  acts precisely once,  $Z'/r^2$  being factored out (see equation (4.4)). It should be noted that  $\psi_0$ , obtained from equation (4.8) is not normalised to unity. However, we may factor the disconnected terms in the numerator of equation (4.5) into a product of terms involving  $U_1$  times all other terms. This second factor is  $\langle \psi_0 | \psi_0 \rangle$ , provided the Exclusion Principle is ignored, and it cancels the denominator.

The terms contributing to equation (4.5) can be represented by diagrams, and the second and third-order diagrams are shown in Figure 4.1. In these diagrams the dotted lines represent interactions with the potential  $U_1$ . From equation (4.5) and the definitions of  $\psi_0$  and  $\psi_1^{(1)}$ , we can see that there is only one second-order diagram, and its contribution,  $\alpha_2$ , to the dipole polarizability of helium is given explicitly by

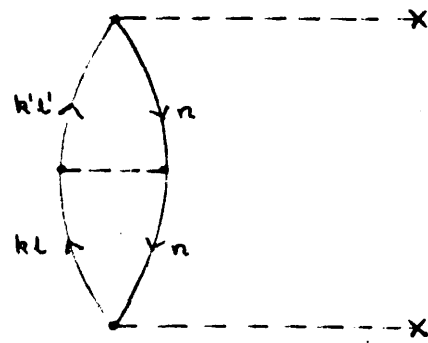
$$\alpha_2 = (-1) \cdot 2 \cdot 2 \langle \phi_0 | U_1 \frac{1}{E_0 - H_0} \Sigma | \rangle \langle | U_1 | \phi_0 \rangle$$

where  $| \rangle$  denotes an excited state of the system. The factor (-1) comes from equation (4.7) and the result is multiplied by 2 because there are two 1s electrons, either of which may be excited. The summation is overall

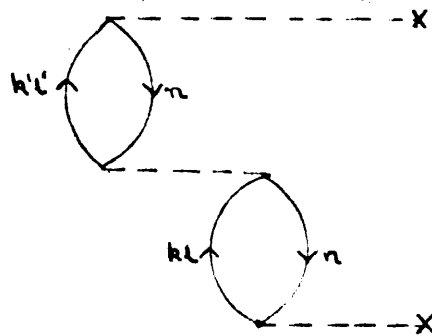
Figure 4.1 Second and third order diagrams which contribute to the polarizability of helium.



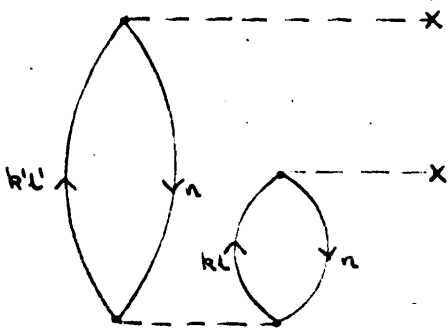
(a).



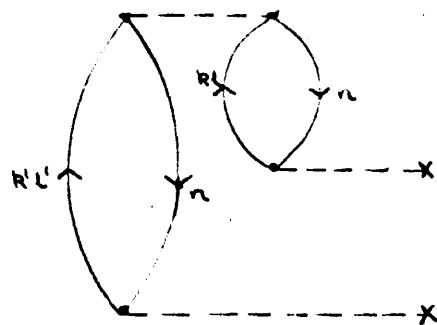
(b).



(c).



(d).



(e).

states of the system excluding the ground state. For helium there are no bound excited states and so as previously, assuming the normalization of the continuum states, as in equation (1.24), we can replace the summation  $\sum_k$  by an integration  $\frac{2}{\pi} \int_0^\infty dk$ . Then

$$\alpha_2 = - \frac{8}{\pi} \int_0^\infty \frac{dk |\langle 1s | r P_1(\cos\theta) | k\ell \rangle|^2}{\epsilon_{1s} - k^2/2} \quad (4.9)$$

where  $\epsilon_{1s}$  is the energy of the ground state,  $1s$ , and where we have substituted for  $U_1$  from equation (4.6).

We next consider the matrix elements,  $U(k)$ , involved in the integrand of equation (4.9),

$$\begin{aligned} U(k) &= \langle 1s | r P_1(\cos\theta) | k\ell \rangle \\ &= \int \phi_{1s0}^*(\underline{r}) r \cos\theta \phi_{k\ell m}(\underline{r}) d\underline{r} \end{aligned}$$

Using the form of  $\phi_{k\ell m}$  given in equation (1.22) we have

$$U(k) = \int_0^\infty \frac{P(1s, r) P(k\ell, r)}{r} dr \int d\hat{r} Y_{00}^*(\hat{r}) Y_{\ell m}(\hat{r}) \cos\theta$$

Now  $\cos\theta = \frac{4\pi}{3} Y_{10}(\hat{r})$  and so the angular part of the integral is  $\frac{1}{3} \delta_{\ell 1} \delta_{m 0}$ . That is, any intermediate state must be a p-state with zero magnetic quantum number ( $\ell = 1$  and  $m = 0$ ). The matrix elements,  $U(k)$ , are therefore given by

$$U(k) = \frac{1}{3} \int_0^\infty \frac{1}{r} P(1s, r) P(kp, r) dr$$

and the polarizability is

$$\alpha_2 = -\frac{8}{\pi} \int_0^{\infty} \frac{dk |U(k)|^2}{\epsilon_{1s} - k^2/2}$$

The integrations over  $r$  and  $k$  in this expression for  $\alpha_2$  were carried out using a Simpson's rule, the first with a mesh of 475 points, the second of 42 points. Each routine was checked by using analytic functions with known integrals.

The second-order contribution to the dipole polarizability of helium was found to be 0.76531, which is 55% of Dalgarno and Kingston's result (1960).

There are four third order contributions to the polarizability (c.f. Chang (1967)) corresponding to the diagrams shown in Figures 4.1, 4.1c, 4.1d and 4.1e. Each involves two interactions with  $U_1$  and one further  $v$  or  $V^{\text{HF}}$  interaction. The  $V^{\text{HF}}$  interactions can be replaced by  $v$  ones, by the definition of the Hartree-Fock potential,  $V^{\text{HF}}$ , equation (1.20). Each of the four diagrams contributes twice, as before, and also there is a double integration over  $k$  and  $k'$ , so that each contribution has an extra external factor of  $-16/\pi^2$ , the minus sign coming from equation (4.7). The contributions are given explicitly by

$$\alpha_{3b} = -\frac{16}{\pi^2} (-1)^3 \int_0^{\infty} dk \int_0^{\infty} dk' \frac{\langle 1s | r \cos \theta | k' \ell' \rangle \langle k' \ell' 1s | v | k \ell 1s \rangle \langle k \ell | r \cos \theta | 1s \rangle}{(\epsilon_{1s} - k'^2/2)(\epsilon_{1s} - k^2/2)}$$

$$\alpha_{3c} = -\frac{16}{\pi^2} (-1)^4 \int_0^{\infty} dk \int_0^{\infty} dk' \frac{\langle 1s | r \cos \theta | k' \ell' \rangle \langle 1s k' \ell' | v | k \ell 1s \rangle \langle k \ell | r \cos \theta | 1s \rangle}{(\epsilon_{1s} - k'^2/2)(\epsilon_{1s} - k^2/2)}$$

$$\alpha_{3d} = \alpha_{3e} = -\frac{16}{\pi^2} (-1)^4 \int_0^{\infty} dk \int_0^{\infty} dk' \frac{\langle 1s 1s | v | k' \ell' k \ell \rangle \langle k \ell | r \cos \theta | 1s \rangle \langle k' \ell' | r \cos \theta | 1s \rangle}{(2\epsilon_{1s} - k'^2/2 - k^2/2)(\epsilon_{1s} - k'^2/2)}$$

The power  $n$  of the additional factor  $(-1)^n$  is the number of closed loops and internal hole lines in each of the diagrams.

Each expression contains a factor  $U(k) U(k')$  and so, the only allowed values of  $l$  and  $l'$  are  $l = 1$ ,  $l' = 1$ , and also  $m = 0 = m'$ . There are two new basic kinds of matrix element,  $\langle k'p \ n | v | k' \ n \rangle$  and  $\langle k'p \ n | v | n \ kp \rangle$ . On carrying out the angular integrations involved in these matrix elements, making use of the expansion for  $\frac{1}{r_1 - r_2}$  given in equation (2.1), we have

$$\langle k'p \ n | v | kp \ n \rangle = \int_0^\infty dr_1 P(k'p, r_1) P(kp, r_1) Q(r_1)$$

where

$$Q(r_1) = \frac{1}{r_1} \int_0^{r_1} P^2(1s, r_2) dr_2 + \int_{r_1}^\infty \frac{1}{r_2} P^2(1s, r_2) dr_2$$

and

$$\langle k'p \ n | v | n \ kp \rangle = \frac{1}{3} \int_0^\infty P(1s, r_1) P(k'p, r_1) f(kp, r_1) dr_1$$

where  $f$  is defined, as in equation (2.7) by

$$f(kp, r_1) = \int_0^\infty dr_2 P(1s, r_2) P(kp, r_2) \frac{r_<}{r_>}$$

with  $r_< = \min(r_1, r_2)$  and  $r_> = \max(r_1, r_2)$ .

A Simpson's rule, with a mesh of 475 points, was used for each of the integrations over  $r_1$  and  $r_2$  and then for the double integration over  $k$  and  $k'$  the mesh was reduced to 42 points.

The contributions  $\alpha_{3b}$ ,  $\alpha_{3c}$  and  $\alpha_{3d}$  were thus evaluated and were 0.2319, -0.0442 and 0.0074 respectively. The polarizability including all second and third order diagrams was found to be  $0.960 a_0^3$ , which is

approximately 70% of the Dalgarno and Kingston (1960) result.

These results differ from those quoted in our paper (Knowles and McDowell 1973) by a factor of three. This is due to the fact that an error was found in our earlier analysis, where we allowed the magnetic quantum numbers  $m$  and  $m'$  to take values other than zero.

It would be straightforward to go onto higher order diagrams, and in particular to sum the infinite series of ladder diagrams, the first two terms of which are Figures 4.1a and 4.1b. But there will be many cancellations and it would be difficult to draw any conclusions from the results. We have shown, however, that the third-order correction to the dipole polarizability of helium is about 25% of the second order term and this suggests that the third order correction to the phase shift might also be non-negligible. This is considered in the next chapter.

CHAPTER V

ESTIMATES OF THE THIRD ORDER CORRECTION  
TO THE PHASE SHIFT

5.1. The distinct diagrams of any order

In this section we give a method of determining all the distinct diagrams of a given order. We apply this in particular to second and third order diagrams, representing them explicitly in algebraic form.

The conditions to be satisfied by a diagram occurring in the  $n$ th order optical potential can be summarised as follows. There must be

- (a)  $n$  horizontal interaction lines, at different levels,
- (b) one incoming line and one outgoing line, each at any level,
- (c) two vertices on any level,
- (d) one line entering and one leaving any vertex.

Consider the first horizontal interaction line as being at level  $A$ , with vertices  $A_1$  and  $A_2$ , the second at level  $B$  with vertices  $B_1$  and  $B_2$ , and so on, and let  $X$  and  $Y$  represent the incoming and outgoing lines respectively. Then the required diagrams of order  $n$  can be written down as permutations of the  $2n+2$  elements  $X, Y, A_1, A_2, B_1, B_2, \dots, N_1, N_2$ . There are several restrictions, however, on the allowed permutations.

(i) Cycles of length one are not allowed, since they correspond to first order diagrams which are cancelled by the choice of the Hartree-Fock potential (see Figure 1.1).

(ii)  $X$  and  $Y$  must occur in the same 'cycle', and this cycle is fixed in that  $X$  must occur at the beginning of it and  $Y$  at the end of it, and there must be at least one other element in between them; that is, the diagrams must be connected ones.



(iii) The elements representing the two vertices on a given level cannot occur next to each other.

(iv)  $A_1$  and  $A_2$  are interchangeable, and similarly  $B_1$  and  $B_2$ , etc. For example, the permutations  $(XA_1 B_1 Y)(A_2 B_2)$ ,  $(XA_1 B_2 Y)(A_2 B_1)$  and  $(XA_2 B_2 Y)(A_1 B_1)$  represent the same diagram.

In the case of second order, we have the six elements  $X$ ,  $Y$ ,  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$  and we obtain four distinct permutations, namely  $(XA_1 B_1 Y)(A_2 B_2)$ ,  $(XA_1 B_1 A_2 B_2 Y)$ ,  $(XB_1 A_1 B_2 A_2 Y)$  and  $(XB_2 A_2 Y)(A_1 B_1)$ . These correspond precisely to the diagrams of Figure 1.2. Clearly we obtain  $1/n$  of the number of diagrams by considering only those permutations in which  $A_1$  follows  $X$  immediately.

In Table 5.1 all the allowed third order permutations are written out. This procedure can easily be applied to higher order diagrams and gives a method of determining all possible distinct diagrams of a given order.

From Table 5.1 we can see that there are exactly eighty-four third order diagrams which contribute to the phase shifts. They can be divided into four groups corresponding to the four second order diagrams shown in Figure 1.2. Clearly it is not feasible to evaluate the contributions from all of these third order diagrams and we choose to consider only those which are simple extensions of the direct scattering diagram, Figure 1.2a. These representative diagrams are shown in Figure 5.1 and estimates of their respective contributions to the phase shifts have been made.

## 5.2. The third order ladder diagram

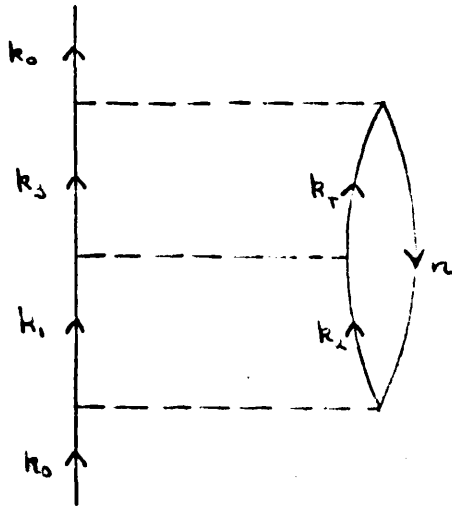
Figure 5.1a is the ladder diagram, the simplest third order extension of the direct scattering diagram, Figure 1.2a, and on physical grounds we

Table 5.1. The permutations representing the third order diagrams

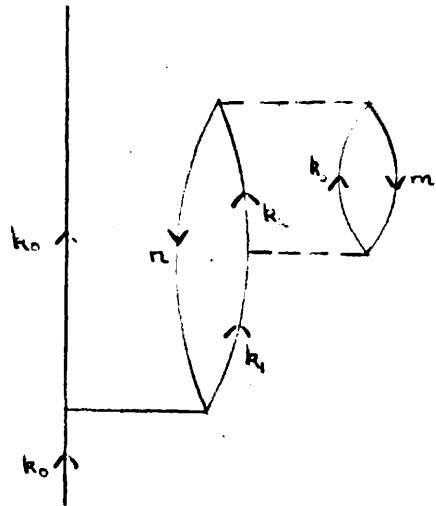
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(XABACECY)	(XBCBACAY)	(XCACBABY)
(XABCABCY)	(XBCABCAY)	(XCABCABY)
(XABCACBY)	(XBCABACY)	(XCABCABY)
(XABCBCAY)	(XBCACBAY)	(XCABACBY)
(XABCBCAY)	(XBCACABY)	(XCABABCY)
(XACABCBY)	(XBABCACY)	(XCBCABAY)
(XACBABCY)	(XBACBCAY)	(XCBACABY)
(XACBACBY)	(XBACBACY)	(XCBACBAY)
(XACBCABY)	(XBACABCY)	(XCBABCAY)
(XACBCBAY)	(XBACACBY)	(XCBABACY)
(XABACY) (BC)	(XBCBAY) (CA)	(XCACBY) (AB)
(XABCAY) (BC)	(XBCABY) (CA)	(XCABCY) (AB)
(XABCBY) (AC)	(XBCACY) (BA)	(XCABAY) (CB)
(XACABY) (BC)	(XBABCY) (CA)	(XCBACAY) (AB)
(XACBAY) (BC)	(XBACBY) (CA)	(XCBACY) (AB)
(XACBCY) (AB)	(XBACAY) (BC)	(XCBABY) (CA)
(XABCY) (ABC)	(XBCAY) (BCA)	(XCABY) (CAB)
(XABCY) (ACB)	(XBCAY) (BAC)	(XCABY) (CBA)
(XACBY) (ABC)	(XBACY) (BCA)	(XCBAY) (CAB)
(XACBY) (ACB)	(XBACY) (BAC)	(XCBAY) (CBA)
(XABY) (ACBC)	(XBCY) (BACA)	(XCAY) (CBAB)
(XACY) (ABCB)	(XBAY) (BCAC)	(XCBY) (CABA)
(XABY) (AC) (BC)	(XBCY) (BA) (CA)	(XCAY) (CB) (AB)
(XACY) (AB) (BC)	(XBAY) (BC) (CA)	(XCBY) (CA) (AB)
(XAY) (ABCBC)	(XBY) (BCACA)	(XCAY) (CABAB)
(XAY) (ACBCB)	(XBY) (BACAC)	(XCAY) (CBABA)
(XAY) (ABC) (BC)	(XBY) (BCA) (CA)	(XCAY) (CAB) (AB)
(XAY) (ACB) (BC)	(XBY) (BAC) (CA)	(XCAY) (CBA) (AB)

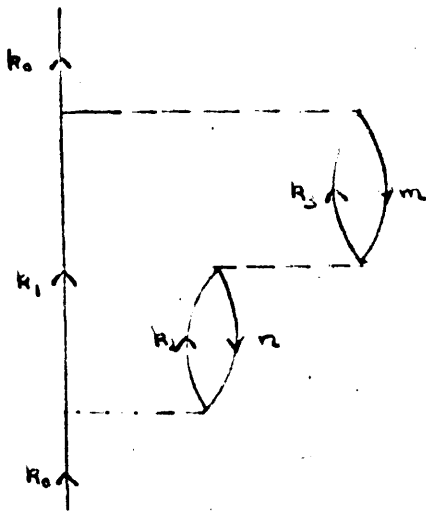
Figure 5.1 Four third order diagrams which are simple extensions of the direct scattering diagram, 1.2a.



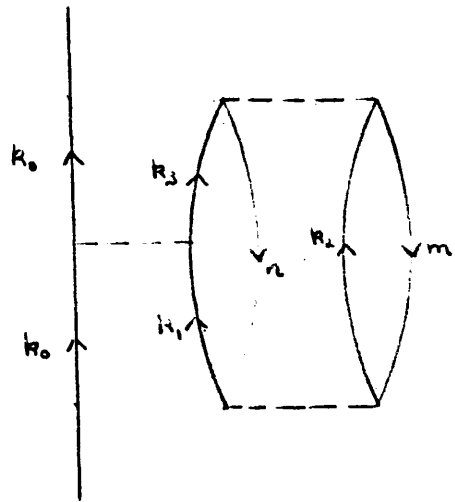
(a).



(b)



(c).



(d)

expect this to give the dominant third order correction to the phase shift. Using equations (1.25) and (1.19) we can write down the contribution, A, of the diagram as

$$A = -\frac{2}{k_0} \langle k_0^{\ell} n | v | \sum_{\underline{k}_3, \underline{k}_4} \frac{\langle k_3^{\ell_3} k_4^{\ell_4} \rangle \langle k_3^{\ell_3} k_4^{\ell_4} | v | \rangle}{D(k_3, k_4)} \sum_{\underline{k}_1, \underline{k}_2} \frac{\langle k_1^{\ell_1} k_2^{\ell_2} \rangle \langle k_1^{\ell_1} k_2^{\ell_2} | v | k_0^{\ell} n \rangle}{D(k_1, k_2)} \rangle \quad (5.1)$$

$$\text{where } D(k_i, k_j) = \epsilon_n + \frac{k_0^2}{2} - \frac{k_i^2}{2} - \frac{k_j^2}{2} \quad (5.2)$$

and each sum is over the complete set of continuum states, the solutions of equation (1.17). The denominator  $D(k_1, k_2)$  is a slowly-varying function of  $k_1, k_2$  in the region of  $\underline{k}_1, \underline{k}_2$ -space where  $\langle k_1^{\ell_1} k_2^{\ell_2} | v | k_0^{\ell} n \rangle$  is large, so that, using the completeness of the states  $\phi_k$  we can approximate by

$$A = -\frac{2}{k_0 D(k_{10}, k_{20})} \left(\frac{2}{\pi}\right)^2 \int_0^\infty dk_3 \int_0^\infty dk_4 \frac{\langle k_0^{\ell} n | v | k_3^{\ell_3} k_4^{\ell_4} \rangle}{D(k_3, k_4)} \times \langle k_3^{\ell_3} k_4^{\ell_4} | v^2 | k_0^{\ell} n \rangle$$

where we have used equation (1.24) to replace the summations over  $\underline{k}_3, \underline{k}_4$  by integrations over  $k_3$  and  $k_4$  and where  $k_{10} = 0.9, k_{20} = 1.1$  when  $k_0 = 1.0$  (see below). This double integral is identical with that of equation (1.26) except that one of the  $v$  matrix elements is replaced by a  $v^2$  matrix element. That is, in one of the radial integrals the usual  $\gamma_\lambda(r_1, r_2)$  function, arising from the expansion for  $|\underline{r}_1 - \underline{r}_2|^{-1}$  (see

equation (2.1)), is replaced by a  $\beta_\lambda(r_1, r_2)$  function, occurring in the expansion for  $|\underline{r}_1 - \underline{r}_2|^{-2}$ . These  $\beta_\lambda(r_1, r_2)$  functions are given explicitly by Sack (1964). The expression for  $\beta_1(r_1, r_2)$  is given in Appendix A; the value  $\lambda = 1$  is the only one we need to use. From equation (2.5) we have

$$\langle k_0 l n | v | k_3 l_3 k_4 l_4 \rangle = \frac{\sqrt{4\pi}}{2l_4+1} I_{l_4}(1s, k_0 l; k_4 l_4, k_3 l_3) \int Y_{l_0}^*(\hat{r}_2) Y_{l_3 m_3}(\hat{r}_2) Y_{l_4 m_4}(\hat{r}_2) d\hat{r}_2 \quad (5.3)$$

where the I integral is defined by

$$I_{l_4}(1s, k_0 l; k_4 l_4, k_3 l_3) = \int_0^\infty dr_1 \int_0^\infty dr_2 P(1s, r_1) P(k_0 l, r_2) P(k_3 l_3, r_2) \times P(k_4 l_4, r_2) \gamma_{l_4}(r_1, r_2) .$$

In a similar manner we can write the  $v^2$  matrix element as

$$\langle k_3 l_3 k_4 l_4 | v^2 | k_0 l n \rangle = \frac{\sqrt{4\pi}}{2l_4+1} J_{l_4}(1s, k_0 l; k_4 l_4, k_3 l_3) \int Y_{l_0}^*(\hat{r}_2) Y_{l_3 m_3}(\hat{r}_2) Y_{l_4 m_4}(\hat{r}_2) d\hat{r}_2$$

where

$$J_{l_4}(1s, k_0 l; k_4 l_4, k_3 l_3) = \int_0^\infty dr_1 \int_0^\infty dr_2 P(k_0 l, r_2) P(1s, r_1) P(k_4 l_4, r_2) P(k_3 l_3, r_2) \beta_{l_4}(r_1, r_2) . \quad (5.5)$$

An accurate evaluation of the integral in (2.8) required a mesh of 1764 pairs of values of  $(k', k'')$ . The replacement of the  $\gamma_\lambda$  coefficients by the  $\beta_\lambda$  causes a large increase in computing time, which was judged

prohibitive since one approximation to A has already been made and since an upper bound on the correction factor A is all that is required.

The dominant contributions to equation (2.8) and also to A, because of the factor  $\langle k_0^{\ell} n | v | k_3^{\ell_3} k_4^{\ell_4} \rangle$ , come from intermediate angular momenta  $\ell'' = 1$ ,  $\ell' = 1$  or 3 (that is  $\ell_4 = 1$ ,  $\ell_3 = 1$  or 3). In this case, the contribution A can be written as

$$A = \frac{-2}{k_0 D(k_{10}, k_{20})} \left(\frac{2}{\pi}\right)^2 \int_0^\infty dk_3 \int_0^\infty \frac{dk_4}{D(k_3, k_4)} \cdot \quad (5.6)$$

$$\left( \frac{6}{5} \frac{I_1(k_4 1, k_3 1)}{3} \frac{J_1(k_4 1, k_3 1)}{3} + \frac{9}{5} \frac{I_1(k_4 1, k_3 3)}{3} \frac{J_1(k_4 1, k_3 3)}{3} \right)$$

where  $I_1(k_4 1, k_3 1) = I_1(1s, k_0 \ell; k_4 1, k_3 1)$  and similarly for the function  $J_1$ . Here we have used the results of §2.3 to evaluate integrals in equations (5.3) and (5.4).

Details of the way in which the J integrals were evaluated are given in Appendix A. In Table 5.2 we compare the numerical values of  $J_1(k_4 1, k_3 1)$  and  $I_1(k_4 1, k_3 1)$  over the  $k_3, k_4$ -region in which the latter peaks, taking  $k_0 = 1.0$  a.u. The integrals  $J_1(k_4 1, k_3 3)$  were found to be negligible compared with the  $J_1(k_4 1, k_3 1)$ . The function  $I_1(k_4 1, k_3 1)$  is sharply peaked at  $k_3 = k_{30}$ ,  $k_4 = k_{40}$  whilst the other function,  $J_1(k_4 1, k_3 1)$ , is very sharply peaked at  $k_3 = k_{30}$  but is slowly varying with  $k_4$  in this neighbourhood. Thus to a good approximation,

$$A = - \frac{2}{k_0 D(k_{10}, k_{20})} \left(\frac{2}{\pi}\right)^2 \int_0^\infty \frac{dk_3 \langle k_3^{\ell_3} k_{40}^{\ell_4} | v^2 | k_0^{\ell} n \rangle}{D(k_3, k_{40})}$$

$$\times \int_0^\infty dk_4 \langle k_0^{\ell} n | v | k_3^{\ell_3} k_4^{\ell_4} \rangle$$

where we are considering the case  $\ell_4 = 1, \ell_3 = 1$ .

Since the  $v^2$  matrix element is very sharply peaked with respect to  $k_3$  we can obtain a rough upper bound on A by replacing  $\langle k_3^{\ell_3} k_4^{\ell_4} | v^2 | k_0^{\ell_n} \rangle$  by its peak value everywhere in  $k_3$ -space. Thus we approximate A by

$$A^{(\mathbf{u})} = - \frac{2}{k_0} \left(\frac{2}{\pi}\right)^2 \frac{\langle k_3^{\ell_3} k_4^{\ell_4} | v^2 | k_0^{\ell_n} \rangle}{D(k_{10}, k_{20}) D(k_{30}, k_{40})} \int_0^\infty dk_3 \int_0^\infty dk_4 \langle k_0^{\ell_n} | v | k_3^{\ell_3} k_4^{\ell_4} \rangle .$$

That is, for  $\ell_3 = 1, \ell_4 = 1$ , from equation (5.6) ,

$$A^{(\mathbf{u})} = - \frac{2}{k_0} \left(\frac{2}{\pi}\right)^2 \frac{6}{5.9} \frac{J_1(k_{40}^1, k_{30}^1)}{D(k_{10}, k_{20}) D(k_{30}, k_{40})} \int_0^\infty dk_3 \int_0^\infty dk_4 I_1(k_4^1, k_3^1) .$$

This is an upper bound since the  $v^2$  matrix element is negative and the  $v$  matrix element positive throughout the region of interest, while both denominators are negative. Hence  $A^{(\mathbf{u})} > A$ .

From our second order work we expect  $k_1$  and  $k_2$  to take values near 0.9 and 1.1 a.u. respectively when  $k_0 = 1.0$  a.u. With the corresponding value of  $D(k_1, k_2)$  we obtain a result for  $A^{(\mathbf{u})}$  of 0.04 which is about 10% larger than the total second order result for the same value of  $k_0$ .

Although this result is an upper bound we do not think it is a gross over-estimate of the actual contribution of the third order ladder diagram to the d-wave phase shift at that energy. That is, in view of the corresponding correction to the polarizability, this third order diagram and its corresponding exchange and EPV diagrams are not negligible. Our result, however, does not give any information on the total contribution of this class of diagrams, since there are several exchange diagrams and

Table 5.2. Comparison of the functions  $I_1(k_4, 1, k_3, 1)$  and  $J_1(k_4, 1, k_3, 1)$

In each box the upper number is  $J_1$  and the lower  $I_1$

$k_3$ $k_4$	.4	.6	.8	.9	1.0	1.1	1.4
.6	-.1926 .0818	-.4037 .1675	-.6084 .2325	-.7306 .2315	-.3585 .1466	.0108 .0541	.0259 -.0129
1.0	-.3817 .1335	-.8099 .2691	-1.264 .3708	-1.523 .3718	-.7643 .2556	-.0084 .1262	-.0196 .0131
1.1	-.4127 .1352	-.8786 .2724	-1.390 .3759	-1.672 .3782	-.8410 .2651	-.0110 .1383	-.0393 .0240
1.2	-.4263 .1329	-.9309 .2679	-1.495 .3708	-1.795 .3744	-.9028 .2671	-.0197 .1462	-.0593 .0348
1.4	-.4655 .1199	-.9918 .2427	-1.651 .3384	-1.961 .3443	-.9841 .2533	-.0016 .1497	-.0945 .0528
2.0	-.4814 .0669	-.9782 .1367	-1.851 .1939	-2.045 .2003	-1.016 .1537	-.0416 .1005	-.1263 .0582
2.5	-.3546 .0228	-.9766 .0463	-1.794 .0653	-1.790 .0671	-.9297 .0505	-0.389 .0317	.0170 .0177



in the second order calculation it was found that the exchange diagram Figure 1.2b gave a non-negligible contribution to the second order phase shift, and also the contribution was opposite in sign to that of the direct diagram, Figure 1.2a. Consequently there will be considerable cancellation and the only conclusion we can draw is that in any accurate work using this optical potential approach, this class of diagrams must be taken into account.

### 5.3. Other third order diagrams

In this section we discuss the contributions to the third order phase shift of the diagrams other than the ladder diagram, shown in Figure 5.1.

The contribution, B, of Figure 5.1c is given by

$$B = -\left(\frac{2}{\pi}\right) \frac{3}{k_0} \int_0^\infty dk_1 \int_0^\infty dk_2 \int_0^\infty dk_3 \frac{\langle mk_0 | v | k_3 k_1 \rangle \langle nk_3 | v | k_2 m \rangle \langle k_1 k_2 | v | k_0 n \rangle}{D(k_1, k_3) D(k_1, k_2)}$$

where the D functions are defined in equation (5.2) and where the angular momenta indices associated with the matrix elements and also the summations over them are implied. This was estimated using a method first proposed by Kelly (1963). We considered the ratio, B', of B to the contribution of the second-order diagram, Figure 1.2a, given by equation (1.26).

That is

$$B' = \frac{\left(\frac{2}{\pi}\right) \int_0^\infty dk_1 \int_0^\infty dk_2 \int_0^\infty dk_3 \frac{\langle mk_0 | v | k_3 k_1 \rangle \langle nk_3 | v | k_2 n \rangle \langle k_1 k_2 | v | k_0 n \rangle}{D(k_1, k_3) D(k_1, k_2)}}{\int_0^\infty dk_1 \int_0^\infty dk_3 \frac{\langle mk_0 | v | k_3 k_1 \rangle \langle k_3 k_1 | v | mk_0 \rangle}{D(k_1, k_3)}} \quad (5.7)$$

This was simplified by using a peaking approximation to fix the values of  $k_1$  and  $k_3$  and so reduce the number of repeated integrals. We now give a summary of this approach.

We consider only contributions from intermediate angular momenta  $\ell_3 = 1$ ,  $\ell_1 = 1$  and 3, since these values give the dominant second order contribution to the d-wave phase shift. There are two kinds of matrix element occurring in the expression (5.7) for  $B'$ , each of which has been dealt with in our earlier work. From equation (2.5), for the d wave ( $\ell = 2$ ), we have

$$\langle 1s k_0 2 | v | k_3 k_1 \ell_1 \rangle = \frac{\sqrt{4\pi}}{3} I_1(1s, k_0 2; k_3 1, k_1 \ell_1) \delta_{m_1, -m_2} \int Y_{20}^*(\hat{r}) Y_{\ell_1, m_1}(\hat{r}) Y_{\ell_2, m_2}(\hat{r}) d\hat{r} \quad (5.8)$$

where  $\delta_{i,j}$  is the Kronecker delta and where the values of the angular spherical harmonic integrals for various values of  $\ell_1$  and  $m_1$  are given in Table 2.2.

The other matrix element  $\langle 1s k_3 1 | v | k_2 \ell_2 1s \rangle$  can, on carrying out the angular integrations in the usual manner, be written as

$$\langle 1s k_3 1 | v | k_2 \ell_2 1s \rangle = \frac{1}{3} Y(k_3 1, k_2 \ell_2) \delta_{m_2, m_3} \delta_{1, \ell_2} \quad (5.9)$$

where the radial Y functions are defined by

$$Y(k_3 1, k_2 \ell_2) = \int_0^\infty P(1s, r_1) P(k_3 1, r_1) f(k_2 \ell_2, r_1) dr_1 \quad (5.10)$$

with  $f$  given by equation (2.7). They have already been computed in the polarizability calculation (Chapter IV).

Clearly, from equations (5.8) and (5.9), there is only a single summation in the numerator of equation (5.7), over  $m_2$  say, and also in the denominator, over  $m_1$  say. The summations were carried out using the expressions for the matrix elements given in equations (5.8) and (5.9) and the results of Table 2.2. The resulting expression for  $B'$  was found to be

$$B' = \frac{2K}{3\pi} \int_0^\infty dk_1 \int_0^\infty dk_2 \int_0^\infty dk_3 \frac{I_1(k_3^1, k_1^{\ell_1})}{3} \frac{I_1(k_2^1, k_1^{\ell_1})}{3} Y(k_3^1, k_2^1)}{D(k_1, k_3)D(k_1, k_2)} \quad (5.11)$$


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$$\int_0^\infty dk_1 \int_0^\infty dk_3 \frac{I_1(k_3^1, k_1^{\ell_1})^2}{3} \frac{K}{D(k_1, k_3)}$$

where  $K = 6/5$  for  $\ell_1 = 1$   
 $= 63/35$  for  $\ell_1 = 3$  .

Now as we have seen in section 5.2 (Table 5.2) the functions  $I_1(k_3^1, k_1^{\ell_1})$  are sharply peaked with respect to  $k_1$  and  $k_3$  and so the expression (5.11) can be simplified by assuming  $k_3$  and  $k_1$  to be fixed, taking values near to those giving the maximum value of  $I_1(k_3^1, k_1^{\ell_1})$ . The final result for the ratio  $B'$  is

$$B' = \frac{\frac{2}{\pi} \int_0^\infty dk_2 \frac{I_1(k_2^1, k_1^{\ell_1})}{3} \frac{1}{3} \frac{Y(k_3^1, k_2^1)}{D(k_1, k_2)}}{\frac{I_1(k_3^1, k_1^{\ell_1})}{3}}$$

where  $\ell_1 = 1$  or  $3$ .

This was evaluated numerically for the two cases  $\ell_1 = 1$  and  $\ell_1 = 3$ , using a 42-point Simpson's rule, and our results for two values

of the incident energy,  $k_0$ , are shown in Table 5.3. It can be seen that the effect of the two-bubble diagram, Figure 5.1c, is negligible.

The contribution, C, of the diagram shown in Figure 5.1b is

$$C = -\left(\frac{2}{\pi}\right)^3 \frac{2}{k_0} \int_0^\infty dk_1 \int_0^\infty dk_2 \int_0^\infty dk_3 \frac{\langle nm|v|k_2 k_3 \rangle \langle k_2 k_3|v|nk_1 \rangle \langle k_0 k_1|v|k_0 n \rangle}{D(k_1, k_0) \left(2\varepsilon_n - \frac{k_2^2}{2} - \frac{k_3^2}{2}\right)}$$

where  $D(k_1, k)$  is defined in equation (5.2) and where the summations over the angular momentum indices implied in the matrix elements have been suppressed. As in the case of the two-bubble diagram, Figure 5.1c, a peaking approximation was used and we discuss this below. The result for C is an upper bound on the contribution of Figure 5.1c to the third order phase shift.

The matrix element  $\langle k_0 \ell k_1 \ell_1 |v| k_0 \ell m \rangle$  peaks sharply, at  $k_1 = k_{10}^{(\ell_1)}$  say, whilst  $D(k_1, k)$  is a slowly-varying function of  $k_1$  in the region of  $k_{10}$  and so we can approximate by

$$C = -\left(\frac{2}{\pi}\right)^3 \frac{2}{k_0} \frac{\langle k_0 \ell k_{10}^{(\ell_1)} \ell_1 |v| k_0 \ell m \rangle}{D(k_{10}, k_0)} \int_0^\infty dk_2 \int_0^\infty dk_3 \frac{\langle nm|v|k_2 k_3 \rangle \langle k_2 k_3|v|nk_{10}^{(\ell_1)} \rangle}{E(k_2, k_3)}$$

where  $E(k_2, k_3) = 2\varepsilon_n - \frac{k_2^2}{2} - \frac{k_3^2}{2}$ .

The matrix element  $\langle k_0 \ell k_{10}^{(\ell_1)} \ell_1 |v| k_0 \ell m \rangle$  can be written down in terms of the usual I integrals by using the results of equation (2.5). From Table 2.2 it can be seen that there are two values of  $\ell_1$  which give non-vanishing angular parts of the matrix element, namely

$\ell_1 = 0$  and  $\ell_1 = 2$ . The corresponding matrix elements are

$$\langle k_o^2 k_{10}^{(0)} | v | k_o^2 m \rangle = I_o(k_{10}^{(0)})_{0, k_o^2}$$

$$\langle k_o^2 k_{10}^{(2)} | v | k_o^2 m \rangle = \frac{2}{7\sqrt{5}} I_2(k_{10}^{(2)})_{2, k_o^2}.$$

That is

$$C = -\frac{2}{k_o} \left(\frac{2}{\pi}\right)^3 \frac{I_o(k_{10}^{(0)})_{0, k_o^2}}{D(k_o, k_{10}^{(0)})} C_o + \frac{2}{7\sqrt{5}} \frac{I_2(k_{10}^{(2)})_{2, k_o^2}}{D(k_o, k_{10}^{(2)})} C_2 \quad (5.12)$$

where

$$C_i = \int_0^\infty dk_2 \int_0^\infty dk_3 \frac{\langle nm | v | k_3^{\ell_3} k_2^{\ell_2} \rangle \langle k_2^{\ell_2} k_3^{\ell_3} | v | k_{10}^{(i)} i m \rangle}{E(k_2, k_3)} \quad (5.13)$$

for  $i = 0, 2$ .

In our second order work it was found that the dominant contribution from the matrix elements  $\langle k_2^{\ell_2} k_3^{\ell_3} | v | k_{10}^{(i)} i m \rangle$  was from

$$(i) \quad \ell_2 = 1 = \ell_3 \text{ for } i = 0$$

and (ii)  $\ell_3 = 1, \ell_2 = 1$  and  $3$  for  $i = 2$ . However, the matrix elements

$\langle nm | v | k_3^{\ell_3} k_2^{\ell_2} \rangle$  vanish unless  $\ell_2 = \ell_3$ , and so we consider only

$\ell_2 = 1, \ell_3 = 1$  in our evaluation of the  $C_i$  functions. Also the

$\langle k_2^{\ell_2} k_3^{\ell_3} | v | k_{10}^{(i)} i m \rangle$  matrix elements vanish unless  $m_2$  and  $m_3$  are

equal and opposite in sign, whilst  $\langle nm | v | k_3^{\ell_3} k_2^{\ell_2} \rangle$  vanishes unless

$m_2 = m_3$ . Consequently the only non-zero contributions to the  $C_i$  functions

come from  $m_2 = 0 = m_3$ .

Now the matrix elements  $\langle k_2^1 k_3^1 | v | k_{10}^{(i)} i m \rangle$  peak very

sharply at  $k_2 = k_{20}^{(i)}, k_3 = k_{30}^{(i)}$  say, and the E functions are slowly-

varying in this  $k_2, k_3$ -region, and so we approximate the integrals in equation (5.13) to obtain a rough upper bound on the functions  $C_i$ .

Using the results of equation (2.5) and Table 2.2 we obtain

$$\langle k_{20}^{(0)1}, k_{30}^{(0)} | v | k_{10}^{(0)0}, m \rangle = \frac{1}{3} I_1(k_{30}^{(0)1}, k_{20}^{(0)1})$$

$$\langle k_{20}^{(2)1}, k_{30}^{(2)1} | v | k_{10}^{(2)0}, m \rangle = \frac{2}{3\sqrt{5}} I_1(k_{30}^{(2)1}, k_{20}^{(2)1})$$

Also  $\langle n m v k_{30}^{(i)1} k_{20}^{(i)1} \rangle = -\frac{1}{3} Y(k_{30}^{(i)1}, k_{20}^{(i)1})$  (see equation 5.10) and so we approximate by

$$C_0 = - \frac{Y(k_{20}^{(0)}, k_{30}^{(0)}) I_1(k_{30}^{(0)1}, k_{20}^{(0)1})}{9E(k_{20}^{(0)}, k_{30}^{(0)})}$$

and

$$C_2 = - \frac{2Y(k_{20}^{(2)}, k_{30}^{(2)}) I_1(k_{30}^{(2)1}, k_{20}^{(2)1})}{9\sqrt{5} E(k_{20}^{(2)}, k_{30}^{(2)})}$$

Hence, using these approximations in equation (5.12) we obtain our results for the contribution  $C$  to the third order phase shift. These are shown in Table 5.4. It can be seen that  $C$  is insignificant.

The correction from the diagram Figure 5.1d was not evaluated because of the expense involved in calculating the 'four-excited state' matrix elements  $\langle k_1 k_2 | v | k_3 k_4 \rangle$ , but, for physical reasons we expect it to be smaller than that from the ladder diagram, Figure 5.1a.

Recently Pindzola and Kelly (1973) have applied the optical potential method to the low energy elastic scattering of electrons by the neutral argon atom. Their work is basically a second order calculation

Table 5.3. Ratio of the contribution B of Figure 5.1c to that of Figure 1.2a for the d-wave phase shift

$k_0$ (a.u.)	$k_1, k_3$	$\ell_1, \ell_3$	Ratio of contributions 5.1c to 1.2a
0.5	0.8, 1.0	1, 1	-.0336
	0.8, 1.0	1, 3	-.0318
1.0	0.8, 1.0	1, 1	-.0416
	0.9, 1.0	1, 1	-.0398
	0.8, 1.0	1, 3	-.0394

Table 5.4. The contribution C from Figure 5.1b compared with the total second order result

	$k_0 = 1.0$ a.u.	$k_0 = 0.5$ a.u.
$k_{10}(0)$	0.5	0.5
$k_{20}(0)$	0.6	0.6
$k_{30}(0)$	1.0	1.0
$k_{10}(2)$	1.1	1.0
$k_{20}(2)$	0.9	0.9
$k_{30}(2)$	1.1	1.1
contribution C	$.254 \times 10^{-4}$	$.282 \times 10^{-4}$
Total second order result	.0352	.00745
C as a %age of total second order	.08%	.38%

but they have considered third order diagrams. Two sets of single-particle states, solutions of equation (1.6), are generated. One set is obtained by choosing the arbitrary one-body potential  $V_i$  to be the Hartree-Fock potential  $V^{HF}$ , as we have done. These states are used as possible states for the scattering electron. A further set of states is generated by  $V_{N-1}$  type potentials in which there are interactions with only  $N-1$  other electrons. These physically represent the bound and continuum states which the atomic electrons can occupy. Pindzola and Kelly have calculated phase shifts and elastic scattering cross-sections and have obtained very good agreement with experiment.

Their use of the  $V_{N-1}$  potential causes cancellations in the third order diagrams which we do not occur with the Hartree-Fock potential. The dominant diagram is expected to be Figure 5.1b, and its contribution to the phase shift to be less than 10% of the second order correction. It is pointed out, however, that further work is required before any conclusions can be drawn on the importance or otherwise of third order diagrams.

#### 5.4. Conclusions

We have seen that for the s and p wave phase shifts there is very good agreement between our second order optical potential results, those of the Green's function method of Yarlagadda et al. (1973), those of the variational calculation of Sinfailam and Nesbet (1972) and those of the polarised orbital treatment of Duxler et al. (1971). Our results for the d-wave phase shifts lie above those of Yarlagadda et al. and about 10% below the results of both Duxler et al. and Sinfailam and Nesbet. The results of all these calculations lie below the results of the phase shift analysis of experimental data by Bransden et al. (1973). It is



likely, however, that this last calculation is not very reliable because of errors in the available experimental data. More accurate data is at the moment being analysed.

From our third order work we conclude that the direct scattering ladder diagram gives a significant contribution to the third order correction to the phase shift. This is the dominant contribution, and since it is positive, we expect the total third order correction to be positive. There will be considerable cancellations, however, due to the corresponding exchange diagrams and so we can draw no conclusions as to how large or small the total third order correction is likely to be.

In any accurate work using this optical potential method, third order diagrams must be considered, but to calculate the third order contribution more accurately than in this present work is at the moment prohibitively expensive.

CHAPTER VI

AN INTRODUCTION TO THE DISPERSION RELATION  
AND PHASE SHIFT ANALYSIS

The method of phase shift analysis of experimental data has been used for some time in elementary particle physics. It has recently been applied very successfully in atomic physics, notably by Bransden and McDowell (1969) and McDowell (1971b) who have considered the problems of electron-helium and electron-neon scattering. Gerjuoy and Krall (1960) have developed dispersion relations appropriate to the scattering of electrons by atoms. These can be used to calculate values of the real part of the forward scattering amplitude which can be used in the phase shift analysis.

The dispersion relation has been tested by Bransden and McDowell (1969) for electron-helium scattering and shown to be consistent within the errors associated with the calculations of the various quantities which are involved. Our aim has been to test the dispersion relation for the more complicated case of electron-neon scattering. In the second part of this thesis we will discuss the progress which has been made. We begin by a brief introduction to the dispersion relation and the phase shift analysis technique, and we review what has already been done for electron-helium scattering.

6.1. The Dispersion Relation

Dispersion relations are expressions which relate the real and imaginary parts of a scattering amplitude. They were first used in optical physics by Kronig and Kramers (1929) and later by workers in meson physics to help analyse the results of high-energy nuclear scattering experiments. Gerjuoy and Krall (1960) conjectured that they

might also prove useful in atomic physics. They developed the dispersion relations appropriate to the elastic scattering of electrons by atomic hydrogen and used them successfully to distinguish between two conflicting experiments.

The dispersion relations for the non-relativistic scattering of a particle by a fixed potential  $V(r)$  (which we shall assume has bounded first and second moments) had previously been derived by Klein and Zemach (1959). The total wavefunction,  $\psi$ , for the system satisfies the Schrödinger equation

$$(H_0 + V - E)\psi = 0 \quad (6.1)$$

where  $E = \hbar^2 k^2 / 2m$ . The potential  $V(r)$  can be treated as an inhomogeneity term added to the homogeneous free Schrödinger equation

$$(H_0 - E)\psi_0 = 0,$$

that is,  $(\nabla^2 + k^2)\psi_0 = 0$  (6.2)

Equation (6.1) can be written in an equivalent integral form

$$\psi(\underline{r}) = \psi_0(\underline{r}) - \int G_0(\underline{r} - \underline{r}') V(\underline{r}') \psi(\underline{r}') d\underline{r}' \quad (6.3)$$

where  $\psi_0$  is an arbitrary solution of (6.2) and  $G_0$  is a Green's function of the operator  $\nabla^2 + k^2$ ,

$$(\nabla^2 + k^2)G_0(\underline{r}) = -\delta(\underline{r})$$

Formally, we can iterate and obtain a solution of (6.1),

$$\psi = \sum_{q=0}^{\infty} (-G_0 V)^q \psi_0 \quad (6.4)$$

where  $\psi_0 = e^{i\mathbf{k}_0 \cdot \mathbf{r}}$  with  $\mathbf{k}_0$  the specified initial energy and

$$G_0 = \lim_{\epsilon \rightarrow 0} \left( \frac{1}{E - H_0 + i\epsilon} \right) \quad (6.5)$$

Equation (6.4) is the Born-Neumann series. Equations (6.3) and (6.5) can be combined to give the Lippmann-Schwinger equation

$$\psi = \psi_0 - (E - H_0 + i\epsilon)^{-1} V \psi$$

Also, if  $G$  is the Green's function for the total Hamiltonian  $H_0 + V$ , that is

$$G = (E - H_0 - V + i\epsilon)^{-1} \quad (6.6)$$

then

$$\begin{aligned} \psi &= \psi_0 - GV\psi_0 \\ &= \psi_0 - (E - H_0 - V + i\epsilon)^{-1} V\psi_0 \end{aligned} \quad (6.7)$$

For scattering from the state  $\mathbf{k}_i$  to the state  $\mathbf{k}_f$ , the exact scattering amplitude is given by

$$f(\theta, E) = -\frac{m}{2\pi} \langle \mathbf{k}_f | V | \psi \rangle \quad (6.8)$$

and the first Born approximation to this is

$$f_B(\theta, E) = -\frac{m}{2\pi} \langle \mathbf{k}_f | V | \psi_0 \rangle$$

Klein and Zemach (1959) showed that the function

$$Q(E) = f(0, E) - f_B(0, E) \quad (6.9)$$

- (i) is an analytic function of  $E$  in the complex energy plane with a branch cut along the positive real axis and  $0 \leq \arg E < 2\pi$ ;
- (ii) has a branch point at  $E = 0$ ;
- (iii) has simple poles at the bound states of the system;
- (iv) vanishes at large complex  $E$ .

It follows from Cauchy's Theorem that

$$\begin{aligned}
 Q(E) &= \frac{1}{2\pi i} \int_{C_1} \frac{Q(E') dE'}{E' - E} \\
 &= \frac{1}{2\pi i} \int_{C_2} \frac{Q(E') dE'}{E' - E} - \sum_j R_j(E)
 \end{aligned} \tag{6.10}$$

where the contours  $C_1$  and  $C_2$  are shown in Figure 6.1 and  $R_j$  are the residues of  $Q(E')(E' - E)^{-1}$  at the poles  $E_j$ . Now  $V$  and  $H_0$  are real quantities and it can be seen from equations (6.8) and (6.7) that

$$f^*(0, E) = f(0, E^*)$$

and similarly for the Born amplitude  $f_B$ . Therefore

$$Q(E + i\epsilon) = Q^*(E - i\epsilon),$$

and

$$\begin{aligned}
 \frac{1}{2\pi i} \int_{C_2} \frac{Q(E') dE'}{E' - E} &= \frac{1}{2\pi i} \int_0^\infty \frac{dE' Q(E' + i\epsilon)}{E' - E} - \int_0^\infty \frac{dE' Q(E' - i\epsilon)}{E' - E} \\
 &= \frac{P}{\pi} \int_0^\infty \frac{dE' \text{Im} Q(E')}{E' - E}
 \end{aligned}$$

where  $P$  denotes that the principle value of the integral is to be taken. Taking the real part of equation (6.10) and noting that  $f_B$  is real, the desired dispersion relation is obtained:

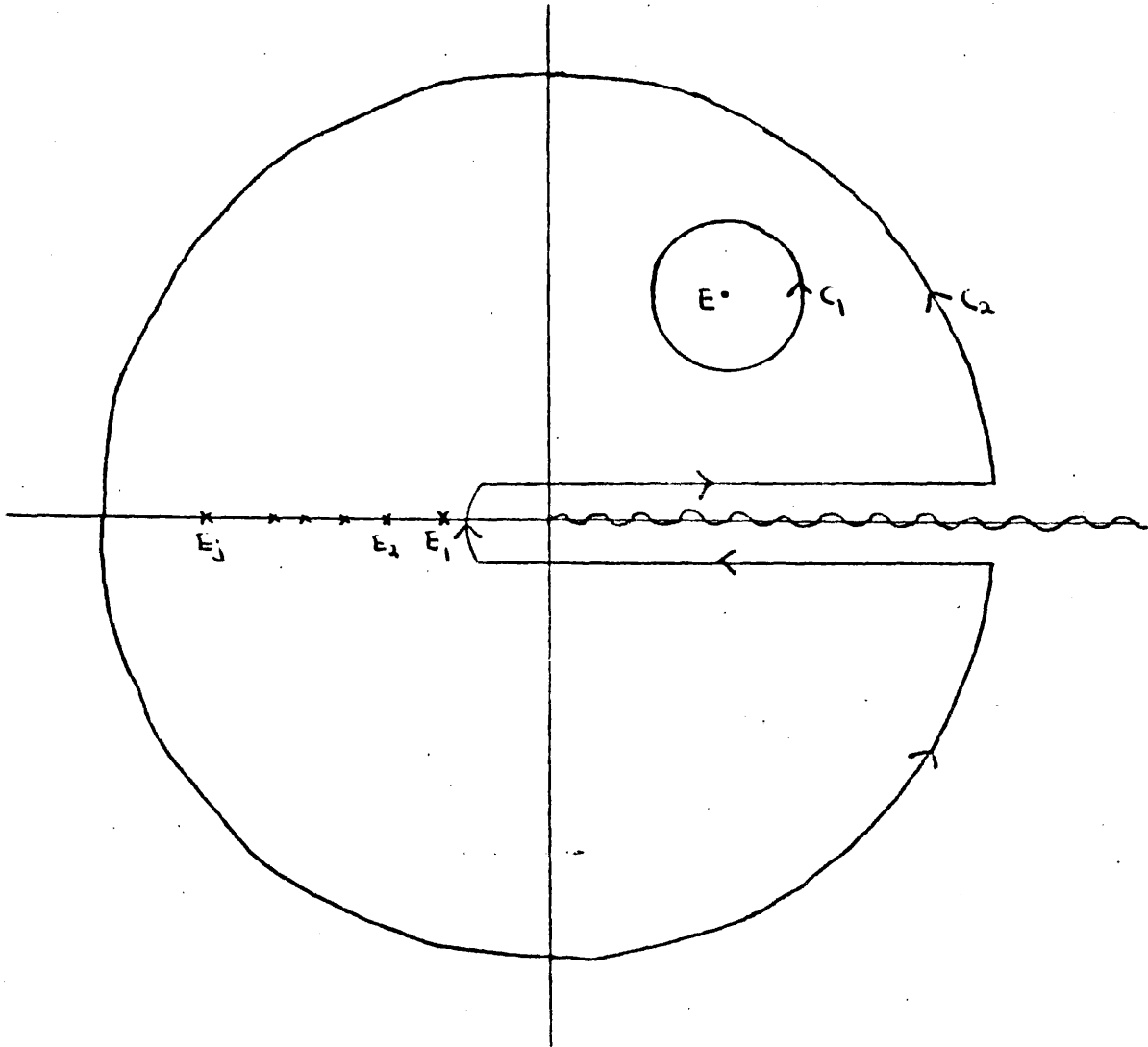


Figure 6.1 The contours of integration in equation (6.10)

$$\operatorname{Re} f(O, E) = f_B(O, E) + \frac{P}{\pi} \int_0^{\infty} \frac{dE' \operatorname{Im} f(O, E')}{E' - E} - \sum_j R_j(E) .$$

By using the optical theorem

$$\operatorname{Im} f(O, k^2) = \frac{k}{4} Q_{\text{TOT}}(k^2)$$

where  $Q_{\text{TOT}}$  is the total electron-atom cross-section, the dispersion relation can be written

$$\operatorname{Re} f(O, E) = f_B(O, E) + \frac{P}{4\pi} \int_0^{\infty} \frac{k' Q_{\text{TOT}}(k'^2) dk'^2}{k'^2 - k^2} - \sum_j R_j . \quad (6.11)$$

Gerjuoy and Krall (1960) suggested that a similar result would hold for many-particle collisions. They assumed that the Green's function of the total Hamiltonian (equation (6.6))

- (i) has poles at the bound states of the system;
- (ii) has a branch point at  $E = 0$  and at every energy  $E_t$  corresponding to the threshold of a new inelastic channel;
- (iii) is single-valued and analytic except at the above poles and branch points if a branch cut is drawn along the positive real axis, with the specification  $0 \leq \arg(E - E_t) < 2\pi$  for each threshold energy  $E_t$ ;
- (iv) has the representation  $\frac{\phi_j(R)\phi_j(R')}{E - E_j}$  near any bound state pole.

These assumptions have not been proved but are known to be consistent in that they lead directly to many accepted formulae in many-particle scattering. If such a Green's function exists with these properties then the function  $Q$  of equation (6.9) can be formed and the analysis of Klein and Zemach follows through. Thus the dispersion relation (6.11)

holds. For cases in which no bound states of the electron-atom system exist the residue term vanishes and we have

$$\operatorname{Re} f(0, k^2) = f_B(0, k^2) + \frac{P}{4\pi} \int_0^\infty \frac{k' Q_{\text{TOT}}(k'^2) dk'^2}{k'^2 - k^2}. \quad (6.12)$$

Now the incident and target electrons are identical and therefore the scattering amplitude  $f(0, k^2)$  is a linear combination of direct and exchange amplitudes,  $f_D(0, k^2)$  and  $f_E(0, k^2)$ .

The dispersion relation (6.12) is applicable to scattering by the rare gases since in such cases no bound states of the complete system exist. For both helium and neon (the two cases which we shall be considering) the direct and exchange amplitudes are related by

$$f(0, k^2) = f_D(0, k^2) - f_E(0, k^2) \quad (6.13)$$

(see for example Schiff (1955)) and we can write

$$\begin{aligned} \operatorname{Re} f(0, k^2) = f_B(0, k^2) - g_B(0, k^2) \\ + \frac{1}{4\pi} P \int_0^\infty \frac{k' Q_{\text{TOT}}(k'^2) dk'^2}{k'^2 - k^2} \end{aligned} \quad (6.14)$$

where  $f_B$  is now the Born approximation to the direct scattering amplitude and  $g_B$  is the exchange Born scattering amplitude.

By choosing a suitable ground state wave function for the atom, the quantities  $f_B$  and  $g_B$  can be calculated. The integral can be evaluated by using direct experimental measurements for the total cross-section  $Q_{\text{TOT}}$ . Thus we can predict, from the dispersion relation, values of the real part of the forward scattering amplitude,  $f(0, k^2)$ .



In the special case of zero energy, the dispersion relation becomes

$$-A = \text{Re } f(0,0) = f_B(0,0) - g_B(0,0) + \frac{1}{4\pi^2} \int_0^\infty \frac{Q_{\text{TOT}}(k'^2) dk'^2}{k'} \quad (6.15)$$

where A is the scattering length defined by

$$-A = \lim_{k \rightarrow 0} \text{Re } f(0, k^2) \quad (6.16)$$

A is known accurately from experiment and so we have in equation (6.15) a means of testing the validity of the dispersion relation.

## 6.2. Phase Shift Analysis of electron-atom scattering

The technique of phase shift analysis of experimental data is applicable in many branches of physics. As we have mentioned before, it has been used for some time in elementary particle physics, notably by Vik and Rugge (1963) and Bransden et al. (1966) in analyses of pion-nucleon data. The first application to atomic scattering data was by Hooper et al. (1968), who analysed the differential cross-section data of Ramsauer and Kollath (1932). This work was extended by Bransden and McDowell (1969) for the case of electron helium scattering. (This will be discussed briefly in the next section.)

For the method of phase shift analysis to be feasible it is necessary to have measurements of several distinct observables of a system, these observables each depending on different combinations of a few variables, within a general theoretical model. Values  $x_i$  of the observables are calculated in terms of these variables and are compared with the measured values of these quantities,  $X_i$ , which are subject to errors  $\delta X_i$ . The sum

$$F = \sum_{i=1}^N \left( \frac{X_i - x_i}{\delta X_i} \right)^2 \quad (6.17)$$

is then formed and minimised with respect to the variables, subject to any necessary constraints. Here  $N$  is the number of independent measurements considered. If  $n$  is the number of parameters used in the theoretical calculation, then there are  $m = (N-n)$  degrees of freedom. The quantity

$$\chi^2 = F/m$$

is used as a test of the quality of the fit which is achieved. For a satisfactory fit,  $\chi^2$  should be less than unity. Several computer programs exist which perform this minimization calculation.

The variables used depend on the particular problem being considered but in the case of electron-atom scattering it is convenient to parameterise the phase shifts. Bransden and McDowell (1969, and McDowell (1971a)) point out that by formulating the theoretical analysis in terms of the  $S$  matrix rather than in terms of the phase shifts directly, unitarity is imposed on the solution. The elastic scattering amplitude, and hence many of the observables for which experimental information is available, can be expressed in terms of this  $S$  matrix.

The  $\ell$ th element of the  $S$  matrix for impact energy  $k^2$  is defined by

$$S(\ell, k) = e^{2i\eta'_\ell} \frac{(kr_\ell^2 - k^2 + \frac{i}{2}\Gamma_\ell)}{(kr_\ell^2 - k^2 - \frac{i}{2}\Gamma_\ell)} \equiv e^{2i\delta_\ell} \quad (6.18)$$

It is assumed that in each partial wave there is at most one resonance, corresponding to an energy  $k_{r\ell}^2$  and with width  $\Gamma_\ell$ .  $\delta_\ell$  is the  $\ell$ th partial wave phase shift and

$$\eta_{\ell}' = \eta_{\ell} - \frac{1}{2} \tan^{-1} \frac{\Gamma_{\ell} - k_{r\ell}^2}{k_{r\ell}^4 - \frac{1}{4} \Gamma_{\ell}^2} \quad (6.19)$$

where  $\eta_{\ell}$  is the potential scattering part of the  $\ell$ th partial wave phase shift and the inverse tangent is such that  $\delta_{\ell}$  approaches  $\eta_{\ell}$  away from the resonance. This is a form of the Breit-Wigner one level resonance formula.

The elastic scattering amplitude is then given by

$$f(\theta, k^2) = \frac{-i}{2k} \sum_{\ell=0}^{\infty} (2\ell+1) (S(\ell, k) - 1) P_{\ell}(\cos\theta)$$

where  $P_{\ell}(x)$  is the Legendre polynomial of order  $\ell$ . Thus

$$\text{Re } f(\theta, k^2) = \frac{1}{2k} \sum_{\ell=0}^{\infty} (2\ell+1) \text{Im } S(\ell, k) P_{\ell}(\cos\theta) \quad (6.20)$$

$$\text{Im } f(\theta, k^2) = -\frac{1}{2k} \sum_{\ell=0}^{\infty} (2\ell+1) (\text{Re } S(\ell, k) - 1) P_{\ell}(\cos\theta) \quad (6.21)$$

In particular, the forward elastic scattering amplitude satisfies

$$\text{Re } f(0, k^2) = \frac{1}{2k} \sum_{\ell=0}^{\infty} (2\ell+1) \text{Im } S(\ell, k) \quad (6.22)$$

The total elastic scattering cross-section,  $Q_{\text{el}}(k^2)$ , is given by

$$Q_{\text{el}}(k^2) = \sum_{\ell=0}^{\infty} Q_{\ell}(k^2)$$

where

$$Q_{\ell}(k^2) = \frac{4}{k^2} (2\ell+1) \sin^2 \eta_{\ell}' \frac{(q+\epsilon)^2}{(1+\epsilon)^2}$$

$q$  and  $\varepsilon$  are the Fano parameters (Fano 1961),

$$q = -\cot\eta_\ell', \quad \varepsilon = 2(k^2 - k_{r\ell}^2) |\Gamma_\ell| .$$

The diffusion cross-section,  $Q_D(k^2)$ , can be written as

$$Q_D(k^2) = \frac{4}{k^2} \sum_{\ell=0}^{\infty} (\ell+1) \sin^2(\delta_\ell - \delta_{\ell+1})$$

and the differential cross-section as

$$I(\theta, k^2) = |f(\theta, k^2)|^2 = |\operatorname{Re} f(\theta, k^2)|^2 + |\operatorname{Im} f(\theta, k^2)|^2$$

where the real and imaginary parts of the scattering amplitude are given by equations (6.20) and (6.21).

Experimental measurements of the total cross-section,  $Q_{\text{TOT}}$ , can also be introduced into the phase shift analysis, by means of the dispersion relation (6.14). If there exist measurements of  $Q_{\text{TOT}}$  over a wide range of energies and calculations of its high energy behaviour in, say, the first Born approximation, then we can evaluate  $\operatorname{Re} f(0, k^2)$  from equation (6.14). The required direct and exchange Born scattering amplitudes can be calculated by choosing a suitable ground state wavefunction. We can thus treat  $\operatorname{Re} f(0, k^2)$  as experimental data. We have another means of testing the validity of the dispersion relation as we can compare the values of  $\operatorname{Re} f(0, k^2)$  obtained in this way with those obtained from equation (6.22).

If the potential scattering phase shifts  $\eta_\ell$  are parameterised, then the S matrix, defined by equations (6.18) and (6.19) can be evaluated in terms of these parameters. Hence theoretical values of the

required observables can be obtained and used in the formation of the sum (6.17). The minimization procedure can then be applied and the optimum values of the parameters used to give values of the phase shifts .

Theoretical results of a very general nature can be introduced as constraints on the minimization procedure. For example, O'Malley et al. (1962) have provided some general results on the energy dependence of the scattering phase shifts in the low energy region, for electron-neutral atom scattering. We require, for atoms in S states,

$$k \cot \eta_0 = -\frac{1}{A} + \frac{\pi\alpha}{3A^2} k + \frac{2\alpha}{3A} k^2 \log \frac{\alpha k^2}{16} + O(k^2)$$

and

$$\eta_\ell = k^2 \left[ \frac{\alpha\pi}{(2\ell-1)(2\ell+1)(2\ell+3)} + O(k) \right], \ell \neq 0,$$

where A is the scattering length and  $\alpha$  the known polarizability.

One further constraint that is usually imposed is that the potential scattering part of the phase shift  $\eta_\ell$  should be a continuous and differentiable function of energy.

### 6.3. Application to electron-helium scattering

As we have mentioned before, the first application of phase shift analysis to atomic scattering data was that of Hoepfer et al. (1968) who analysed the data of Ramsauer and Kollath (1932) on the differential cross-section  $I(\theta, k^2)$ . They obtained results for the phase shifts which were in disagreement with those from all theoretical models. A similar analysis was carried out by Andrick et al. (1970) who used their own measurements of  $I(\theta, k^2)$  and obtained good agreement with theoretical phase shifts.

Recently Bransden and McDowell (1969, 1960) and McDowell (1971a) have extended the analysis to include  $I(\theta, k^2)$ ,  $Q_{e\ell}(k^2)$ ,  $Q_{p\ell}(k^2)$  and  $\text{Re } f(0, k^2)$ , the last being derived from measurements of the total cross-section via the dispersion relation (6.14). In their first paper they considered two sets of measurements of  $I(\theta, k^2)$ , by (a) Ramsauer and Kollath (1932), and (b) Gibson and Dolder (1969), in the energy range 3.1 to 19.1 eV. They adopted the values of  $Q_{e\ell}(k^2)$  given by Golden and Bandel (1965) and those of  $Q_{p\ell}(k^2)$  by Frost and Phelps (1964), together with values of  $\text{Re } f(0, k^2)$  obtained from the dispersion relation, and they investigated their consistency compared with the two sets of data on  $I(\theta, k^2)$ . The resulting values of  $\chi^2$  were (a) 3.54 and (b) 1.18, indicating that the Gibson-Dolder differential cross-sections are far superior to those of Ramsauer and Kollath.

Bransden and McDowell (1969) also predicted s, p and d wave phase shifts using the data mentioned above. They compared them with those from the extended polarised orbital calculation of Callaway et al. (1968) and the optical potential model of Pu and Chang (1966). For the s and p waves they concluded that all the experimental information which they used was consistent with the theoretical values to within 5%. The d-wave phase shifts, however, were not determined by the available experimental data to better than 25%.

Further experimental data has since become available, and the calculation of the phase shifts has been repeated. (A minor error in the earlier work in the calculation of the Born exchange amplitude  $g_{p\ell}(0, k^2)$  has also been corrected.) The results have already been discussed in §3.2 and are shown in Figures 3.1, 3.2 and 3.3 where they are also compared with various other theoretical models. We have seen

that although there is reasonable agreement between the theory and the phase shift analysis results for s and p wave phase shifts, the d-wave results are still inconsistent.

Bransden and McDowell (1969, 1970) also compared the values of the real part of the forward scattering amplitude,  $f(0, k^2)$ , obtained from their phase shift analysis calculations, via equation (6.22), with those predicted by the dispersion relation (6.14). They considered two energy ranges, 3.1 to 19.1 eV and 100 to 500 eV, and in each case found agreement. It was concluded that within the errors associated with the various calculated and experimental quantities the measured cross-sections were consistent with the dispersion relation.

There are two errors which arise in the calculation of  $\text{Re } f(0, k^2)$  using the dispersion relation (6.14). These are relatively easily dealt with in the case of electron-helium scattering, but for larger atoms the problem is much more complicated, as we shall see in the next chapter. In the next section we shall discuss these errors.

#### 6.4. Errors in $\text{Re } f(0, k^2)$ calculated from the dispersion relation

There are two important sources of error in the dispersion relation calculation of  $\text{Re } f(0, k^2)$ . First, there are uncertainties in the adopted values of the total cross-section  $Q_{\text{TOT}}(k^2)$ . Direct measurements of  $Q_{\text{TOT}}$  are available only over a limited range of energies (below 100 eV) and even these are subject to experimental errors. At high energies the Born approximation should be reliable, but it is necessary to interpolate for the intermediate region. The error in  $\text{Re } f(0, k^2)$  which can be attributed to this procedure is difficult to estimate. It is certainly small at low and high energies, but may be as

large as 15% in the intermediate energy range.

The second source of error is in the calculation of the Born approximation to the scattering amplitude and is due to the fact that the ground state wavefunction is only known approximately. For helium, the direct and exchange Born amplitudes are given by

$$f_B(0, k^2) = -\frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 |\psi(\underline{r}_1, \underline{r}_2)|^2 V(\underline{r}_1, \underline{r}_2, \underline{r}_3)$$

$$g_B(0, k^2) = -\frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \psi(\underline{r}_1, \underline{r}_2) \psi(\underline{r}_3, \underline{r}_2) e^{ik \cdot (\underline{r}_3 - \underline{r}_1)} V(\underline{r}_1, \underline{r}_2, \underline{r}_3)$$

where  $V(\underline{r}_1, \underline{r}_2, \underline{r}_3) = -\frac{2}{r_3} + \frac{1}{|\underline{r}_1 - \underline{r}_3|} + \frac{1}{|\underline{r}_2 - \underline{r}_3|}$ , and  $\psi(\underline{r}_1, \underline{r}_2)$  is the ground state wavefunction of the helium atom. The helium wavefunction adopted by Bransden and McDowell (1969) is

$$\psi(\underline{r}_1, \underline{r}_2) = N(e^{-zr_1} + ce^{-2zr_1})(e^{-zr_2} + ce^{-2zr_2}), \quad c = 0.6, \quad z = 1.4558 \quad (6.23)$$

This provides the value  $f_B(0, k^2) = .7878$  which may be compared with the value .7913 obtained by Pekeris (1959) using a many-parameter wavefunction, and Kim and Inokuti's (1968) sum-rule value of .7911. In fact the function  $f_B$  is relatively insensitive to the particular wavefunction chosen. The exchange amplitude,  $g_B$ , however, is much more sensitive. At large energies this is unimportant since the function decreases rapidly with energy, but at low energies  $g_B$  must be known accurately. Lawson et al. (1966) have used two different wavefunctions and compared the values of the forward scattering intensity at zero energy. The error arising from a simple Hartree-Fock wave function as compared with a many-parameter variational wave function was quite considerable. Although it decreases rapidly with energy, it will still



be significant below 10 eV. This problem can be overcome in several ways, the most obvious being by choosing a suitably accurate wavefunction. For example, one could take correlation into account by using a configuration interaction type of wavefunction. We shall consider this approach in Chapter VIII. An alternative procedure was adopted by Bransden and McDowell (1969) but we do not expand on it here.

It has been shown by Bransden and McDowell that the method of phase shift analysis can be successfully applied to atomic scattering data. The consistency of different sets of experimental measurements can be tested and inaccurate data can be distinguished. Phase shifts can be obtained from the data, their accuracy being limited by the accuracy of the data. In the case of electron-helium scattering the dispersion relation has been tested and shown to be consistent within the errors associated with it. It is very important, however, to have an accurate ground state wave function for the calculation of the Born approximation to the exchange scattering amplitude.

In the next chapter we consider the application of this technique to the more complicated case of electron-neon scattering.

## CHAPTER VII

### THE DISPERSION RELATION FOR NEON

The dispersion relation for the scattering of electrons by the neon atom is given in equation (6.14). In order to test its validity, we require three quantities. First, values of the total cross-section,  $Q_{TOT}$ , at all energies, are needed for the evaluation of the integral in equation (6.14). Secondly, we need values of the real part of the forward scattering amplitude, including the particular case of the scattering length. These are obtained from a phase shift analysis of the available experimental data, apart from  $Q_{TOT}$ . Finally, the Born approximations to the direct and exchange forward scattering amplitudes must be evaluated. In this chapter we consider each of these in turn.

#### 7.1. The total scattering cross-section

For energies below 20 eV, detailed experimental measurements by Salop and Nakano (1970) of the total cross-section,  $Q_{TOT}$ , are available. It is shown by Inokuti et al. (1967) that at high energies the total inelastic cross-section,  $\sigma_{inel}$ , can be obtained from a sum rule. They tested their result by making an accurate evaluation of  $\sigma_{inel}$  for the helium atom and obtained excellent agreement with experimental data. The total elastic cross-section can be expressed in terms of the atomic form factor  $F(K)$ , which has been calculated accurately by Peixoto et al. (1969). By combining these results for  $\sigma_{el}$  and  $\sigma_{inel}$ , a high energy form for the total cross-section,  $Q_{TOT}$ , can be found. We shall discuss this briefly.

The atomic form factor  $F(K)$  and the incoherent scattering function  $S_{inc}(K)$  for a neutral atom of atomic number  $Z$  are defined as follows:

$$F(K) = \sum_{j=1}^Z \langle 0 | e^{i\mathbf{K} \cdot \mathbf{r}_j} | 0 \rangle \quad (7.1)$$

$$S_{inc}(K) = \frac{1}{Z} \left[ \sum_{j,k=1}^Z \langle 0 | e^{i\mathbf{K} \cdot (\mathbf{r}_j - \mathbf{r}_k)} | 0 \rangle - |F(K)|^2 \right] \quad (7.2)$$

where  $\mathbf{K}$  is the momentum transfer and  $\mathbf{r}_j$  the radial vector from the nucleus to the  $j$ th electron. Following Kim and Inokuti (1968) we have, in the first Born approximation,

$$d\sigma_{el} = \frac{4a_0^2}{(Ka_0)^4} |Z - F(K)|^2 d\Omega \quad (7.3)$$

$$d\sigma_{inel} = \frac{4a_0^2}{(Ka_0)^4} Z S_{inc}(K) \quad (7.4)$$

where  $d\sigma_{el}$  is the differential cross-section for the elastic scattering of electrons by an atom and  $d\sigma_{inel}$  is that summed over all inelastic collisions, assuming that the momentum of the incident electron is very large compared to the momentum transfer.

The generalised oscillator strength  $f_s(K)$  for the transition from the ground state to the state  $s$  is defined by

$$f_s(K) = \frac{E_s}{K^2} \left| \langle 0 | \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} | s \rangle \right|^2 \quad (7.5)$$

and the optical oscillator strength is

$$f_s = \lim_{K \rightarrow 0} f_s(K)$$

$E_s$  is the excitation energy of the state  $s$  measured from the ground state. Clearly

$$\sum_s \frac{f_s(k)}{E_s} = S_{inc}(k) \quad (7.6)$$

We further define the moment of the optical oscillator strength  $S(\mu)$  by

$$S(\mu) = \sum_s f_s(E_s)^\mu \quad (7.7)$$

In equations (7.5) - (7.7) the summations are over all discrete and continuous states, excluding the initial one.

It is shown by Inokuti et al. (1967) that

$$\sigma_{inel} = \frac{4\pi}{E} \{ M^2 \log(4CE) + \dots \} \quad (7.8)$$

where  $E$  is the energy of the system in Rydbergs, and where

$$M^2 = \sum_s f_s E_s^{-1} = S(-1) \quad (7.9)$$

Further, they show that

$$M^2 \log C = -2L(-1) + I_1 - I_2 \quad (7.10)$$

where  $L(-1) = \sum_s f_s E_s^{-1} \log E_s = \left. \frac{\partial S(\mu)}{\partial \mu} \right|_{\mu=-1}$  (7.11)

$$I_1 = \int_1^\infty Z S_{inc}(k) \frac{dk^2}{k^4}$$

$$I_2 = \int_0^1 \{ M^2 - Z S_{inc}(k)/k^2 \} \frac{dk^2}{k^4}$$

Values of the incoherent scattering function  $S_{inc}(K)$  for neon have been tabulated by Peixoto et al. (1969). (Note that their variable  $s$  is given by  $K = 0.53 s$ .) McDowell has used these results to evaluate the integrals  $I_1$  and  $I_2$  approximately, and obtains

$$I_1 = 2.993, \quad I_2 = 0.64 \quad .$$

The quantity  $L(-1)$  is the slope of the curve  $S(\mu)$  at the point  $\mu = -1$ . The required values of  $S(\mu)$  are given by Piech and Levinger (1964),

$$S(-2) = \alpha/16 = .67 \quad ,$$

where  $\alpha$  is the atomic polarisability,

$$S(-1) = 1.925, \quad S(0) = 10.0 = Z,$$

$$S(1) = 293.7, \quad S(2) = (11.2 \pm 0.6) \times 10^4 \quad .$$

(The value of  $S(-1)$  is that of Dalgarno and Kingston (1960).) It is found graphically that  $L(-1) = 2.6 \pm 0.2$ . Substituting these results into equation (7.8) we find the high energy form for the total inelastic cross-section to be

$$\sigma_{inel}(k^2) = \frac{4}{k^2} \{1.925 \log 4k^2 - 2.847\} \cdot (\pi a_0^2) \quad (7.12)$$

which is in good agreement with an independent derivation by Saxon (1973).

For elastic scattering, we have from equation (7.3)

$$\sigma_{el}(k^2) = \frac{8}{k^2} \int_{K_{min}}^{K_{max}} K^{-3} |Z - F(K)|^2 dK \quad (\pi a_0^2) \quad .$$

This integral has been evaluated by McDowell, using the tabulated values for  $F(K)$  given by Peixoto et al. (1969). It is noted that for elastic scattering,  $K_{min} = 0$  and  $K_{max} = 2k$ , and so for  $k^2 \geq 25$ ,

$$\begin{aligned}\sigma_{\text{el}}(k^2) &= \frac{8}{k^2} \int_0^{\infty} K^{-3} |Z - F(K)|^2 dK \\ &= \frac{17.55}{k^2},\end{aligned}$$

for lower energies, a correction for  $\int_{K_{\text{max}}}^{\infty}$  has to be made and McDowell obtains the better approximation to the total elastic cross-section

$$\sigma_{\text{el}}(k^2) = \left( \frac{17.55}{k^2} - \frac{71.05}{k^4} \right) (\pi a_0^2) \quad (7.13)$$

The total scattering cross-section,  $\sigma_{\text{TOT}}$ , is given by

$$\sigma_{\text{TOT}}(k^2) = \sigma_{\text{inel}}(k^2) + \sigma_{\text{el}}(k^2) .$$

Thus for high energies we have, from equations (7.12) and (7.13)

$$\sigma_{\text{TOT}}(k^2) \approx \frac{4}{k^2} \left[ 4.433 \log_{10} k^2 + 4.22 - \frac{17.6}{k^2} \right] \quad (7.14)$$

Further work is in progress and will be reported elsewhere (Inokuti and McDowell 1973).

We have therefore a means of calculating the total cross-sections for high energies, and for low energies we have the experimental data of Salop and Nakano (1970). However, in the intermediate energy range, no information is available, and so it is necessary to interpolate. As we have mentioned before, this introduces errors into the evaluation of the integral in the dispersion relation (6.14).

## 7.2. Phase Shift analysis of electron-neon scattering

The technique of phase shift analysis has been applied by McDowell (1971b) to the scattering of slow electrons by neon. The analysis is parallel to that described in §6.2, the aim being to find a set of phase shifts which will give a simultaneous fit to the experimental data on the total elastic, the diffusion, and the elastic differential cross-sections, over a wide range of energies. The phase shifts are restricted by requiring them to be continuous functions of the energy, away from the resonances, and to satisfy the Spruch bounds. The results are compared with those from the most important theoretical model, the polarised orbital calculation of Thomson (1966).

The only available absolute measurements of the elastic differential cross-section  $I(\theta, k^2)$ , for electron-neon scattering at that time were those of Ramsauer and Kollath (1932). It was found in the helium work of Bransden and McDowell (1969) that the data of Ramsauer and Kollath was unreliable at small energies and small angles. The data used in this work was therefore restricted to exclude such regions.

The experimental values of the diffusion cross-section used by McDowell were those of Crompton and Robertson, which were taken in a swarm experiment on the drift velocities of slow electrons in neon (see Frost and Phelps 1964).

The total elastic scattering cross-section data of Salop and Nakano (1970) was also used in the phase shift analysis.

This experimental data and also the corresponding theoretical results, in terms of the S matrix (see §6.2) are used in the formation of the sum F, defined by equation (6.17). This function is then

minimised with respect to the parameters involved in the phase shifts.

McDowell parameterises the phase shifts in the following way:

$$\tan \eta_0(k^2) = -a_{01}k^2 - \frac{4}{3} a_{01} \alpha k^3 \log k + \sum_{i=2}^5 a_{0i} k^{i+1}$$

$$\eta_\ell(k^2) = \frac{\pi \alpha k^2}{(2\ell-1)(2\ell+1)(2\ell+3)} + \sum_{i=1}^3 a_{\ell i} k^{i+2}, \quad \ell = 1, 2 \quad .$$

The polarizability,  $\alpha$ , is taken to be  $2.67 a_0^3$ . The higher phase shifts are assumed to be dominantly due to the long range polarization interaction,

$$V_{\text{pol}} = -\frac{\alpha}{r^4} \quad (\text{ryd}) \quad .$$

They are calculated in the first Born approximation. This parameterisation of the lower order phase shifts is chosen so that the leading terms are of the form predicted by O'Malley (1963). At very small values of  $k$  it agrees with O'Malley's effective range expansion to order  $k^3$ ; additional terms are introduced to represent the behaviour of the phase shifts over the range  $0 < k < 1.5$  a.u. McDowell points out that such a choice of parameterization is empirical and is not rigorously deduced from a theoretical model. The phase shifts are also required to be continuous and differentiable functions of energy.

The minimization procedure is then performed by using the computer program (VAO4A) of Powell and Fletcher (1964).

The resulting value of  $\chi^2$  obtained by fitting the neon data mentioned above was 0.66. This indicates a high degree of consistency between the three experiments considered, within their assigned errors.



The phase shifts obtained from the parameters giving this optimum value of  $\chi^2$  should therefore be reliable in the low energy region. They are in good agreement with the theoretical values of Thomson (1966) except for the p-wave. It is suggested by McDowell that an extended polarised orbital calculation, which includes exchange polarization and non-adiabatic effects, will lead to better agreement.

The parameter  $a_{01}$  is simply the scattering length and is found to be 0.22. This agrees well with the value 0.24 obtained by O'Malley, but disagrees with the Thomson polarised orbital value of 0.35. McDowell points out that his value is determined largely by the accurate very low energy diffusion cross-section data of Crompton and Robertson.

Values of the real part of the forward scattering amplitude can be obtained from this phase shift analysis by means of equation (6.22). In addition, the scattering length can be used to test the zero-energy form of the dispersion relation, equation (6.15).

### 7.3. The Born exchange amplitude $g_B(0, k^2)$

In this section we give a detailed account of the analysis involved in the calculation of the Born exchange scattering amplitude,  $g_B(0, k^2)$ , for the elastic scattering of an electron with energy  $k^2$  a.u. by the neon atom. In the case of zero energy, this analysis is a special case of that for scattering by an N-electron atom which is discussed in Chapter IX.

We consider the neon atom to have a wave function which is a single Slater determinant built up of ten Clementi-type one-electron orbitals. These can be written as

$$\begin{aligned}\phi_{1s}(\underline{r}) &= \sum_{k=1}^2 d_k e^{-\xi_k r} + \sum_{k=3}^6 d_k r e^{-\xi_k r} \\ \phi_{2s}(\underline{r}) &= \sum_{k=1}^2 e_k e^{-\delta_k r} + \sum_{k=3}^6 e_k r e^{-\delta_k r} \\ \phi_{2pm}(\underline{r}) &= \sum_{k=1}^4 c_k e^{-\zeta_k r} r Y_{1m}(\hat{r})\end{aligned}\tag{7.15}$$

$$\text{where for } k = 1, 2: \quad d_k = \frac{d_k' (2\xi_k)^{3/2}}{\sqrt{8\pi}}, \quad e_k = \frac{e_k' (2\delta_k)^{3/2}}{\sqrt{8\pi}}$$

$$\text{for } k = 3-6: \quad d_k = \frac{(2\xi_k)^{5/2} d_k'}{\sqrt{96\pi}}, \quad e_k = \frac{e_k' (2\delta_k)^{5/2}}{\sqrt{96\pi}}$$

$$\text{and for } k = 1-4: \quad c_k = \frac{(2\zeta_k)^{5/2} c_k'}{\sqrt{24}}$$

The coefficients  $d_k'$ ,  $e_k'$ ,  $c_k'$  and the exponents  $\xi_k$ ,  $\delta_k$ ,  $\zeta_k$  are tabulated by Clementi (1965) (see §7.6 for a further discussion of the neon wave function).

We label the orbitals in the following manner:

$$\begin{aligned}\phi_1 &= \phi_{1s\alpha}, & \phi_2 &= \phi_{1s\beta}, & \phi_3 &= \phi_{2s\alpha}, & \phi_4 &= \phi_{2s\beta}, \\ \phi_5 &= \phi_{2p_1\alpha}, & \phi_6 &= \phi_{2p_0\alpha}, & \phi_7 &= \phi_{2p_{-1}\alpha}, & \phi_8 &= \phi_{2p_1\beta}, \\ \phi_9 &= \phi_{2p_0\beta}, & \phi_{10} &= \phi_{2p_{-1}\beta},\end{aligned}$$

where  $\alpha$  and  $\beta$  denote spin-up and spin-down states respectively.

The Born exchange amplitude is given by

$$g_B(0, k^2) = -\frac{1}{2\pi} \int d\underline{r}_1 \dots d\underline{r}_{11} e^{i\mathbf{k} \cdot \underline{r}_{11}} D\{\phi_1(1) \dots \phi_{10}(10)\} V \quad (7.16)$$

$$\sum_{j \in S} D\{\phi_1^*(1) \dots \phi_j^*(11) \dots \phi_{10}^*(10)\} e^{-i\mathbf{k} \cdot \underline{r}_j}$$

where the potential V is

$$V = -\frac{10}{r_{11}} + \sum_{i=1}^{10} \frac{1}{|\underline{r}_i - \underline{r}_{11}|} \quad (7.17)$$

(see for example Burhop (1961)). D denotes the Slater determinant of the ten orbitals in the bracket following it. The set S is the set of spin-up orbitals and comprises  $\phi_1, \phi_3, \phi_5, \phi_6$  and  $\phi_7$ . The incoming particle can only exchange with one of the same spin, and we suppose this to be spin-up. We write

$$g_B(0, k^2) = \sum_{k=1}^3 I_k \quad (7.18)$$

where

$$I_1 = -\frac{1}{2\pi} \int d\underline{r}_1 \dots d\underline{r}_{11} D\{\phi_1(1) \dots \phi_{10}(10)\} \left(-\frac{10}{r_{11}}\right) \quad (7.19)$$

$$\times \sum_{j \in S} D\{\phi_1^*(1) \dots \phi_j^*(11) \dots \phi_{10}^*(10)\} e^{i\mathbf{k} \cdot (\underline{r}_{11} - \underline{r}_j)}$$

$$I_2 = -\frac{1}{2\pi} \int d\underline{r}_1 \dots d\underline{r}_{11} D\{\phi_1(1) \dots \phi_{10}(10)\} \sum_{j \in S} \sum_{n=1}^{10} \left( \frac{1}{|\underline{r}_n - \underline{r}_{11}|} - \frac{1}{|\underline{r}_{11} - \underline{r}_j|} \right) \quad (7.20)$$

$$\times D\{\phi_1^*(1) \dots \phi_j^*(11) \dots \phi_{10}^*(10)\} e^{i\mathbf{k} \cdot (\underline{r}_{11} - \underline{r}_j)}$$

and

$$I_3 = -\frac{1}{2\pi} \int d\underline{r}_1 \dots d\underline{r}_{11} D\{\phi_1(1) \dots \phi_{10}(10)\} \sum_{j \in S} e^{i\mathbf{k} \cdot (\underline{r}_{11} - \underline{r}_j)} \quad (7.21)$$

$$\times \frac{1}{|\underline{r}_{11} - \underline{r}_j|} D\{\phi_1^*(1) \dots \phi_j^*(11) \dots \phi_{10}^*(10)\} .$$

We consider each of these integrals in turn.

(i) We can rewrite equation (7.19) as

$$I_1 = \frac{5}{\pi} \sum_{j \in S} \int \frac{d\underline{r}_1 \dots d\underline{r}_{11}}{r_{11}} \alpha(11) \phi_1(1) \dots \phi_{10}(10) e^{i\mathbf{k} \cdot (\underline{r}_{11} - \underline{r}_j)} \alpha(j)$$

$$\times \begin{vmatrix} \phi_1(1) & \dots & \phi_1(11) & \dots & \phi_1(10) \\ \vdots & & \vdots & & \vdots \\ \phi_j(1) & \dots & \phi_j(11) & \dots & \phi_j(10) \\ \vdots & & \vdots & & \vdots \\ \phi_{10}(1) & \dots & \dots & \dots & \phi_{10}(10) \end{vmatrix}^*$$

where the asterisk indicates that the complex conjugate of each element is to be taken and where  $\alpha(j)$  denotes the spin of the particle  $j$ .

Now for a non-zero contribution, because of the orthogonality of the states  $\phi_i$ , there is only one surviving term from the determinant, namely the product of the diagonal elements. Thus

$$I_1 = \frac{5}{\pi} \sum_{j \in S} \int d\underline{r}_j \int \frac{d\underline{r}_{11}}{r_{11}} \phi_j(j) \phi_j^*(11) e^{i\mathbf{k} \cdot (\underline{r}_{11} - \underline{r}_j)} .$$

For a given  $j$  the integrations over  $\underline{r}_j$  and  $\underline{r}_{11}$  are separable and so

$$I_1 = \frac{5}{\pi} \sum_{j \in S} X(j) Y(j)$$

where 
$$X(j) = \int d\underline{r}_j e^{-ik \cdot \underline{r}_j} \phi_j(\underline{r}_j) \quad (7.22)$$

and 
$$Y(j) = \int d\underline{r}_{11} e^{ik \cdot \underline{r}_{11}} \frac{\phi_j(\underline{r}_{11})}{r_{11}} \quad (7.23)$$

Now the integrals  $X(j)$  and  $Y(j)$  vanish unless  $\phi_j$  has magnetic quantum number zero and so  $I_1$  reduces to

$$I_1 = \frac{5}{\pi} (X(1)Y(1) + X(3)Y(3) + X(6)Y(6)) \quad (7.24)$$

Using the expansions (7.15) for the one electron orbitals we obtain the following expressions for the X and Y functions

$$X(1) = \sum_{k=1}^2 d_k K(\epsilon_k, 0) + \sum_{k=3}^6 d_k K(\epsilon_k, 1)$$

$$Y(1) = \sum_{k=1}^2 d_k K(\epsilon_k, -1) + \sum_{k=3}^6 d_k K(\epsilon_k, 0)$$

$$X(3) = \sum_{k=1}^2 e_k K(\delta_k, 0) + \sum_{k=3}^6 e_k K(\delta_k, 1)$$

$$Y(3) = \sum_{k=1}^2 e_k K(\delta_k, -1) + \sum_{k=3}^6 e_k K(\delta_k, 0)$$

$$X(6) = i\sqrt{\frac{3}{4\pi}} \sum_{k=1}^4 c_k K_p(\zeta_k, 0)$$

$$Y(6) = -i\sqrt{\frac{3}{4\pi}} \sum_{k=1}^4 c_k K_p(\zeta_k, -1)$$

where 
$$K(\lambda, n) = \int d\underline{r} e^{ik \cdot \underline{r}} e^{-\lambda r} r^n \quad (7.25)$$

and 
$$K_p(\lambda, n) = \frac{\partial}{\partial k} (K(\lambda, n))$$

Values of the  $K$  and  $K_p$  integrals for various values of  $n$  are given in Table 7.1. They satisfy the recurrence relations

$$K(\lambda, n) = -\frac{\partial K}{\partial \lambda}(\lambda, n-1); \quad K_p(\lambda, n) = -\frac{\partial K_p}{\partial \lambda}(\lambda, n-1) \quad (7.26)$$

(ii) In equation (7.20) we can see that the potential part of the integrand is independent of  $\underline{r}_j$ , and so there is an external factor, in  $I_2$ , of

$$\int d\underline{r}_j \phi_j(\underline{r}_j) e^{-i\mathbf{k} \cdot \underline{r}_j}$$

that is, of  $X(j)$  (see equation (7.22)) and this is zero unless  $j=1, 3$  or  $6$ . Thus we can write

$$I_2 = \sum_{j=1,3,6} I_2^{(j)}$$

We consider first  $I_2^{(1)}$ , which from equation (7.20) is given by

$$I_2^{(1)} = -\frac{1}{2\pi} \sum_{n=2}^{10} \int d\underline{r}_1 \dots d\underline{r}_{11} \frac{1}{\sqrt{10!}} \phi_1(1) \dots \phi_{10}(10) e^{i\mathbf{k}(\underline{r}_{11} - \underline{r}_j)}$$

$$\times \frac{1}{|\underline{r}_n - \underline{r}_{11}|} \frac{1}{\sqrt{10!}} \begin{vmatrix} \phi_1(11) & \dots & \phi_1(10) \\ \phi_j(11) & \dots & \phi_j(10) \\ \phi_{10}(1) & \dots & \phi_{10}(10) \end{vmatrix}^*$$

Since, for a given  $n$ , only  $\underline{r}_1$ ,  $\underline{r}_{11}$  and  $\underline{r}_n$  are involved in the integrand, apart from in the wavefunctions, this reduces to

$$I_2^{(1)} = -\frac{1}{2\pi} X(1) \sum_{n=2}^{10} \int d\underline{r}_n \int d\underline{r}_{11} \frac{\phi_n^{(n)} e^{i\mathbf{k} \cdot \underline{r}_{11}}}{|\underline{r}_{11} - \underline{r}_n|}$$

$$\times \left[ \phi_1^*(11) \phi_n^*(n) - \phi_n^*(11) \phi_1^*(n) \delta_{m_n \alpha} \right]$$

Table 7.1

Values of the  $K$  and  $K_p$  functions

n	$K(\lambda, n)$	$K_p(\lambda, n)$
-3	-	$-\frac{4\pi}{k}\left(1 - \frac{\lambda}{k} \tan^{-1} \frac{k}{\lambda}\right)$
-2	-	$\frac{4\pi}{k^2}\left(\frac{\lambda k}{k^2 + \lambda^2} - \tan^{-1} \frac{k}{\lambda}\right)$
-1	$\frac{4\pi}{k^2 + \lambda^2}$	$-\frac{8\pi k}{(k^2 + \lambda^2)^2}$
0	$\frac{8\pi\lambda}{(k^2 + \lambda^2)^2}$	$-\frac{32\pi k\lambda}{(k^2 + \lambda^2)^3}$
1	$\frac{8\pi(3\lambda^2 - k^2)}{(k^2 + \lambda^2)^3}$	$+\frac{32\pi k(k^2 - 5\lambda^2)}{(k^2 + \lambda^2)^4}$
2	$\frac{96\pi\lambda(\lambda^2 - k^2)}{(k^2 + \lambda^2)^4}$	$-\frac{64\pi k\lambda(15\lambda^2 - 9k^2)}{(k^2 + \lambda^2)^5}$
3	$\frac{96\pi(k^4 - 10k^2\lambda^2 + 5\lambda^4)}{(k^2 + \lambda^2)^5}$	-

where  $\delta_{m_n \alpha} = 1$  if  $\phi_n$  has spin  $\alpha$  and is zero otherwise. Thus, if we define the functions  $K_n$  and  $R_n$  by

$$K_n(1s) = \int d\underline{r}_1 \int \frac{d\underline{r}_2 e^{i\underline{k} \cdot \underline{r}_1}}{|\underline{r}_1 - \underline{r}_2|} \phi_1^*(\underline{r}_1) |\phi_n(\underline{r}_2)|^2$$

and

$$R_n(1s) = \int d\underline{r}_1 \int d\underline{r}_2 e^{i\underline{k} \cdot \underline{r}_1} \frac{\phi_1^*(\underline{r}_2) \phi_n^*(\underline{r}_1) \phi_n(\underline{r}_2)}{|\underline{r}_1 - \underline{r}_2|}$$

then

$$I_2^{(1)} = -\frac{1}{2\pi} X(1) \left[ \sum_{\substack{n=2 \\ n \neq 1}}^{10} K_n(1s) - \sum_{\substack{n \in S \\ n \neq 1}} R_n(1s) \right]$$

The other two terms,  $I_2^{(3)}$  and  $I_2^{(6)}$  are similar, and we have the general result

$$I_2^{(j)} = -\frac{1}{2\pi} X(j) \left[ \sum_{\substack{n=1 \\ n \neq j}}^{10} K_n(j) - \sum_{\substack{n \in S \\ n \neq j}} R_n(j) \right] \quad (7.27)$$

By using the forms for the wave functions given in equation (7.15) we can express the functions  $K_n$  and  $R_n$  in terms of P integrals, which are of the form

$$\int d\underline{r} \int d\underline{R} \frac{e^{i\underline{k} \cdot \underline{r}} e^{-\lambda r} e^{-\mu R} R^s r^t}{|\underline{r} - \underline{R}|} Y_{\ell m}(\hat{\underline{R}}) Y_{\ell' m'}(\hat{\underline{r}}),$$

s and t being non-negative integers and the  $Y_{\ell m}$  being spherical harmonics. We give a list of these P functions in Appendix D, where we also express them in terms of the K and  $K_p$  functions defined in equation (7.25). We therefore treat them as known functions.

Considering first the function  $I_2^{(1)}$  we obtain



$$\begin{aligned}
 K_2(1s) &= \int d\underline{r} \int d\underline{R} \frac{e^{i\underline{k} \cdot \underline{r}} \phi_1^*(r) |\phi_2(R)|^2}{|\underline{r} - \underline{R}|} \\
 &\equiv G_1(\underline{d}, \underline{\xi}, \underline{d}, \underline{\xi}, \underline{d}, \underline{\xi}) , \text{ say} \\
 &= \sum_{j=1}^2 d_j \left[ \sum_{k=1}^2 \sum_{\ell=1}^2 d_k d_\ell P_1(\xi_j, \alpha_{k\ell}) \right. \\
 &\quad + \sum_{k=1}^2 \sum_{\ell=3}^6 d_k d_\ell P_7(\xi_j, \alpha_{k\ell}) + \sum_{k=3}^6 \sum_{\ell=1}^2 d_k d_\ell P_7(\xi_j, \alpha_{k\ell}) \\
 &\quad \left. + \sum_{k=3}^6 \sum_{\ell=3}^6 d_k d_\ell P_2(\xi_j, \alpha_{k\ell}) \right] \\
 &\quad + \sum_{j=3}^6 d_j \left[ \sum_{k=1}^2 \sum_{\ell=1}^2 d_k d_\ell P_5(\xi_j, \alpha_{k\ell}) + \sum_{k=1}^2 \sum_{\ell=3}^6 d_k d_\ell P_3(\xi_j, \alpha_{k\ell}) \right. \\
 &\quad \left. + \sum_{k=3}^6 \sum_{\ell=1}^2 d_k d_\ell P_3(\xi_j, \alpha_{k\ell}) + \sum_{k=3}^6 \sum_{\ell=3}^6 d_k d_\ell P_6(\xi_j, \alpha_{k\ell}) \right]
 \end{aligned}$$

where  $\alpha_{k\ell} = \xi_k + \xi_\ell$ .

Similarly

$$K_3(1s) = K_4(1s) = G_1(\underline{d}, \underline{\xi}, \underline{e}, \underline{\delta}, \underline{e}, \underline{\delta}) .$$

For  $i \in [5, 10]$ , we have

$$K_i(1s) = \int d\underline{r} \int d\underline{R} \frac{e^{i\underline{k} \cdot \underline{r}} \phi_1^*(r) |\phi_i(R)|^2}{|\underline{r} - \underline{R}|} .$$

These six terms can be added together by noting that

$$|Y_{10}|^2 + 2|Y_{11}|^2 = 3/4\pi . \quad \text{We obtain}$$

$$\sum_{i=5}^{10} K_i(1s) = \frac{6}{4\pi} \left[ \sum_{k=1}^2 d_k \sum_{j=1}^4 \sum_{\ell=1}^4 c_j c_\ell P_2(\xi_k, \zeta_j + \zeta_\ell) \right. \\ \left. + \sum_{k=3}^6 d_k \sum_{j=1}^4 \sum_{\ell=1}^4 c_j c_\ell P_6(\xi_k, \zeta_j + \zeta_\ell) \right] \\ \equiv G_2(\underline{d}, \underline{\xi}, \underline{c}, \underline{\zeta}, \underline{c}, \underline{\zeta}), \text{ say.}$$

We now consider the R functions, first  $R_3(1s)$ :

$$R_3(1s) = \int d\underline{r} \int d\underline{R} \phi_3^*(\underline{r}) e^{\underline{i}k \cdot \underline{r}} \phi_3(\underline{R}) \phi_1^*(\underline{R}) \\ G_1(\underline{e}, \underline{\delta}, \underline{d}, \underline{\xi}, \underline{e}, \underline{\delta}) .$$

The remaining three R functions can be added together,

$$\sum_{i=5}^7 R_i(1s) = \sum_{i=5}^7 \int d\underline{r} \int d\underline{R} \frac{\phi_1^*(\underline{R}) e^{\underline{i}k \cdot \underline{r}} \phi_i^*(\underline{r}) \phi_i(\underline{R})}{|\underline{r} - \underline{R}|} \\ \equiv G_3'(\underline{d}, \underline{\xi}, \underline{c}, \underline{\zeta}, \underline{c}, \underline{\zeta}), \text{ say} \\ = \sum_{k=1}^2 \sum_{j=1}^4 \sum_{\ell=1}^4 d_k c_j c_\ell P_4(\zeta_j, \xi_k + \zeta_\ell) \\ - \sum_{k=3}^6 \sum_{j=1}^4 \sum_{\ell=1}^4 d_k c_j c_\ell P_8(\zeta_j, \xi_k + \zeta_\ell) .$$

These are all the functions we need to evaluate  $I_2^{(1)}$ . The integrals involved in  $I_2^{(3)}$  ( $K_n(2s)$  and  $R_n(2s)$ ) can be written down in an analogous way. They are:

$$K_1(2s) = K_2(2s) = G_1(\underline{e}, \underline{\delta}, \underline{d}, \underline{\xi}, \underline{d}, \underline{\xi})$$

$$K_4(2s) = G_1(\underline{e}, \underline{\delta}, \underline{e}, \underline{\delta}, \underline{e}, \underline{\delta})$$

$$\sum_{i=5}^{10} K_i(2s) = G_2(\underline{e}, \underline{\delta}, \underline{c}, \underline{\zeta}, \underline{c}, \underline{\zeta})$$

$$R_1(2s) = G_1(\underline{d}, \underline{\xi}, \underline{e}, \underline{\delta}, \underline{d}, \underline{\xi})$$

$$\sum_{i=5}^7 R_i(2s) = G_3'(\underline{e}, \underline{\delta}, \underline{c}, \underline{\zeta}, \underline{c}, \underline{\zeta}) .$$

The remaining case is  $I_2^{(6)}$ . We have

$$\begin{aligned} K_1(2p) &= \int d\underline{r} \int d\underline{R} \frac{\phi_6^*(\underline{r}) |\phi_1(\underline{R})|^2 e^{i\underline{k} \cdot \underline{r}}}{|\underline{r} - \underline{R}|} \\ &= G_4(\underline{c}, \underline{\zeta}, \underline{d}, \underline{\xi}, \underline{d}, \underline{\xi}) \\ &= \sum_{\ell=1}^4 \left[ \sum_{k=1}^2 \sum_{j=1}^2 c_\ell d_k d_j P_9(\zeta_\ell, \xi_k + \xi_j) \right. \\ &\quad - 2 \sum_{k=3}^6 \sum_{j=1}^2 c_\ell d_k d_j P_{15}(\zeta_\ell, \xi_k + \xi_j) \\ &\quad \left. + \sum_{k=3}^6 \sum_{j=3}^6 c_\ell d_k d_j P_{10}(\zeta_\ell, \xi_k + \xi_j) \right] . \end{aligned}$$

Similarly  $K_3(2p) = K_4(2p) = G_4(\underline{c}, \underline{\zeta}, \underline{e}, \underline{\delta}, \underline{e}, \underline{\delta})$  .

Also

$$\begin{aligned} R_1(2p) &= G_5(\underline{d}, \underline{\xi}, \underline{c}, \underline{\zeta}, \underline{d}, \underline{\xi}) \\ &= \sum_{\ell=1}^4 c_\ell \left\{ \sum_{k=1}^2 \sum_{j=1}^2 P_{13}(\xi_k, \zeta_\ell + \xi_j) \right. \\ &\quad \left. - \sum_{k=3}^6 \sum_{j=1}^2 P_{16}(\xi_k, \zeta_\ell + \xi_j) \right\} \end{aligned}$$

$$\begin{aligned}
 & - \sum_{k=1}^2 \sum_{\ell=3}^6 P_{17}(\xi_k, \zeta_\ell + \xi_j) \\
 & + \left. \sum_{k=3}^6 \sum_{j=3}^6 P_{14}(\xi_k, \zeta_\ell + \xi_j) \right\} d_k d_j,
 \end{aligned}$$

and  $R_3(2p) = G_5(\underline{c}, \underline{\delta}, \underline{c}, \underline{\zeta}, \underline{e}, \underline{\delta})$ .

The remaining integrals can be combined (see equations D4 and D5) and we obtain the expressions

$$\begin{aligned}
 \sum_{\substack{i=5 \\ i \neq 6}}^{10} K_i(2p) &= \sum_{k=1}^4 \sum_{\ell=1}^4 \sum_{j=1}^4 c_j c_k c_\ell P_{11}(\zeta_j, \zeta_\ell + \zeta_k) \\
 R_5(2p) + R_7(2p) &= \sum_{k=1}^4 \sum_{\ell=1}^4 \sum_{j=1}^4 c_j c_k c_\ell P_{12}(\zeta_j, \zeta_\ell + \zeta_k).
 \end{aligned}$$

We have now considered all the functions necessary to evaluate the second term in the expansion (7.17) for  $g_B(0, k^2)$ .

(iii) We next consider the third integral,  $I_3$ , which contributes to  $g_B(0, k^2)$ ; it is given by equation (7.21). We have

$$\begin{aligned}
 I_3 &= -\frac{1}{2\pi} \int_{j \in S} \frac{dr_1 - dr_{11}}{|r_{11} - r_i|} e^{ik \cdot (r_{11} - r_j)} \phi_1(1) \dots \phi_{10}(10) \\
 &\times \begin{vmatrix} \phi_1(1) & \dots & \phi_1(11) & \dots & \phi_1(10) \\ \vdots & & & & \\ \phi_j(1) & \dots & \dots & \dots & \phi_j(10) \\ \vdots & & & & \\ \phi_{10}(1) & \dots & \dots & \dots & \phi_{10}(10) \end{vmatrix} *
 \end{aligned}$$

Now for a given  $j$  only  $\underline{r}_j$  and  $\underline{r}_{11}$  are involved in the integrand apart from in the wave function, and so, because of the orthogonality of the one electron functions  $\phi_i$ , there is only one non-vanishing term in the determinant. Thus

$$I_3 = -\frac{1}{2\pi} \sum_{j \in S} \int d\underline{r}_j \int d\underline{r}_{11} \frac{e^{i\mathbf{k} \cdot (\underline{r}_{11} - \underline{r}_j)}}{|\underline{r}_j - \underline{r}_{11}|} \phi_j(j) \phi_j^*(11) \quad (7.28)$$

$$\equiv \sum_{j \in S} I_3^{(j)}, \text{ say,}$$

where  $j$  takes the values 1, 3, 5, 6 and 7. If we define the function  $M(\lambda, \mu)$  by

$$M(\lambda, \mu) = \int d\underline{r} \int d\underline{R} \frac{e^{i\mathbf{k} \cdot (\underline{r} - \underline{R})} e^{-\lambda r - \mu R}}{|\underline{r} - \underline{R}|} \quad (7.29)$$

and use the expressions (7.15) for the one-electron orbitals  $\phi_i$ , we can write  $I_3^{(1)}$  in the form

$$I_3^{(1)} = -\frac{1}{2\pi} \sum_{k=1}^2 \sum_{j=1}^2 d_k d_j M(\xi_k, \xi_j) + \sum_{k=1}^2 \sum_{j=3}^6 d_k d_j \frac{\partial}{\partial \xi_j} M(\xi_k, \xi_j) \quad (7.30)$$

$$+ \sum_{k=3}^6 \sum_{j=1}^2 d_k d_j \frac{\partial M(\xi_k, \xi_j)}{\partial \xi_k} + \sum_{k=3}^6 \sum_{j=3}^6 d_k d_j \frac{\partial^2 M(\xi_k, \xi_j)}{\partial \xi_j \partial \xi_k}$$

The integral  $M$  is rather complicated but was evaluated by Bransden et al. (1954) and details of the analysis are given in Appendix B. The result obtained is

$$M(\lambda, \mu) = \frac{32\pi^2}{k(\lambda^2 - \mu^2)^2} \left\{ k \left( \frac{\mu}{\lambda^2 + k^2} + \frac{\lambda}{\mu^2 + k^2} \right) - \frac{4\mu\lambda}{\lambda^2 - \mu^2} \left( \tan^{-1} \frac{\lambda}{k} - \tan^{-1} \frac{\mu}{k} \right) \right\} \quad (7.31)$$

The derivative of  $M(\lambda, \mu)$  with respect to  $\lambda$ ,  $M^{(\lambda)}(\lambda, \mu)$  is thus given by

$$M^{(\lambda)}(\lambda, \mu) = \frac{32\pi^2}{k} \left( \frac{k}{(\mu^2 + k^2)^2 (\lambda^2 - \mu^2)^2} - \frac{4\lambda^3 k}{(\mu^2 + k^2)(\lambda^2 - \mu^2)^3} - \frac{2\lambda\mu k}{(\lambda^2 + k^2)^2 (\lambda^2 - \mu^2)^2} - \frac{8\lambda\mu k}{(\lambda^2 + k^2)(\lambda^2 - \mu^2)^3} - \frac{4\mu}{(\lambda^2 - \mu^2)^3} \left\{ \tan^{-1} \left( \frac{\lambda}{k} \right) - \tan^{-1} \left( \frac{\mu}{k} \right) \right\} \left( 1 - \frac{6\lambda^2}{\lambda^2 - \mu^2} \right) \right) \quad (7.32)$$

Since  $M(\lambda, \mu)$  is symmetric in  $\lambda$  and  $\mu$ ,  $\frac{\partial M(\lambda, \mu)}{\partial \mu}$  is obtained by interchanging  $\lambda$  and  $\mu$  in this last equation. Also, by differentiating the function  $M^{(\lambda)}(\lambda, \mu)$  with respect to  $\mu$ , we obtain the function  $M_1(\lambda, \mu)$ ,

$$M_1(\lambda, \mu) = \frac{\partial^2 M(\lambda, \mu)}{\partial \lambda \partial \mu} = \frac{64\pi^2}{k(\lambda^2 - \mu^2)^3} \left\{ \frac{2(5\lambda^4 + 5\mu^4 + 38\lambda^2\mu^2)}{(\lambda^2 - \mu^2)^2} \left( \tan^{-1} \frac{\lambda}{k} - \tan^{-1} \frac{\mu}{k} \right) - \frac{4k}{(\lambda^2 - \mu^2)} \left( \frac{\mu(\mu^2 + 5\lambda^2)}{\mu^2 + k^2} + \frac{\lambda(\lambda^2 + 5\mu^2)}{\lambda^2 + k^2} \right) + k \left( \frac{\mu(3\lambda^2 + \mu^2)}{(\mu^2 + k^2)^2} - \frac{\lambda(3\mu^2 + \lambda^2)}{(\lambda^2 + k^2)^2} \right) \right\} \quad (7.33)$$

The expressions (7.31), (7.32) and (7.33) are valid for  $\lambda \neq \mu$ . When  $\lambda$  and  $\mu$  are equal it is necessary to expand these expressions in powers of  $(\lambda^2 - \mu^2)$  and take the limit  $\lambda \rightarrow \mu$ . We use the results

$$\tan^{-1} A - \tan^{-1} B = \tan^{-1} \left( \frac{A - B}{AB + 1} \right)$$

and

$$\tan^{-1} x = x - \frac{x^3}{3} + \frac{x^5}{5} + O(x^7)$$

and then after a considerable amount of straightforward but tedious analysis we obtain

$$M(\lambda, \lambda) = \frac{4\pi^2}{\lambda^3} \left[ \frac{3k^4 + 10\lambda^2 k^2 + 15\lambda^4}{3(k^2 + \lambda^2)^3} \right],$$

$$M^{(\lambda)}(\lambda, \lambda) = \frac{2\pi^2}{2\lambda^4 (k^2 + \lambda^2)^6} \left[ -9k^{10} - 55k^8 \lambda^2 - 138k^6 \lambda^4 - 222k^4 \lambda^6 - 205k^2 \lambda^8 - 75\lambda^{10} \right]$$

(7.34)

and

$$M_1(\lambda, \lambda) = \frac{4\pi^2}{3\lambda^5 (k^2 + \lambda^2)^5} \left[ 9k^8 + 46\lambda^2 k^6 + \frac{484}{5} \lambda^4 k^4 + 82\lambda^6 k^2 + 99\lambda^8 \right].$$

It was at this point that an error in the helium work of Bransden and McDowell (1969) arose. The order of limit-taking and differentiation was reversed and  $M_1(\lambda, \lambda)$  was taken to be  $\frac{\partial^2 M(\lambda, \lambda)}{\partial \lambda^2}$ . It is easily seen that this is incorrect and not the same as

$\lim_{\mu \rightarrow \lambda} M_1(\lambda, \mu)$ .

We can thus evaluate the function  $I_3^{(1)}$ , given by equation (7.30). The second term which contributes to  $I_3$  is  $I_3^{(3)}$ . The analysis is exactly parallel to that described above for  $I_3^{(1)}$  with the constants  $d_k$  and  $\xi_k$  which appear in (7.30) replaced by  $e_k$  and  $\delta_k$  respectively.

The function  $I_3^{(6)}$  is given by

$$I_3^{(6)} = -\frac{1}{2\pi} \int_{\underline{r}_1} d\underline{r}_1 \int_{\underline{r}_2} d\underline{r}_2 \frac{e^{i\underline{k} \cdot (\underline{r}_1 - \underline{r}_2)} \phi_6^*(\underline{r}_1) \phi_6(\underline{r}_2)}{|\underline{r}_2 - \underline{r}_1|}$$

$$= -\frac{1}{2\pi} \sum_{k=1}^4 \sum_{j=1}^4 c_k c_j M_2(\zeta_k, \zeta_j)$$

where

$$M_2(\lambda, \mu) = \frac{\partial^2 N(\lambda, \mu)}{\partial \lambda \partial \mu}$$

with

$$N(\lambda, \mu) = \int_{\underline{r}_1} d\underline{r}_1 \int_{\underline{r}_2} d\underline{r}_2 \frac{e^{i\underline{k} \cdot (\underline{r}_1 - \underline{r}_2)} e^{-\lambda r_1} e^{-\mu r_2}}{|\underline{r}_1 - \underline{r}_2|} Y_{10}^*(\hat{\underline{r}}_1) Y_{10}^*(\hat{\underline{r}}_2)$$

Now it is easily seen that

$$\frac{1}{2\pi^2} \int \frac{dp}{p^2} e^{i\underline{p} \cdot (\underline{r}_1 - \underline{r}_2)} = \frac{1}{|\underline{r}_1 - \underline{r}_2|} \quad (7.35)$$

and thus

$$N(\lambda, \mu) = \frac{1}{2\pi^2} \int \frac{dp}{p^2} \left( \int_{\underline{r}_1} d\underline{r}_1 e^{i(\underline{k} + \underline{p}) \cdot \underline{r}_1} e^{-\lambda r_1} Y_{10}^*(\hat{\underline{r}}_1) \right) \left( \int_{\underline{r}_2} d\underline{r}_2 e^{-i(\underline{k} + \underline{p}) \cdot \underline{r}_2} e^{-\mu r_2} Y_{10}(\hat{\underline{r}}_2) \right) \quad (7.36)$$

But  $e^{i\underline{k} \cdot \underline{r}} = 4\pi \sum_{\alpha=0}^{\infty} \sum_{\beta=-\alpha}^{\alpha} i^{\alpha} j_{\alpha}(kr) Y_{\alpha\beta}^*(\hat{\underline{k}}) Y_{\alpha\beta}(\hat{\underline{r}})$ , and hence, on putting

$\underline{k} + \underline{p} = \underline{k}$  and carrying out the angular integration over  $\underline{r}_1$  we obtain for the  $\underline{r}_1$  integral involved in  $N(\lambda, \mu)$  the result

$$\int_{\underline{r}_1} d\underline{r}_1 e^{i(\underline{k} + \underline{p}) \cdot \underline{r}_1} e^{-\lambda r_1} Y_{10}^*(\hat{\underline{r}}_1) = 4\pi Y_{10}^*(\hat{\underline{k}}) i \int_0^{\infty} r_1^2 e^{-\lambda r_1} j_1(kr_1) dr_1$$



where  $j_1$  is the spherical Bessel function of order one. Since  $j_1(kr) = (\sin kr - kr \cos kr)/(kr)^2$  this radial integral has the value  $2k/(\lambda^2+k^2)^2$ . A similar result is obtained from the  $r_2$  integration in equation (7.36) and thus

$$N(\lambda, \mu) = 32 \int \frac{d\underline{p}}{p^2} \frac{Y_{10}^*(\underline{\hat{K}}) Y_{10}(\underline{\hat{K}}) K^2}{(\lambda^2+k^2)^2 (\mu^2+k^2)^2} .$$

But  $\underline{p} = \underline{K} - \underline{k}$ , and so, choosing the axes so that  $\underline{k}$  lies along the line  $\theta_k = 0$ , we have

$$N(\lambda, \mu) = 32 \int_0^\infty \frac{K^4 dK}{(\lambda^2+k^2)^2 (\mu^2+k^2)^2} \int_0^{2\pi} d\phi \int_0^\pi \frac{\sin\theta_K d\theta_K Y_{10}^*(\underline{\hat{K}}) Y_{10}(\underline{\hat{K}})}{k^2+K^2-2Kk \cos\theta_K}$$

Now  $Y_{10}(\underline{\hat{K}}) = \sqrt{\frac{3}{4\pi}} \cos\theta_K$  and so, making the substitution  $x = \cos\theta_K$ , the angular part of  $N(\lambda, \mu)$  is

$$\frac{3}{2} \int_{-1}^1 \frac{x^2 dx}{(k^2+K^2-2Kkx)}$$

That is,

$$N(\lambda, \mu) = 48 \int_0^\infty \frac{K^4 dK}{(K^2+\lambda^2)^2 (K^2+\mu^2)^2} \int_{-1}^1 \frac{x^2 dx}{(K^2+k^2-2Kkx)} . \tag{7.37}$$

We now turn to the remaining functions,  $I_3^{(5)}$  and  $I_3^{(7)}$  which contribute to  $I_3$ . From equations (7.28) and (7.15) we obtain

$$I_3^{(5)} = I_3^{(7)} = -\frac{1}{2\pi} \sum_{k=1}^4 \sum_{j=1}^4 c_k c_j M_3(\zeta_k, \zeta_j)$$

where  $M_3(\lambda, \mu) = \frac{\partial^2 N_3(\lambda, \mu)}{\partial \lambda \partial \mu}$  (7.38)

with

$$N_3(\lambda, \mu) = \int_{\underline{r}_1} d\underline{r}_1 \int_{\underline{r}_2} d\underline{r}_2 \frac{e^{i\underline{k} \cdot (\underline{r}_1 - \underline{r}_2)}}{|\underline{r}_1 - \underline{r}_2|} e^{-\lambda r_1} e^{-\mu r_2} Y_{11}^*(\hat{\underline{r}}_1) Y_{11}(\hat{\underline{r}}_2) .$$

This function  $N_3$  can be simplified by following through the method just described for  $N$ , to give

$$N_3(\lambda, \mu) = 24 \int_0^\infty \frac{K^4 dK}{(K^2 + \lambda^2)^2 (K^2 + \mu^2)^2} \int_{-1}^1 \frac{(1-x^2) dx}{(K^2 + k^2 - 2K kx)} .$$

By comparison with equation (7.37) we see that

$$N_3(\lambda, \mu) = 24 \int_0^\infty \frac{K^4 dK}{(K^2 + \lambda^2)^2 (K^2 + \mu^2)^2} \int_{-1}^1 \frac{dx}{(K^2 + k^2 - 2K kx)} - \frac{1}{2} N(\lambda, \mu) .$$

The contribution  $I_3^{(A)}$  to  $I_3$  from the three terms  $I_3^{(5)}$ ,  $I_3^{(6)}$  and  $I_3^{(7)}$  is therefore given by

$$I_3^{(A)} = \sum_{j=5,6,7} I_3^{(j)} = -\frac{1}{2\pi} \sum_{j=1}^4 \sum_{k=1}^4 c_k c_j M^A(\zeta_k, \zeta_j) \quad (7.39)$$

where

$$M^A(\lambda, \mu) = \frac{\partial^2 M^A(\lambda, \mu)}{\partial \lambda \partial \mu} \quad (7.40)$$

and  $N^A(\lambda, \mu) = N(\lambda, \mu) + 2N_3(\lambda, \mu) .$

That is

$$N^A(\lambda, \mu) = 48 \int_0^\infty \frac{K^4 dK}{(K^2 + \lambda^2)^2 (K^2 + \mu^2)^2} \int_{-1}^1 \frac{dx}{(K^2 + k^2 - 2K kx)} .$$

The integration over  $x$  is now trivial and we obtain as the final expression for  $N^A(\lambda, \mu)$ ,

$$N^A(\lambda, \mu) = \frac{48}{k} \int_0^{\infty} \frac{K^3 dK}{(K^3 + \lambda^2)^2 (K^2 + \mu^2)^2} \log \left| \frac{K + k}{K - k} \right| \quad (7.41)$$

The function  $M^A(\lambda, \mu)$  given by equations (7.40) and (7.41) can be evaluated numerically by using Gauss-Laguerre and Krilov quadratures, and details are given in Appendix C. Thus we can evaluate the final contribution to  $I_3$ , namely  $I_3^{(A)}$ , given by equation (7.39).

This completes the analysis involved in the calculation of the Born exchange amplitude,  $g_B(0, k^2)$  for non-zero energy,  $k^2$ .

#### 7.4. The Special Case of Zero Energy

In the case of zero energy ( $k^2 = 0$ ) for the incoming electron, many of the integrals and functions involved in the calculation of the Born exchange amplitude,  $g_B(0, k^2)$ , simplify. It can be seen from Table 7.1 that each of the  $K_p$  functions vanishes whilst the  $K$  functions remain non-zero. Thus several of the  $P$  functions, namely,  $P_9, P_{10}, P_{11}, P_{12}, P_{13}, P_{14}, P_{15}, P_{16}$  and  $P_{17}$  are zero, and the others are much simpler. Also  $X(6)$  and  $Y(6)$ , defined by equations (7.22) and (7.23) vanish. Therefore, both  $I_1$  and  $I_2$  simplify considerably since they are composed entirely of  $X, Y$  and  $P$  functions.

We have in equations (7.31), (7.32) and (7.33) expressions for the functions  $M, M^{(\lambda)}$  and  $M_1$  (for  $\lambda \neq \mu$ ) which are involved in the term  $I_3^{(1)}$  of the Born exchange amplitude. We cannot put  $k^2$  equal to zero in these equations immediately, but by expanding in powers of  $k$  and taking the limit as  $k \rightarrow 0$  we easily obtain the required results (see also Chapter IX). For  $\lambda = \mu$  the results for the limiting case are obvious from equations (7.34).

The remaining function we need to consider is  $M^A(\lambda, \mu)$  (see equation (7.39)). It is related to the function  $N^A$  (which is given by

equation (7.41)) by equation (7.40). We can take the limit as  $k^2$  tends to zero in equation (7.41) if we expand the logarithmic term, and we obtain

$$N_0^A(\lambda, \mu) = \lim_{k^2 \rightarrow 0} N^A(\lambda, \mu) = 96 \int_0^\infty \frac{K^2 dK}{(K^2 + \lambda^2)^2 (K^2 + \mu^2)^2} .$$

This integral is analytic and can be evaluated by integrating round a sufficiently large semi-circular contour in the positive imaginary plane with centre at the origin. Inside this contour, there are double poles at the points  $K = \lambda i$  and  $K = \mu i$ . The residues at these poles are easily found to be

$$-\frac{i(\mu^2 + 3\lambda^2)}{4\lambda(\mu^2 - \lambda^2)^3} \quad \text{and} \quad -\frac{i(\lambda^2 + 3\mu^2)}{4\mu(\lambda^2 - \mu^2)^3} ,$$

respectively. Therefore by the Residue Theorem,

$$N_0^A(\lambda, \mu) = \frac{24\pi}{\lambda\mu(\lambda+\mu)^3} ,$$

and by equation (7.40)

$$\lim_{k^2 \rightarrow 0} M^A(\lambda, \mu) = \frac{96\pi(\lambda^2 + 5\lambda\mu + \mu^2)}{\lambda^2 \mu^2 (\lambda + \mu)^5} .$$

The value of the Born exchange scattering amplitude at zero energy is therefore found by the methods of the previous section, §7.3, with the simplifications mentioned above.

### 7.5. The Born Direct Scattering Amplitude $f_B(0, k^2)$

In this section we discuss the Born approximation to the direct part of the forward scattering amplitude for elastic electron-neon collisions. This is given by

$$f_B(0, k^2) = -\frac{1}{2\pi} \int d\underline{r}_1 \dots d\underline{r}_{11} D\{\phi_1(1) \dots \phi_{10}(10)\} \cdot V D\{\phi_1^*(1) \dots \phi_{10}^*(10)\}$$

where D denotes the Slater determinant of the one-electron orbitals

$\phi_i$  ( $i = 1-10$ ) which are given by equation (7.15). The potential is defined in equation (7.17) and can be written as

$$V = \sum_{i=1}^{10} \left( \frac{1}{|\underline{r}_i - \underline{r}_{11}|} - \frac{1}{r_{11}} \right)$$

Then, since the orbitals are orthogonal, we have

$$f_B(0, k^2) = -\frac{1}{2\pi} \sum_{i=1}^{10} \int d\underline{r}_1 \dots d\underline{r}_{11} \phi_i(\underline{r}_i) \phi_i^*(\underline{r}_i) \left( \frac{1}{|\underline{r}_i - \underline{r}_{11}|} - \frac{1}{r_{11}} \right)$$

where the summation is over the states  $\phi_i$ .

Now by using the expansion (2.1) it can be shown that

$$\int d\underline{r}_{11} \left( \frac{1}{|\underline{r}_i - \underline{r}_{11}|} - \frac{1}{r_{11}} \right) = -\frac{2\pi}{3} r_i^2$$

Therefore

$$f_B(0, k^2) = \frac{1}{3} \sum_{i=1}^{10} \int d\underline{r} |\phi_i(\underline{r})|^2 r^2 = \frac{1}{3} \sum_{i=1}^{10} F_i$$

where  $F_i = \int d\underline{r} r^2 |\phi_i(\underline{r})|^2$ . The integrals  $F_i$  can be evaluated by using equation (7.15). For  $i = 1$ , we have

$$F_1 = \int d\underline{r} r^2 \left( \sum_{k=1}^2 \sum_{j=1}^2 d_k d_j e^{-(\xi_k + \xi_j)r} + 2r \sum_{k=1}^2 \sum_{j=3}^6 d_k d_j e^{-(\xi_k + \xi_j)r} + r^2 \sum_{k=3}^6 \sum_{j=3}^6 d_k d_j e^{-(\xi_k + \xi_j)r} \right)$$

Now  $\int r^n e^{-\alpha r} dr = \frac{4\pi(n+2)!}{\alpha^{n+3}}$  and thus

$$F_1 = 4\pi \left( 24 \sum_{k=1}^2 \sum_{j=1}^2 \frac{d_k d_j}{(\xi_k + \xi_j)^5} + 240 \sum_{k=1}^2 \sum_{j=3}^6 \frac{d_k d_j}{(\xi_k + \xi_j)^6} + 720 \sum_{k=3}^6 \sum_{j=3}^6 \frac{d_k d_j}{(\xi_k + \xi_j)^7} \right).$$

Clearly  $F_2 = F_1$  and  $F_3 = F_4$ ;  $F_3$  is obtained from  $F_1$  by replacing the constants  $d_k, d_j, \xi_k$  and  $\xi_j$  by  $e_k, e_j, \delta_k$  and  $\delta_j$  respectively. The remaining integrals  $F_i$  can be summed and we have

$$\sum_{i=5}^{10} F_i = 2 \int d\underline{r} r^2 \sum_{k=1}^4 \sum_{\ell=1}^4 c_k c_\ell e^{-(\zeta_k + \zeta_\ell)} r^2 \left[ |Y_{10}(\underline{\hat{r}})|^2 + 2|Y_{11}(\underline{\hat{r}})|^2 \right].$$

But  $|Y_{10}(\underline{\hat{r}})|^2 + 2|Y_{11}(\underline{\hat{r}})|^2 = \frac{3}{4\pi}$ . Therefore

$$\begin{aligned} \sum_{i=5}^{10} F_i &= \frac{6}{4\pi} \int d\underline{r} r^4 \sum_{k=1}^4 \sum_{\ell=1}^4 c_k c_\ell e^{-(\zeta_k + \zeta_\ell)} r \\ &= \frac{6}{4\pi} 4\pi \sum_{k=1}^4 \sum_{\ell=1}^4 \frac{c_k c_\ell 720}{(\zeta_k + \zeta_\ell)^7}. \end{aligned}$$

The final result for the direct scattering amplitude is then

$$\begin{aligned} f_D(0, k^2) &= \frac{8\pi}{3} \left[ 24 \sum_{k=1}^2 \sum_{j=1}^2 \left( \frac{d_k d_j}{(\xi_k + \xi_j)^5} + \frac{e_k e_j}{(\delta_k + \delta_j)^5} \right) \right. \\ &\quad + 240 \sum_{k=1}^2 \sum_{j=3}^6 \left( \frac{d_k d_j}{(\xi_k + \xi_j)^6} + \frac{e_k e_j}{(\delta_k + \delta_j)^6} \right) \\ &\quad \left. + 720 \sum_{k=3}^6 \sum_{j=3}^6 \left( \frac{d_k d_j}{(\xi_k + \xi_j)^7} + \frac{e_k e_j}{(\delta_k + \delta_j)^7} \right) + \frac{2160}{4\pi} \sum_{k=1}^4 \sum_{j=1}^4 \frac{c_k c_j}{(\zeta_k + \zeta_j)^7} \right] \end{aligned} \quad (7.42)$$

It can be seen that  $f_D(0, k^2)$  is independent of the energy  $k^2$ .

Table 7.2

The parameters in the Ne ground state wavefunction

<u>Type</u>	<u>k</u>	<u><math>\xi_k = \delta_k</math></u>	<u><math>d_k</math></u>	<u><math>e_k</math></u>	<u>Type</u>	<u><math>\zeta_k</math></u>	<u><math>c_k</math></u>
<u>(a) Clementi 6-state</u>							
1s	1	9.5735	0.9309	-0.2317	2p	1.4700	0.2243
1s	2	15.4496	0.0461	-0.0044	2p	2.3717	0.5183
2s	3	1.9550	-0.0009	0.1820	2p	4.4545	0.3390
2s	4	2.8462	0.0032	0.6611	2p	9.4550	0.0177
2s	5	4.7746	-0.0018	0.3237			
2s	6	7.7131	0.0354	-0.1424			
<u>(b) Clementi 5-state</u>							
1s	1	9.0670	0.9447	-0.1646	2p	2.3717	0.5183
1s	2	14.0938	0.0866	-0.0502	2p	4.4545	0.3390
2s	3	3.8312	0.0056	0.5313	2p	1.4700	0.2243
2s	4	9.7569	-0.0315	-0.1022	2p	9.4550	0.0177
2s	5	2.3498	-0.0009	0.5688			
<u>(c) Weber et al.</u>							
1s	1	14.2938	0.08088	-0.00685	2p	9.4550	0.0170
1s	2	8.0964	1.12920	-0.29117	2p	4.5545	0.3236
2s	3	8.7569	-0.23474	0.00215	2p	2.3217	0.6040
2s	4	3.4312	-	0.78810	2p	1.3052	0.1566
2s	5	1.9656	-	0.31173			

### 7.6. Results for the Born scattering amplitudes

(a)  $\underline{f_B(0, k^2) = f_B}$

The Born approximation to the direct scattering amplitude, as given in equation (7.42), was evaluated using the Clementi wavefunction which is given in equation (7.15). The values of the constants  $d_k$ ,  $e_k$ ,  $c_k$ ,  $\xi_k$ ,  $\delta_k$  and  $\zeta_k$  are shown in Table 7.2; we shall refer to this wavefunction as the Clementi 6-state wavefunction. It is obtained by Clementi who uses the Roothaan-Hartree-Fock method, which is discussed in detail by Roothaan and Bagus (1963). Clementi also gives a different wavefunction in which each of the 1s and 2s orbitals involves only five exponents and five coefficients. We have calculated  $f_B$  using this Clementi 5-state wavefunction. The results obtained for  $f_B$  from these two types of wavefunction were respectively 3.125 and 3.123.

Recently, Weber et al. (1970), whilst maintaining the Clementi form of wavefunction (see equation (7.15)), have placed constraints on its behaviour at  $r = 0$  and  $r = \infty$ . First, the long-range behaviour is forced so that each orbital  $\phi_i$  dies off exponentially according to its own orbital energy  $\epsilon_i$ . In the Roothaan and Bagus (1963) calculations, for atoms with only s electrons the orbitals had the asymptotic form

$$\phi_i \sim e^{-\sqrt{-2\epsilon_i} r} \quad (7.43)$$

If, however, p and d electrons were present, the asymptotic form was

$$\phi_i \sim e^{-\sqrt{-2\epsilon_s} r}$$

where  $\epsilon_s$  was the minimum of all the orbital energies of the electrons present. That is, for neon, the 1s, 2s and 2p orbitals die off with the same exponential behaviour. Weber et al. suggest that this is a mathematical anomaly of the Hartree-Fock method and they enforce the form



(7.43) for each of the orbitals. Secondly, they require the orbitals to satisfy the nuclear cusp condition for small  $r$ . That is, if  $\phi_i(r) = a_0 + a_1 r + a_2 r^2 + \dots$ , then  $a_1 = -za_0$  for  $s$  functions and  $a_0 = 0$ ,  $a_2 = -\frac{1}{2}(za_0)$  for  $p$  functions. Weber et al. have imposed both these constraints and recalculated the Hartree-Fock orbitals. They thus obtain wavefunctions which should be more accurate than the Clementi ones at both small and large values of  $r$ .

A point to note is that the standard  $1s$  orbitals, as reported by Clementi, have radial nodes. These 'spurious' nodes do not appear, however, in the orbitals of Weber et al.

The value of the Born direct scattering amplitude,  $f_B$ , which we obtained by using the Weber et al. orbitals was 3.133, which differs from the Clementi value by less than 1%. We conclude therefore that  $f_B$  is relatively insensitive to the neon ground state wavefunction employed.

$f_B$  can be calculated in an alternative way involving the atomic form factor,  $F(K)$ , which is defined by equation (7.1). For elastic scattering,  $f_B$  is given by

$$f_B(0, k^2) = \lim_{K \rightarrow 0} \frac{2|Z - F(K)|}{K^2}$$

where  $\underline{K}$  is the momentum transfer (c.f. equation (7.3)). By expanding  $F(K)$  in powers of the momentum transfer,

$$F(K) = Z + a_0 K^2 + a_1 K^3 + \dots$$

and using the results of Peixoto et al. (1969) McDowell has obtained the value 3.324 for the Born direct scattering amplitude. This differs from our earlier values by about 5%.

(b)  $g_B(0, k^2)$

We have calculated the Born exchange scattering amplitude,  $g_B(0, k^2)$ , using each of the Clementi 5-state, the Clementi 6-state and the Weber et al. wavefunctions. Our results are shown in Table 7.3. We can see that for zero  $k^2$ , the three wavefunctions yield values of  $g_B(0, 0)$  which differ by as much as 6%. This indicates that  $g_B$  is much more sensitive to the neon ground state wavefunction than is  $f_B$ .

(c) The dispersion relation

Our aim is to test the validity of the dispersion relation for neon and we shall consider the special case of zero energy, for which equation (6.15) is the postulated dispersion relation. To evaluate the integral on the right hand side we require the total cross-section,  $Q_{TOT}$ , at all energies. At low energies, the experimental data of Salop and Nakano (1970) is available, and in §7.1 we have derived a high energy form for  $Q_{TOT}$  (see equation (7.14)). In the intermediate energy range it is necessary to interpolate. Bransden has evaluated the integral

$$\frac{1}{4\pi} P \int_0^{\infty} \frac{Q_{TOT}(k'^2) dk'^2}{k'} \quad (7.44)$$

and obtained the value 4.115. Thus, the dispersion relation (6.15) reduces to

$$-A = f_B - g_B(0, 0) + 4.115 \quad (7.45)$$

In his phase shift analysis, McDowell has predicted the scattering length  $A$ , to be 0.22 (see §7.2). Also the most accurate value of the Born direct scattering amplitude,  $f_B$ , is 3.324, and so we have

$$g_B(0, 0) = 7.659$$

Table 7.3

Values of  $g_B(0, k^2)$

<u>Energy <math>k^2</math> a.u.</u>	<u>Clementi 5-state</u>	<u>Clementi 6-state</u>	<u>Weber et al.</u>
0.0	5.018	5.120	5.321
0.1	5.293	5.368	5.543
0.2	5.406	5.461	5.608
0.5	5.386	5.403	5.456
1.0	4.854	4.850	4.823
2.0	3.664	3.660	3.629
5.0	1.836	1.837	1.845
10.0	0.9730	0.9734	0.9723
20.0	0.5462	0.5465	0.5443
100.0	0.0682	0.0682	0.0672
1000.0	-0.00808	-0.00808	-0.00858

This compares with our best value for  $g_B(0, 0)$  of 5.32. Thus we have a definite discrepancy.

There are two conclusions which can be drawn at this point.

Either the conjectured dispersion relation is not valid, or, there are errors in our calculations of the quantities in the dispersion relation.

We shall now investigate more closely this second possibility.

There are two important sources of error in our calculations, as we have discussed in §6.4. First, there are uncertainties in the total cross-section  $Q_{TOT}$ , because of the lack of experimental measurements, and the resulting interpolation in the intermediate energy range. Bransden predicts a value of 3.4 for  $Q_{TOT}$  at 100 eV which may be compared with the

Normand (1930) experimental value of 2.75. If this latter set of data is correct, then our adopted values of  $Q_{\text{TOT}}$  (which should be correct by energies as high as 300 eV) should be reduced in the energy range 100 to 300 eV. This implies a correction to the integral in the dispersion relation of

$$\frac{1}{2\pi} \int_{7.0}^{21.0} \delta Q(x) dx \approx \frac{14}{2\pi} \cdot (0.5) \approx 1.2 .$$

That is, the integral (7.44) becomes

$$\frac{1}{4\pi} \cdot 2 \int_0^{\infty} (Q_{\text{TOT}}(x) - \delta Q(x)) dx \approx 2.98 .$$

Equation (7.45) would then yield a value for  $g_{\text{B}}(0, 0)$  of 6.459.

The second source of error is in the choice of the neon ground-state wavefunction. We have already noted that the exchange amplitude is very sensitive to the form of wavefunction chosen, and it could be that the Clementi and Weber et al. functions are not accurate enough. These Hartree-Fock wavefunctions do not include correlation effects at low energies. To investigate the importance of this, we shall now recalculate the Born exchange scattering amplitude at zero energy using a highly correlated configuration interaction wavefunction.

CHAPTER VIII

ACCURATE WAVEFUNCTIONS

8.1. The Configuration Interaction Wavefunction

In the Hartree self-consistent field method of solution of the Schrödinger equation for an N-electron atom the wavefunction is a product of N one-electron orbitals; there is no correlation between the motion of individual electrons. The Hartree-Fock method improves on this by having an antisymmetrised determinantal wavefunction, which introduces a type of correlation between electrons of the same spin: no two electrons of the same spin can occupy the same point of space. For a lot of situations this is sufficient, but there are cases where it is not, and we then have the configuration interaction (CI) approach. We start with a complete set of one-electron orbitals and from them form all possible determinantal functions of order N. This gives us a complete set of functions in terms of which we can expand any anti-symmetrized eigenfunction of the system. By including sufficient configurations we would obtain the exact wavefunction for the system.

The wavefunction for an N-electron atom can thus be written in the form

$$\Psi = \sum_{j=1}^{M_0} c_j \Psi_j \quad (8.1)$$

where the  $\Psi_j$  are the eigenfunctions for possible configurations of the atom, and the  $c_j$  are their corresponding weights. It is convenient to choose the  $\Psi_j$  to be simultaneous eigenfunctions of the commuting set of operators,  $\tilde{L}^2$ ,  $\tilde{S}^2$ ,  $\tilde{L}_z$ ,  $\tilde{S}_z$  and H;  $\tilde{L}$  is the total orbital angular momentum of the atom,  $\tilde{S}$  is the total spin angular momentum, and  $\tilde{L}_z$  and  $\tilde{S}_z$  are their respective z components. In order to determine  $\Psi_j$  for a given

configuration we form all possible Nth order determinants and find the combination of them which makes  $\psi_j$  an eigenfunction of  $\tilde{S}^2$ ,  $\tilde{L}^2$ ,  $\tilde{S}_z$  and  $\tilde{L}_z$ .

We consider the general determinantal function

$$D\{\phi(n_1 \ell_1 m_1 s_1) \phi(n_2 \ell_2 m_2 s_2) \dots \phi(n_N \ell_N m_N s_N)\},$$

where the  $\phi(n_i \ell_i m_i s_i)$  are one-electron orbitals, in the usual notation.

It is easily shown that such a function is already an eigenfunction of  $\tilde{L}_z$  and  $\tilde{S}_z$ , but not of  $\tilde{S}^2$  and  $\tilde{L}^2$  (see, for example, Eyring Walter and Kimball (1944)). We next consider the linear combination

$$A = \sum_i a_i D_i \tag{8.2}$$

where  $D_i$  is one of the set of determinants arising for the given configuration. We wish A to be an eigenfunction of  $\tilde{L}^2$ . Now

$$\begin{aligned} \tilde{L}^2 D\{(n_1 \ell_1 m_1 s_1) (n_2 \ell_2 m_2 s_2) \dots\} = \\ \frac{\hbar^2}{4\pi^2} \left\{ \left[ \sum_i \ell_i (\ell_i + 1) + 2 \sum_{i>j} m_i m_j \right] D\{(n_1 \ell_1 m_1 s_1) (n_2 \ell_2 m_2 s_2) \dots\} \right. \\ + \sum_{i \neq j} \left[ \ell_i (\ell_i + 1) - m_i (m_i + 1) \right]^{\frac{1}{2}} \left[ \ell_j (\ell_j + 1) - m_j (m_j - 1) \right]^{\frac{1}{2}} \\ \left. \times D_i(n_1 \ell_1 m_1 s_1) \dots (n_i \ell_i m_i + 1, s_i) \dots (n_j \ell_j m_j - 1, s_j) \dots \right\} \end{aligned} \tag{8.3}$$

and we see that  $\tilde{L}^2$  does not alter the value of  $M_L (=m_1+m_2+\dots)$ . A similar result holds for  $\tilde{S}^2$  and  $M_S$ . Thus only D functions with the same  $M_L$  and  $M_S$  values will be involved in the sum (8.2). We want A to satisfy

$$\tilde{L}^2 A = \frac{\hbar^2}{4\pi} L(L+1)A$$

for some value of  $L$ . That is, noting equation (8.2)

$$\sum_i (L_{ji}^2 - \frac{L(L+1)\hbar^2}{4\pi^2} \delta_{ij}) a_i = 0 \quad (8.4)$$

where  $L_{ji}^2 = \int D_j^* \tilde{L}^2 D_i d\tau$ .

These equations (8.4) can be solved to give values of  $a_i$ , and hence  $A$ . In this way we obtain a set of  $A$ 's which are eigenfunctions of  $\tilde{L}^2$ ,  $\tilde{L}_z$  and  $\tilde{S}_z$ . The same procedure can be repeated with  $\check{S}^2$  instead of  $\tilde{L}^2$  and using the  $A$ 's as the starting functions. We obtain a set of functions  $B_i$  which satisfy

$$\tilde{L}^2 B_i = L_i(L_i+1) \frac{\hbar^2}{4\pi} B_i$$

$$\check{S}^2 B_i = S_i(S_i+1) \frac{\hbar^2}{4\pi} B_i$$

$$\tilde{L}_z B_i = M_{L_i} \frac{\hbar}{2\pi} B_i$$

$$\check{S}_z B_i = M_{S_i} \frac{\hbar}{2\pi} B_i$$

We will now look briefly at one example, the result of which we shall use later in this chapter. We require a 'S state, that is  $L = 0$ ,  $S = 0$ ,  $M_L = 0$ ,  $M_S = 0$ , of the configuration  $(1s)^2(2s)^2(2p)^4(3s)^2$ . There are fifteen possible  $D$  functions, but only three of these have  $M_L$  and  $M_S$  both zero. They are

$$\begin{aligned} \psi_1 &= (100\frac{1}{2})(100\frac{1}{2})(200\frac{1}{2})(200\frac{1}{2})(211\frac{1}{2})(210\frac{1}{2})(210\frac{1}{2})(21\bar{1}\frac{1}{2})(300\frac{1}{2})(300\frac{1}{2}) \\ \psi_2 &= (100\frac{1}{2})(100\frac{1}{2})(200\frac{1}{2})(200\frac{1}{2})(211\frac{1}{2})(210\frac{1}{2})(210\frac{1}{2})(21\bar{1}\frac{1}{2})(300\frac{1}{2})(300\frac{1}{2}) \\ \psi_3 &= (100\frac{1}{2})(100\frac{1}{2})(200\frac{1}{2})(200\frac{1}{2})(211\frac{1}{2})(211\frac{1}{2})(21\bar{1}\frac{1}{2})(21\bar{1}\frac{1}{2})(300\frac{1}{2})(300\frac{1}{2}) \end{aligned} \quad (8.5)$$

We have denoted each determinant D by the elements of its principal diagonal. Equation (8.3) yields the results

$$\begin{aligned}\tilde{L}^2 \psi_1 &= \frac{\hbar^2}{4\pi^2} (2\psi_1 + 2\psi_3) \\ \tilde{L}^2 \psi_2 &= \frac{\hbar^2}{4\pi^2} (2\psi_2 - 2\psi_3) \\ \tilde{L}^2 \psi_3 &= \frac{\hbar^2}{4\pi^2} (2\psi_1 - 2\psi_2 + 4\psi_3) .\end{aligned}$$

For a non-vanishing set of coefficients  $a_i$  we have, from equation (8.4),  $L = 0, 1$  or  $2$ , and the resulting eigenfunctions are

$$\begin{aligned}A_7 &= \frac{1}{\sqrt{3}} (-\psi_1 + \psi_2 + \psi_3) \\ A_8 &= \frac{1}{\sqrt{2}} (\psi_1 + \psi_2) \\ A_9 &= \frac{1}{\sqrt{6}} (\psi_1 - \psi_2 + 2\psi_3) .\end{aligned}\tag{8.6}$$

These A functions are already eigenfunctions of  $\tilde{S}^2$  and so can be used as B functions. In particular  $\tilde{S}^2 A_7 = 0$ , and so  $A_7$  corresponds to a 'S' state and is the function we require. That is, the function  $A_7$  is an eigenfunction of  $\tilde{L}^2$ ,  $\tilde{S}^2$ ,  $\tilde{L}_z$  and  $\tilde{S}_z$  corresponding to a 'S' state of the configuration  $(1s)^2(2s)^2(2p)^4(3s)^2$ .

To summarise then, we can expand the total wavefunction of an atom as a linear combination of the functions  $\Psi_j$ , as in equation (8.1). These  $\Psi_j$ 's are each linear combinations of Slater determinants which are composed of one electron orbitals  $\phi_i$ . We suppose these to be of the form

$$\phi_i = \frac{1}{r} P(n_i, \ell_i, r) Y_{\ell m}(\theta, \phi) X(m_{s_i})$$



where  $Y_{\ell m}$  is a spherical harmonic and  $X(m_{s_i})$  is a spin eigenfunction. We assume that the radial functions  $P(n\ell, r)$  associated with a given quantum number  $\ell$  form an orthonormal set

$$\int P(n\ell, r)P(n'\ell, r)dr = \delta_{nn'}$$

In order to obtain the total wavefunction  $\Psi$  we need to know two sets of quantities, the weights  $c_j$  ( $j=1, \dots, M_0$ ) and the radial wavefunctions  $P(n_i\ell_i, r)$ . They are determined from the fact that the total energy must be stationary with respect to variations in these quantities. Computer programs exist to perform this calculation, one of the most notable being that of Fischer (1969). She describes in some detail the multi-configuration Hartree-Fock (MCHF) solution of the problem.

Basically, two problems are solved repetitively. First, given the weights  $c_j$ , the radial functions  $P(n\ell, r)$  are determined for a stationary energy. Then with these radial functions the weights are recalculated, again for a stationary energy, and so on.

If  $H$  is the total Hamiltonian for the  $N$ -electron atom, then the total energy is given by

$$E = \langle \Psi | H | \Psi \rangle$$

where  $\Psi$  is the total wavefunction for a bound state of the system. Thus, by equation (8.1)

$$E = \sum_{j=1}^{M_0} \sum_{i=1}^{M_0} c_i c_j E_{ij} \left( \sum_{i=1}^{M_0} c_i^2 \right) \quad (8.7)$$

where  $E_{ij} = \langle \Psi_i | H | \Psi_j \rangle \quad (8.8)$

Following Slater (1960) we can write the energy  $E$  in the form

$$\begin{aligned}
 E = & \sum_{j=1}^{M_0} E_j(\text{average}) + \sum_{m=1}^{MF} a_m c_{j_m} c_{j'_m} F^k(i_{m j_m}; i'_{m j'_m}) \\
 & + \sum_{m=1}^{NG} b_m c_{j_m} c_{j'_m} G^k(i_{m j_m}; i'_{m j'_m}) \\
 & + \sum_{m=1}^{NR} d_m c_{j_m} c_{j'_m} R^k(i_m i_{m j_m}; i'_m i'_{m j'_m})
 \end{aligned} \tag{8.9}$$

where  $i$  and  $ii$  specify the index of a wavefunction and  $j$  the configuration to which it belongs.  $E_j(\text{average})$  is the average energy of the configuration  $j$ , and is calculated by the Fischer program. The radial integrals  $R^k$  are defined by

$$\begin{aligned}
 R^k(i_a, i'_a) = & \int_0^\infty R^*(n_i \ell_i, r_1) R^*(n_a \ell_a, r_2) R(n_i', \ell_i', r_1) \\
 & R(n_a', \ell_a', r_2) \frac{2r_<^k}{r_>^{k+1}} r_1^2 r_2^2 dr_1 dr_2
 \end{aligned}$$

with the special cases

$$F^k(i, i') = R^k(ii', ii') \tag{8.10}$$

$$\text{and } G^k(i, i') = R^k(ii', i'i)$$

The indices  $j$  and  $j'$ , appearing in equation (8.9) which denote the configurations, are not involved in the  $R$  integrals. These integrals are calculated by the program, but their coefficients  $a_m$ ,  $b_m$  and  $d_m$  are required as input data. We shall return to this point later in this section.

As we have mentioned before, the aim of the MCHF method is to solve the set of coupled integro-differential equations satisfied by the radial functions  $P(n\ell, r)$  and determine a set of weight factors  $c_j$ . The

integro-differential equations are solved iteratively by the self-consistent field method. As is shown by Hartree (1955) the functions  $P(n\ell, r)$  satisfy the Fock equations

$$\left\{ \frac{d^2}{dr^2} + \frac{2}{r}(Z-Y(n\ell, r)) - \epsilon_{n\ell, n\ell} - \frac{\ell(\ell+1)}{r^2} \right\} P(n\ell, r) = X(n\ell, r) + \sum_{n' \neq n} \epsilon_{n\ell, n'\ell} P(n'\ell, r) \quad (8.11)$$

where  $P(n\ell, 0) = 0 = P(n\ell, \infty)$

and  $Y(n\ell, r) = - \sum_{n\ell} q(n\ell) Y_0(n\ell, n\ell, r) + \sum_k \alpha_{\ell k} Y_k(n\ell, n\ell, r)$

$$X(n\ell, r) = - \frac{2}{r} \sum_{n'\ell'k} \beta_{\ell\ell'k} Y_k(n\ell, n'\ell', r) P(n'\ell', r)$$

with

$$Y_k(n\ell, n'\ell', r) = r \int_0^\infty \gamma_k(r, s) P(n\ell, s) P(n'\ell', s) ds$$

and  $\gamma_k(r, s) = [\min(r, s)]^k / [\max(r, s)]^{k+1}$ .

The constants  $\alpha$  and  $\beta$  are tabulated by Condon and Shortley (1930) and  $q(n\ell)$  is the number of electrons in the  $(n\ell)$  shell. The solutions of these equations oscillate near the origin and Fischer (1969) finds it convenient to make the substitution  $\rho = \log Zr$ . The resulting equations are then solved numerically.

The differential equations for all the radial functions are solved repetitively until the results are self-consistent, that is until the estimated functions differ from the solutions of the equations by an amount not exceeding the allowed tolerance. Initially the wavefunctions are estimated and orthogonalised and the energy parameters,  $\epsilon_{n\ell, n'\ell}$  are

determined. Each equation is solved and the  $\epsilon_{n\ell, n'\ell}$  redetermined. The program then searches for and solves the equation which has the largest change in its solution. This last process is repeated several times and then each of the equations is solved in turn and the  $\epsilon_{n\ell, n'\ell}$ 's redetermined. This entire procedure is repeated for either a specified number of times or until self-consistency is attained, whichever occurs first.

Having determined a set of radial functions, the energy matrix ( $E_{ij}$ ) is computed and hence the weights  $c_j$  which make the total energy  $E$  a minimum (see equation (8.7)). This whole process is repeated several times, to obtain consistency between the radial functions and the weights.

Thus, values of the coefficients  $c_j$  and the numerical radial wavefunctions are calculated by the Fischer program. We have modified this program to run on the CDC6600 computer and have reproduced the test results for C+2 exactly. We have also obtained good results for the single configuration, the ground state of the neon atom,  $(1s)^2 (2s)^2 (2p)^6$ . However, we have so far been unable to get reasonable convergence of the results for the two configuration example which we will be discussing later.

Dr. Wilson at Chelsea College (University of London) has very kindly given us a copy of an unpublished MCHF program of Bagus. This retains the majority of the Fischer program but improves the methods of solution of the differential equations for the radial functions, resulting in better convergence. It also allows more configurations to be included in the calculation. We have modified this program to run on the CDC 6600 and have obtained preliminary results for the two configuration example. We shall consider these in Chapter X.

The data required as input for both the Fischer and Bagus MCHF programs is discussed in detail by Fischer (1969). We shall only consider

here the coefficients  $a_m, b_m, d_m$  which appear in the expression (8.9) for the total energy. We look at the special case of a two configuration approximation to the ground state of the neon atom in which we have the configurations

- (i)  $(1s)^2(2s)^2(2p)^6$
- (ii)  $(1s)^2(2s)^2(2p)^4(3s)^2$

with corresponding wavefunctions  $\Psi_1$  and  $\Psi_2$ . These are simultaneous eigenfunctions of  $L^2, \tilde{S}^2, \tilde{L}_z$  and  $\tilde{S}_z$  with  $L = 0$  and  $S = 0$ . Since the first configuration is a closed shell the wavefunction  $\Psi_1$  is a single Slater determinant composed of ten one-electron orbitals. We have already seen, equation (8.6), that  $\Psi_2$  is given by

$$\Psi_2 = \frac{1}{\sqrt{3}} (-\psi_1 + \psi_2 + \psi_3) \quad (8.11)$$

where  $\psi_1, \psi_2$  and  $\psi_3$  are given in equation (8.5).

The expression for the total energy can be worked out very easily in this case. The first configuration, being a closed shell, has only one multiplet, a 'S state. Therefore

$$\langle \Psi_1 | H | \Psi_1 \rangle = E_1(\text{average})$$

where  $E_1(\text{average})$  is the average energy of the configuration. Details of its evaluation are given in Slater (Volume I, 1960). He also shows that the 'S multiplet energy of the second configuration is

$$\langle \Psi_2 | H | \Psi_2 \rangle = E_2(\text{average}) + \frac{12}{25} F^2(2p, 2p)$$

where  $F$  is defined in equation (8.10).

The matrix element  $E_{12} = \langle \Psi_1 | H | \Psi_2 \rangle$  can be evaluated by using the results of Slater (Volume II, 1960) and is given by

$$\langle \Psi_1 | H | \Psi_2 \rangle = \frac{1}{\sqrt{3}} G'(2p, 3s) .$$

Thus, from equation (8.7) we have

$$E = c_1^2 E_1(\text{average}) + c_2^2 E_2(\text{average}) \\ + \frac{12}{25} c_2^2 F^2(2p, 2p) + \frac{2}{\sqrt{3}} c_1 c_2 G'(2p, 3s) .$$

We have not given here much detail of this calculation, as these results are very easily obtained from Slater. Also this approach becomes unfeasible when more complicated configurations are involved. Moreover it is unnecessary, since Hibbert (1971) has written a computer program which calculates the coefficients  $a_m$ ,  $b_m$ ,  $d_m$  required as input in the MCHF programs.

Thus we have in the configuration interaction approach a means of producing one-electron orbitals which, because they include correlation, are more accurate than the standard Clementi-type wave functions. There are computer programs which calculate these orbitals and output them in a numerical form, together with the configuration weighting factors,  $c_j$ .

## 8.2. Analytic forms for the CI wavefunctions

To calculate the Born exchange scattering amplitude  $g_B(0, 0)$  it is convenient to have the one-electron orbitals in an analytic form. We have therefore written a program which fits to such a form the numerical wavefunctions which are output by the CI program and which we store on

magnetic tape. We choose the orbitals to be of the Clementi (1965) type; we assume the s and p orbitals with which we shall be concerned to have the general forms

$$\phi_{ns}(\underline{r}) = \sum_{k=1}^M d_k e^{-\xi_k r} + \sum_{k=M+1}^{M'} d_k r e^{-\xi_k r} + \sum_{k=i'+1}^{M''} d_k r^2 e^{-\xi_k r} \quad (8.12)$$

for  $n = 1, 2, 3$  and

$$\phi_{npm}(\underline{r}) = \left( \sum_{k=1}^L c_k r e^{-\zeta_k r} + \sum_{k=L+1}^{L'} c_k r^3 e^{-\zeta_k r} \right) Y_{lm}(\hat{r}) \quad (8.13)$$

for  $n = 2, 3$ , respectively. The constants  $M, M', M'', L$  and  $L'$  are specified initially, and depend on which orbitals occur in the problem. Considering the s orbitals, if only the 1s orbital is occupied, only the first term in the sum (8.12) appears. If there are 1s and 2s orbitals, the first two terms are present, and if there are 1s, 2s and 3s orbitals, each of the three terms occurs. Similarly, for the p orbitals, only the first term in equation (8.13) is used when 3p orbitals are absent, otherwise both terms are present. The coefficients and exponents  $d_k, \xi_k, c_k$  and  $\zeta_k$  are to be varied so that the forms (8.12) and (8.13) give good representations of the numerical functions.

We denote by  $P_i(r_j)$  the radial part of the  $i$ th numerical wavefunction at the  $j$ th value of  $r$  for which it is calculated by the CI program. The corresponding function in our analytic fit is  $Q_i(r_j)$ . A point to note is that for s orbitals we have included the spherical harmonic  $Y_{00}(\hat{r}) (= (4\pi)^{-1/2})$  in the constants  $d_k$ . We aim for an accuracy of 1 part in  $10^{-2}$  in our fitting and so we form the sum

$$F_i = \sum_{j=1}^{N_i} \left( \frac{P_i(r_j) - Q_i(r_j)}{10^{-2} P_i(r_j)} \right)^2$$

where  $r_{N_i}$  is the last value of  $r$  for which  $P_i(r_j)$  is greater than  $10^{-3}$ . For  $r$  greater than this value the numerical wavefunction is not reliable enough for a fit to be feasible. The program VAO4A of Powell and Fletcher (1964) is then used to minimise this sum with respect to the variables  $d_k$  and  $\xi_k$  for  $s$  orbitals, and  $c_k$  and  $\zeta_k$  for  $p$  orbitals. We impose, however, a constraint on the values which can be taken by the exponents  $\xi_k$  and  $\zeta_k$ . The 'ns' part of an 'ns' wavefunction (that is, the term in the sum (8.12) which contains a factor  $r^{n-1}$ ) is forced to behave as an 'ns' function for large values of  $r$ . That is

$$\begin{aligned} \xi_k &> \alpha_{1s} & 1 \leq k \leq M \\ \xi_k &> \alpha_{2s} & M < k \leq M' \\ \xi_k &> \alpha_{3s} & M' < k \leq M'' \end{aligned}$$

where  $\alpha_{ns} = \sqrt{-\epsilon_{ns}}$ ,  $\epsilon_{ns}$  being the orbital energy of the 'ns' orbital, in rydbergs. Similarly for  $p$  orbitals

$$\begin{aligned} \zeta_k &> \alpha_{2p} & 1 \leq k \leq L \\ \zeta_k &> \alpha_{3p} & L < k \leq L' \end{aligned}$$

The program VAO4A varies the parameters  $\xi_k$  in the range  $(-\infty, \infty)$ ; the above constraint is imposed by making the substitution

$$x_k = \log\left(\frac{\xi_k - \alpha_k}{\alpha_k}\right) \quad (8.14)$$

and varying the new parameters  $x_k$ .



Our fitting program requires initial values of the parameters involved in  $Q_i$ . In cases where they are available we use the Clementi (1965) values, otherwise it is a matter of trial and error.

To summarise then, we make initial estimates of the parameters involved in the orbitals which we choose to be of the forms (8.12) and (8.13). We apply the substitution (8.14) to the exponent parameters and then form the sum  $F_i$  for each wavefunction  $i$  involved in the problem. The numerical CI wavefunctions,  $P_i$ , are read from magnetic tape. The sum  $F_i$  is then minimised by the program VA04A and we aim for a low value of

$$\chi_i^2 = F_i/m_i$$

where  $m_i$  is the number of degrees of freedom. We thus obtain analytic forms for the CI wavefunctions, and we now go on to use these in the calculation of the Born exchange scattering amplitude,  $g_B(0, 0)$ .

CHAPTER IX

THE BORN EXCHANGE SCATTERING AMPLITUDE AT ZERO ENERGY

In this chapter we consider the Born exchange scattering amplitude for zero energy for an N-electron atom. We assume that we have a configuration interaction (CI) type of wavefunction,  $\Psi$ , which is a 'S state of the atom and which is given, as in equation (8.1), by

$$\Psi = \sum_{i=1}^{M_0} c_i \Psi_i \quad . \quad (9.1)$$

The constants  $c_i$  are the weights of the single configuration wavefunctions  $\Psi_i$ . These  $\Psi_i$  are 'S multiplets which represent possible states of the atom and, as we have seen in §8.1, they can be written in the form

$$\Psi_i = \sum_{j=1}^{M_{ij}} \alpha_{ij} D_{ij} \quad . \quad (9.2)$$

The  $\alpha_{ij}$  are constants and the  $D_{ij}$  are Slater determinants composed of one-electron orbitals  $\phi_i$ . We have already discussed in §8.1 how the functions  $\Psi_i$ , and hence the  $\alpha_{ij}$  and  $D_{ij}$  are determined for a given configuration. Combining equations (9.1) and (9.2) we obtain

$$\Psi = \sum_{i=1}^{M_0} \sum_{j=1}^{M_{ij}} c_i \alpha_{ij} D_{ij} \quad . \quad (9.3)$$

The Born exchange amplitude  $g_B(0, 0)$  for the elastic forward scattering of an electron by an N-electron atom in the state  $\Psi$  is given by

$$g_B(0, 0) = -\frac{1}{2\pi} \langle \Psi(1, \dots, N) | V | \Psi(1, \dots, N-1, N+1) \rangle \quad (9.4)$$

$$\text{where } V = -\frac{N}{r_{N+1}} + \sum_{i=1}^{N+1} \frac{1}{|r_i - r_{N+1}|} \quad (9.5)$$

Thus, combining equations (9.3) and (9.4) we have

$$\mathcal{E}_B(0, 0) = -\frac{1}{2\pi} \sum_{i=1}^{M_0} \sum_{j=1}^{M_{ij}} \sum_{i'=1}^{M_0} \sum_{j'=1}^{M_{i'j'}} c_i c_{i'} \alpha_{ij} \alpha_{i'j'} \quad (9.6)$$

$$\langle D_{ij}(1, \dots, N) | V | D_{i'j'}(1, \dots, N-1, N+1, \dots, N) \rangle .$$

As we have mentioned above, the determinants  $D_{ij}$  are composed of one-electron orbitals  $\phi_i$ , and we assume these to be either 1s, 2s, 3s, 2p or 3p orbitals. They are calculated numerically by the CI program and then fitted to the analytic forms (8.12) and (8.13) as described in §8.2. We shall therefore assume the orbitals to be of the forms (8.12) and (8.13) and denote them by

$$\begin{aligned} \phi_{1s} &= \langle \underline{d}, \underline{\xi} \rangle, & \phi_{2s} &= \langle \underline{e}, \underline{\delta} \rangle, & \phi_{3s} &= \langle \underline{b}, \underline{\chi} \rangle, \\ \phi_{2p} &= \langle \underline{c}, \underline{\zeta} \rangle, & \phi_{3p} &= \langle \underline{a}, \underline{\sigma} \rangle. \end{aligned}$$

That is, the 2s orbital is of the form (8.12) with the constants  $d_k$  and  $\xi_k$  replaced by  $e_k$  and  $\delta_k$  respectively ( $k = 1-M''$ ), and similarly for the other orbitals. We thus have eighteen orbitals and we label them in the following manner:

$$\begin{aligned} \phi_1 &= \phi_{1s\alpha}, & \phi_2 &= \phi_{1s\beta}, \\ \phi_3 &= \phi_{2s\alpha}, & \phi_4 &= \phi_{2s\beta}, \end{aligned}$$

$$\phi_5 = \phi_{2p_1\alpha}, \quad \phi_6 = \phi_{2p_0\alpha}, \quad \phi_7 = \phi_{2p_{-1}\alpha},$$

$$\phi_8 = \phi_{2p_1\beta}, \quad \phi_9 = \phi_{2p_0\beta}, \quad \phi_{10} = \phi_{2p_{-1}\beta},$$

$$\phi_{11} = \phi_{3s\alpha}, \quad \phi_{12} = \phi_{3s\beta},$$

$$\phi_{13} = \phi_{3p_1\alpha}, \quad \phi_{14} = \phi_{3p_0\alpha}, \quad \phi_{15} = \phi_{3p_{-1}\alpha},$$

$$\phi_{16} = \phi_{3p_1\beta}, \quad \phi_{17} = \phi_{3p_0\beta}, \quad \phi_{18} = \phi_{3p_{-1}\beta}$$

$\alpha$  and  $\beta$  denote spin-up and spin-down states respectively.

We now discuss the way in which we have evaluated the matrix elements appearing in equation (9.6). The method is a modification of that used in §7.3, and much of the notation used there is carried over.

We write

$$\langle D_{ij}(1, \dots, N) | V | D_{i'j'}(1, \dots, N-1, N+1) \rangle = \sum_{k=1}^3 I_k(ij, i'j') \quad (9.7)$$

where the functions  $I_k(ij, i'j')$  are defined in an exactly parallel way to equations (7.19), (7.20) and (7.21). We consider each of these in turn, but first we make one further assumption. We neglect single excitations on the grounds that they are unimportant in practice compared with double excitations. In each case, therefore, we have two cases to consider,

- (i)  $D_{ij} = D_{i'j'}$ ,
- (ii)  $D_{ij}$  and  $D_{i'j'}$  differ by two orbitals.

We define  $S$  to be the subset of the spin-up orbitals which are occupied in  $D_{ij}$ . Then

$$S C\{\phi_1, \phi_3, \phi_5, \phi_6, \phi_7, \phi_{11}, \phi_{13}, \phi_{14}, \phi_{15}\}$$

Let  $D_{ij} = \{\phi_i, \dots, \phi_t\}$ .

a)  $I_1(ij, i'j')$

From equations (9.5) and (9.7) and by comparison with equation (7.19) we have

$$I_1(ij, i'j') = \frac{N}{2\pi} \langle D_{ij}(1, \dots, N) | \frac{1}{r_{N+1}} | D_{i'j'}(1, \dots, N-1, N+1) \rangle$$

Since  $r_{N+1}$  is the only term involved in the integrand apart from in the wavefunctions, and since the orbitals are orthogonal, we must have the two determinants containing identical orbitals. Thus  $I_1(ij, i'j')$  is zero unless  $D_{ij} = D_{i'j'}$ . In that case

$$I_1(ij, ij) = \frac{N}{2\pi} \int dr_1 \dots dr_{N+1} \frac{\alpha^{(N+1)}}{r_{N+1}} \phi_i(1) \dots \phi_j(\ell) \dots \phi_t(N) \\ \times \sqrt{N!} \sum_{j_o \in S} D_{ij}\{1, 2, \dots, \ell-1, N+1, \ell+1, \dots, N\}.$$

There is only one non-zero contribution from the determinant, namely the product of the diagonal elements. Thus

$$I_1(ij, ij) = \sum_{j_o \in S} \frac{N}{2\pi} \int dr_\ell \int dr_{N+1} \frac{\phi_{j_o}(\ell) \phi_{j_o}^*(N+1)}{r_{N+1}}.$$

That is,

$$I_1(ij, ij) = \frac{N}{2\pi} \sum_{j_o \in S} X(j_o) Y(j_o)$$

where the X and Y functions are defined by

$$\begin{aligned}
 X(j_o) &= \int d\underline{r} \phi_{j_o}(\underline{r}) \\
 \text{and } Y(j_o) &= \int d\underline{r} \frac{\phi_{j_o}(\underline{r})}{r} .
 \end{aligned}
 \tag{9.8}$$

Now X vanishes unless the state  $\phi_{j_o}$  has zero quantum numbers, m and  $\ell$  and so  $j_o$  can take only the values 1, 3 and 11, according as these states are occupied or not in  $D_{ij}$ . Using the expansion (8.12) we obtain

$$\begin{aligned}
 X(1s) = X(\underline{d}, \underline{\xi}) &= \sum_{k=1}^M d_k K(\xi_k, 0) + \sum_{M+1}^{M'} d_k K(\xi_k, 1) + \sum_{M'+1}^{M''} d_k K(\xi_k, 2) \\
 Y(1s) = Y(\underline{d}, \underline{\xi}) &= \sum_1^M d_k K(\xi_k, -1) + \sum_{M+1}^{M'} d_k K(\xi_k, 0) + \sum_{M'+1}^{M''} d_k K(\xi_k, 1)
 \end{aligned}$$

where  $K(\lambda, n) = \int d\underline{r} e^{-\lambda r} r^n$  analogous to our previous definition in §7.3.

The recurrence relation (7.26) is still valid. Similarly

$$K(2s) = X(\underline{c}, \underline{\lambda}), \quad X(3s) = X(\underline{b}, \underline{\chi}) \quad \text{and} \quad Y(2s) = Y(\underline{e}, \underline{\delta}), \quad Y(3s) = Y(\underline{b}, \underline{\chi}).$$

The values of the K functions are given in Table 9.1.

(b)  $I_3(ij, i'j')$

By comparison with equation (7.21) we have

$$\begin{aligned}
 I_3(ij, i'j') &= -\frac{1}{2\pi} \langle D_{ij}(1, \dots, N) \left| \sum_{\ell=1}^N \frac{1}{|\underline{r}_\ell - \underline{r}_{N+1}|} \right| \\
 &\quad \left. D_{i'j'}(1, \dots, \ell-1, N+1, \ell+1, \dots, N) \right\rangle .
 \end{aligned}$$

Table 9.1

Values of the K functions for  $g_{\mathbb{B}}(0, 0)$

$K(\lambda, -1) = 4\pi\lambda^{-2}$	$K(\lambda, 0) = 8\pi\lambda^{-3}$
$K(\lambda, 1) = 24\pi\lambda^{-4}$	$K(\lambda, 2) = 96\pi\lambda^{-5}$
$K(\lambda, 3) = 480\pi\lambda^{-6}$	$K(\lambda, 4) = 2880\pi\lambda^{-7}$
$K(\lambda, 5) = 20160\pi\lambda^{-8}$	$K(\lambda, 6) = 161280\pi\lambda^{-9}$
$K(\lambda, 7) = 1451520\pi\lambda^{-10}$	$K(\lambda, 8) = 14515200\pi\lambda^{-11}$

Clearly, because of the form of the integrand and the orthogonality of the one-electron orbitals, this vanishes unless the determinants  $D_{ij}$  and  $D_{i'j'}$  differ by at most one orbital. Therefore, because we are not allowing single excitations,  $I_3$  vanishes unless  $D_{ij} = D_{i'j'}$ . If this latter condition is satisfied the analysis of §7.3 part (iii) holds and we obtain

$$\begin{aligned}
 I_3(ij, ij) &= -\frac{1}{2\pi} \sum_{j_0 \in S} \int_{\underline{r}} d\underline{r} \frac{\phi_{j_0}(\underline{r}) \phi_{j_0}^*(\underline{r}_{N+1})}{\underline{r} - \underline{r}_{N+1}} \\
 &= \sum_{j_0 \in S} I_3^{(j_0)}, \text{ say} \quad . \quad (9.9)
 \end{aligned}$$

In the case of non-zero energy, the functions  $I_3^{(i)}$  had an extra exponential term which made the analysis rather complicated (see equation (7.28)). For zero energy however this term is absent, and we can see by

comparing equation (7.29) with the P functions defined in Appendix D that  $M(\lambda, \mu)$  is simply  $P_1(\lambda, \mu)$ . Similar simplifications hold for the other functions involved in  $I_3$ .

The first possible term occurring in the summation of equation (9.9) is  $I_3^{(1)}$ . (Note that if the state  $\phi_1$  is not occupied in the determinant  $D_{ij}$ , then  $I_3^{(1)}$  is zero.) By using the expansion (8.12) for the 1s orbital we have

$$\begin{aligned}
 I_3^{(1)} &= -\frac{1}{2\pi} \left\{ \sum_{k=1}^M \sum_{j=1}^M P_1(\xi_k, \xi_j) + 2 \sum_{k=M+1}^{M'} \sum_{j=1}^M P_5(\xi_k, \xi_j) \right. \\
 &\quad + 2 \sum_{k=M+1}^{M'} \sum_{j=1}^M P_2(\xi_j, \xi_k) + \sum_{k=M+1}^{M'} \sum_{j=M+1}^{M'} P_3(\xi_k, \xi_j) \\
 &\quad \left. + 2 \sum_{k=M'+1}^{M''} \sum_{j=M'+1}^{M'} P_6(\xi_j, \xi_k) + \sum_{k=M'+1}^{M''} \sum_{j=M'+1}^{M''} P_{13}(\xi_k, \xi_j) \right\} d_k d_j \\
 &\equiv I_3^{(1)}(\underline{d}, \underline{\xi}), \text{ say.}
 \end{aligned}$$

The P functions are defined in Appendix D in terms of the K functions which are given in Table 9.1. Similarly,

$$\begin{aligned}
 I_3^{(3)} &= I_3^{(1)}(\underline{e}, \underline{\delta}) \quad \text{and} \\
 I_3^{(11)} &= I_3^{(1)}(\underline{b}, \underline{\chi}).
 \end{aligned}$$

The remaining  $I_3^{(1)}$  functions are of the form ( $n = 2$  or  $3$ )

$$I_3^{(nm)} = -\frac{1}{2\pi} \int d\underline{r} \frac{\int d\underline{R} \phi_{n|m}(\underline{r}) \phi_{n|m}^*(\underline{R})}{|\underline{r} - \underline{R}|}$$



For  $n = 2$ , using equation (8.13) we have

$$\begin{aligned}
 I_3^{(2n)} = & -\frac{1}{2^n} \left\{ \sum_{k=1}^{L'} \sum_{j=1}^{L'} c_k c_j P_{25}(\zeta_k, \zeta_j) \right. \\
 & + 2 \sum_{k=1}^{L'} \sum_{j=L+1}^{L'} c_k c_j \frac{\partial^2}{\partial \zeta_j^2} P_{25}(\zeta_k, \zeta_j) \\
 & \left. + \sum_{k=L+1}^{L'} \sum_{j=L+1}^{L'} c_k c_j \frac{\partial^4}{\partial \zeta_j^2 \partial \zeta_k^2} P_{25}(\zeta_k, \zeta_j) \right\} .
 \end{aligned}$$

We now show that the function  $P_{25}(\lambda, \mu)$  which is defined by

$$P_{25}(\lambda, \mu) = \int \underline{dr} \int \underline{dR} \frac{e^{-\lambda r} e^{-\mu R}}{|r-R|} Y_{1m}^*(\underline{\hat{r}}) Y_{1m}(\underline{\hat{R}}) rR \quad (9.10)$$

is independent of  $m$ . We have

$$\begin{aligned}
 P_{25}(\lambda, \mu) = & \int \underline{dr} \int \underline{dR} e^{-\lambda r} e^{-\mu R} rR Y_{1m}^*(\underline{\hat{r}}) Y_{1m}(\underline{\hat{R}}) \\
 & \times \sum_{\alpha, \beta} \frac{4\pi}{2\alpha+1} \gamma_\alpha(r, R) Y_{\alpha\beta}(\underline{\hat{r}}) Y_{\alpha\beta}^*(\underline{\hat{R}})
 \end{aligned}$$

where we have used the expansion (2.1) for  $|r-R|^{-1}$ . The angular integrations are trivial, yielding the contribution  $\delta_{\alpha 1} \delta_{\beta m}$ . Thus

$$P_{25}(\lambda, \mu) = \int_0^\infty r^2 dr \int_0^\infty R^2 dR e^{-\lambda r} e^{-\mu R} rR \frac{4\pi}{3} \gamma_1(r, R) .$$

Clearly, this is independent of  $m$ , and we have

$$\begin{aligned}
 I_3^{(5)} = I_3^{(6)} = I_3^{(7)} &= -\frac{1}{2\pi} \left\{ \sum_{k=1}^L \sum_{j=1}^L c_k c_j P_{25}(\zeta_k, \zeta_j) \right. \\
 &+ 2 \sum_{k=1}^L \sum_{j=L+1}^{L'} c_k c_j P_{27}(\zeta_k, \zeta_j) + \left. \sum_{k=L+1}^{L'} \sum_{j=L+1}^{L'} c_k c_j P_{30}(\zeta_k, \zeta_j) \right\} \\
 &\equiv I_3^{(5)}(\underline{c}, \underline{\zeta}), \text{ say,}
 \end{aligned}$$

where  $P_{27}(\lambda, \mu) = \frac{\partial^2 P_{25}}{\partial \mu^2}(\lambda, \mu)$  and

$$P_{30}(\lambda, \mu) = \frac{\partial^4}{\partial \lambda^2 \partial \mu^2} P_{25}(\lambda, \mu) .$$

These last two P functions are easily expressed in terms of K functions by using the results of Appendix E and the recurrence relation (7.26).

Similarly

$$I_3^{(13)} = I_3^{(14)} = I_3^{(15)} = I_3^{(5)}(\underline{a}, \underline{\sigma}) .$$

There are therefore only two basic types of integrals involved in the evaluation of the contribution  $I_3$  to the Born exchange amplitude, namely  $I_3^{(1)}(\underline{d}, \underline{\xi})$  and  $I_3^{(5)}(\underline{c}, \underline{\zeta})$ .

(c)  $I_2(ij, i'j')$

By analogy with equation (7.20) we have

$$\begin{aligned}
 I_2(ij, i'j') &= -\frac{1}{2\pi} \int d\underline{r}_1, \dots, d\underline{r}_{N+1} \sqrt{N!} \phi_i(1) \dots \phi_{j_0}(\ell) \dots \phi_t(N) \\
 &\times \left( \sum_{n=1}^N \frac{1}{|\underline{r}_n - \underline{r}_{N+1}|} - \frac{1}{|\underline{r}_{N+1} - \underline{r}|} \right) D_{i'j'} \{1, \dots, \ell-1, N+1, \ell+1, \dots, N\} .
 \end{aligned}$$

As before, since the potential part of the integrand is independent of  $\underline{r}_\ell$ , there is an outside factor in  $I_2$  of

$$\int d\underline{r}_\ell \phi_{j_0}^{(\ell)}$$

which is  $X(j_0)$ . (See equation (9.8).) This vanishes unless  $j_0 = 1, 3$  or  $11$ . Thus

$$I_2 = \sum_{j_0=1,3,11} I_2^{(j_0)}(i,j, i'j')$$

We consider first the case in which  $D_{ij}$  and  $D_{i'j'}$  are identical. Then the analysis of §7.3 follows through and we obtain

$$I_2^{(j)} = -\frac{1}{2\pi} X(j) \left\{ \sum_{\substack{n=1 \\ n \neq j}}^N K_n(j) - \sum_{\substack{n \in S \\ n \neq j}} R_n(j) \right\} \quad (9.11)$$

where

$$K_n(j) = \int d\underline{r} \int d\underline{R} \frac{\phi_j^*(\underline{r}) |\phi_n(\underline{R})|^2}{|\underline{r}-\underline{R}|}$$

and 
$$R_n(j) = \int d\underline{r} \int d\underline{R} \phi_j^*(\underline{R}) \phi_n^*(\underline{r}) \phi_n(\underline{R}) .$$

Once again these  $K_n$  and  $R_n$  functions can be expressed in terms of simple P functions.

First, considering the contribution  $I_2^{(1)}$  to  $I_2$ , we have

$$K_2(1s) = \int_{\underline{r}}^{\underline{R}} \frac{|\phi_1^*(\underline{r}) \phi_2(\underline{R})|^2}{|\underline{r}-\underline{R}|} d\underline{r} \equiv G_1(\underline{d}, \underline{\xi}, \underline{d}, \underline{\xi}, \underline{d}, \underline{\xi}), \quad \text{say.} \quad (9.12)$$

By using the expansion (8.12) for the 1s function and writing

$\alpha_{k\ell} = \xi_k + \xi_j$  we obtain

$$\begin{aligned} K_2(1s) = & \sum_{j=1}^M d_j \left\{ \sum_{k=1}^M \sum_{\ell=1}^M P_1(\xi_j, \alpha_{k\ell}) + \sum_{k=1}^M \sum_{\ell=M+1}^{M'} P_7(\xi_j, \alpha_{k\ell}) \right. \\ & + \sum_{k=1}^M \sum_{\ell=M'+1}^{M''} P_2(\xi_j, \alpha_{k\ell}) + \sum_{k=M+1}^{M'} \sum_{\ell=1}^M P_7(\xi_j, \alpha_{k\ell}) \\ & + \sum_{k=M+1}^{M'} \sum_{\ell=M+1}^{M'} P_2(\xi_j, \alpha_{k\ell}) + \sum_{k=M+1}^{M'} \sum_{\ell=M'+1}^{M''} P_{39}(\xi_j, \alpha_{k\ell}) \\ & + \sum_{k=M'+1}^{M''} \sum_{\ell=1}^M P_2(\xi_j, \alpha_{k\ell}) + \sum_{k=M'+1}^{M''} \sum_{\ell=M+1}^{M'} P_{39}(\xi_j, \alpha_{k\ell}) \\ & \left. + \sum_{k=M'+1}^{M''} \sum_{\ell=M'+1}^{M''} P_{40}(\xi_j, \alpha_{k\ell}) \right\} d_k d_\ell \\ & + \sum_{j=M+1}^{M'} d_j F(k, \ell) + \sum_{j=M'+1}^{M''} d_j H(k, \ell) . \end{aligned}$$

$F(k, \ell)$  is similar to the expression in the curly brackets but with the functions  $P_1, P_2, P_7, P_{39}$  and  $P_{40}$  replaced by  $P_5, P_6, P_3, P_{41}$  and  $P_{42}$  respectively. In  $H(k, \ell)$  these functions are replaced by  $P_2', P_{43}, P_6', P_{44}$  and  $P_{45}$ . Here, prime denotes that the arguments  $\lambda$  and  $\mu$  of  $P_i(\lambda, \mu)$

are interchanged. The P functions are defined in Appendix D.

Similarly,

$$K_3(1s) = K_4(1s) = G_1(\underline{d}, \underline{\xi}, \underline{e}, \underline{\delta}, \underline{e}, \underline{\delta})$$

and  $K_{11}(1s) = K_{12}(1s) = G_1(\underline{d}, \underline{\xi}, \underline{b}, \underline{\chi}, \underline{b}, \underline{\chi})$ .

$$\begin{aligned} \text{Now } K_5(1s) &= \int d\underline{r} \frac{\int d\underline{R} \phi_1(\underline{r}) |\phi_5(\underline{R})|^2}{|\underline{r}-\underline{R}|} \\ &\equiv G_2(\underline{d}, \underline{\xi}, \underline{c}, \underline{\zeta}, \underline{c}, \underline{\zeta}), \text{ say.} \end{aligned} \tag{9.13}$$

It is easily shown that  $K_5$  is independent of the magnetic quantum number of the state  $\phi_5$ . For

$$\begin{aligned} K_5(1s) &= \int d\underline{r} \int d\underline{R} \phi_1(\underline{r}) R_{2p}^2(\underline{R}) |Y_{1m}(\underline{R})|^2 \sum_{\alpha\beta} \frac{4\pi}{2\alpha+1} \gamma_\alpha(\underline{r}, \underline{R}) \\ &\quad \times Y_{\alpha\beta}(\hat{\underline{r}}) Y_{\alpha\beta}^*(\hat{\underline{R}}) \end{aligned}$$

where, as can be seen from equation (3.12),  $\phi_1(\underline{r})$  is purely radial, and where we have written  $\phi_{2pm}(\underline{r}) = R_{2p}(\underline{r}) Y_{1m}(\hat{\underline{r}})$  ( $m = 1$ ). We have used the expansion (2.1) for  $|\underline{r} - \underline{R}|^{-1}$ . The angular  $\hat{\underline{r}}$  integration is trivial and yields  $\sqrt{4\pi} \delta_{\alpha 0} \delta_{\beta 0}$ . Thus

$$\begin{aligned} K_5(1s) &= 4\pi \int_0^\infty r^2 dr \int_0^\infty R^2 R_{2p}^2(\underline{R}) dR \gamma_0(\underline{r}, \underline{R}) \phi_1(\underline{r}) \\ &= \frac{1}{4\pi} \int d\underline{r} \int d\underline{R} \frac{\phi_1(\underline{r}) R_{2p}^2(\underline{R})}{|\underline{r}-\underline{R}|} \end{aligned}$$

Clearly, this is independent of  $m$ . Therefore

$$K_i(1s) = G_2(\underline{d}, \underline{\xi}, \underline{c}, \underline{\zeta}, \underline{c}, \underline{\zeta}) \quad \text{for } i \in [5, 10].$$

Now by using the expansions (8.12) and (8.13), and writing

$\beta_{j\ell} = \zeta_j + \zeta_\ell$ , we obtain

$$\begin{aligned}
 G_2(\underline{d}, \underline{\xi}, \underline{c}, \underline{\zeta}, \underline{c}, \underline{\zeta}) &= \frac{1}{4\pi} \sum_{k=1}^M d_k \left\{ \sum_{j=1}^L \sum_{\ell=1}^L P_2(\xi_k, \beta_{j\ell}) \right. \\
 &+ \sum_{j=1}^L \sum_{\ell=L+1}^{L'} P_{40}(\xi_k, \beta_{j\ell}) + \sum_{j=L+1}^{L'} \sum_{\ell=1}^L P_{40}(\xi_k, \beta_{j\ell}) \\
 &+ \left. \sum_{j=L+1}^{L'} \sum_{\ell=L+1}^{L'} 4\pi P_{18}(\xi_k, \beta_{j\ell}) \right\} c_j c_\ell \\
 &+ \frac{1}{4\pi} \sum_{k=M+1}^{M'} d_k \left\{ \sum_{j=1}^L \sum_{\ell=1}^L P_6(\xi_k, \beta_{j\ell}) + \sum_{j=1}^L \sum_{\ell=L+1}^{L'} P_{42}(\xi_k, \beta_{j\ell}) \right. \\
 &+ \sum_{j=L+1}^{L'} \sum_{\ell=1}^L P_{42}(\xi_k, \beta_{j\ell}) + \sum_{j=L+1}^{L'} \sum_{\ell=L+1}^{L'} 4\pi P_{21}(\xi_k, \beta_{j\ell}) \left. \right\} c_j c_\ell \\
 &+ \frac{1}{4\pi} \sum_{k=M'+1}^{M''} d_k \left\{ \sum_{j=1}^L \sum_{\ell=1}^L P_{43}(\xi_k, \beta_{j\ell}) + \sum_{j=L+1}^{L'} \sum_{\ell=1}^L P_{45}(\xi_k, \beta_{j\ell}) \right. \\
 &+ \sum_{j=1}^L \sum_{\ell=L+1}^{L'} P_{45}(\xi_k, \beta_{j\ell}) + \sum_{j=L+1}^{L'} \sum_{\ell=L+1}^{L'} 4\pi P_{24}(\xi_k, \beta_{j\ell}) \left. \right\} c_j c_\ell .
 \end{aligned}$$

The relevant P functions are defined in Appendix D.

In a similar way, for  $i \in [13, 18]$  we have

$$K_i(1s) = G_2(\underline{d}, \underline{\xi}, \underline{a}, \underline{\sigma}, \underline{a}, \underline{\sigma}) .$$

The  $K_1(2s)$  and  $K_1(3s)$  functions follow an identical pattern. They are obtained from the corresponding  $K_1(1s)$  functions by replacing the array  $(\underline{d}, \underline{\xi})$  which occurs first in the  $G_1$  or  $G_2$  function by the arrays  $(\underline{e}, \underline{\delta})$  and  $(\underline{b}, \underline{\chi})$  respectively. Thus there are only two basic types of integral occurring in the functions  $K_1(ns)$ , namely  $G_1$  and  $G_2$ .

We now proceed to the  $R_1(ns)$  functions. In view of equation (9.11) we need only consider these for the state  $\phi_1$  belonging to the set of spin-up orbitals. We have

$$R_3(1s) = \int \underline{d\underline{r}} \int \underline{d\underline{R}} \frac{\phi_1^*(\underline{R})\phi_3^*(\underline{r})\phi_3(\underline{R})}{|\underline{r}-\underline{R}|}$$

which is simply  $G_1(\underline{e}, \underline{\delta}, \underline{d}, \underline{\xi}, \underline{e}, \underline{\delta})$ . Similarly

$$R_{11}(1s) = G_1(\underline{b}, \underline{\chi}, \underline{d}, \underline{\xi}, \underline{b}, \underline{\chi})$$

$$R_1(2s) = G_1(\underline{d}, \underline{\xi}, \underline{e}, \underline{\delta}, \underline{d}, \underline{\xi})$$

$$R_{11}(2s) = G_1(\underline{b}, \underline{\chi}, \underline{e}, \underline{\delta}, \underline{d}, \underline{\xi})$$

$$R_1(3s) = G_1(\underline{d}, \underline{\xi}, \underline{b}, \underline{\chi}, \underline{d}, \underline{\xi})$$

$$R_3(3s) = G_1(\underline{e}, \underline{\delta}, \underline{b}, \underline{\chi}, \underline{e}, \underline{\delta}) .$$

For  $k = 5, 6$  or  $7$

$$R_k(ns) = \int \underline{d\underline{r}} \int \underline{d\underline{R}} \phi_{ns}^*(\underline{r})\phi_{2pm}^*(\underline{R})\phi_{2pm}(\underline{r})$$

By noting the expansions (8.12) and (8.13) and the definition of  $P_{2s}(\lambda, \mu)$ , equation (9.10), it is easily seen that  $R_k(ns)$  involves sums of various derivatives of  $P_{25}$ . We have already shown that  $P_{25}$  is independent of the magnetic quantum number  $m$ , and it follows that

$$R_5(ns) = R_6(ns) = R_7(ns) .$$

We can express  $R_5(1s)$  in terms of P functions in the following way:

$$\begin{aligned}
 R_5(1s) = & \sum_{k=1}^M d_k \left\{ \sum_{j=1}^L \sum_{\ell=1}^L P_{25}(\zeta_j, \gamma_{\ell k}) \right. \\
 & + \sum_{j=1}^L \sum_{\ell=L+1}^{L'} P_{27}(\zeta_j, \gamma_{\ell k}) + \sum_{j=L+1}^{L'} \sum_{\ell=1}^L P_{27}(\gamma_{\ell k}, \zeta_j) \\
 & \left. + \sum_{j=L+1}^{L'} \sum_{\ell=L+1}^{L'} P_{30}(\zeta_j, \gamma_{\ell k}) \right\} c_\ell c_j \\
 & + \sum_{k=M+1}^{M'} d_k \left\{ \sum_{j=1}^L \sum_{\ell=1}^L P_{26}(\zeta_j, \gamma_{\ell k}) + \sum_{j=1}^L \sum_{\ell=L+1}^{L'} P_{28}(\zeta_j, \gamma_{\ell k}) \right. \\
 & \left. + \sum_{j=L+1}^{L'} \sum_{\ell=1}^L P_{33}(\zeta_j, \gamma_{\ell k}) + \sum_{j=L+1}^{L'} \sum_{\ell=L+1}^{L'} P_{31}(\zeta_j, \gamma_{\ell k}) \right\} c_\ell c_j \\
 & + \sum_{k=M'+1}^{M''} d_k \left\{ \sum_{j=1}^L \sum_{\ell=1}^L P_{27}(\zeta_j, \gamma_{\ell k}) + \sum_{j=1}^L \sum_{\ell=L+1}^{L'} P_{29}(\zeta_j, \gamma_{\ell k}) \right. \\
 & \left. + \sum_{j=L+1}^{L'} \sum_{\ell=1}^L P_{30}(\zeta_j, \gamma_{\ell k}) + \sum_{j=L+1}^{L'} \sum_{\ell=L+1}^{L'} P_{32}(\zeta_j, \gamma_{\ell k}) \right\} c_\ell c_j
 \end{aligned} \tag{9.14}$$



where  $\gamma_{\ell k} = \xi_{1k} + \zeta_{\ell}$ . The P functions are given in terms of  $P_{25}$  in Appendix E. If we define the function  $G_3$  by

$$G_3(1s, 2p, 3p) = \int d\underline{r} \int d\underline{R} \phi_{1s}^*(\underline{r}) \phi_{2p}^*(\underline{R}) \phi_{3p}(\underline{r}) \quad (9.15)$$

and similarly for other combinations of s and p states then

$$R_5(ns) = R_6(ns) = R_7(ns) = G_3(ns, 2p, 2p)$$

and  $R_{13}(ns) = R_{14}(ns) = R_{15}(ns) = G_3(ns, 3p, 3p)$ .

This completes the analysis for  $I_2$  when the determinants  $D_{ij}$  and  $D_{i'j'}$  are identical. Next we suppose that they differ by two orbitals.

Let  $\phi_i$  and  $\phi_k$  be the orbitals which are occupied in  $D_{ij}$ , but not in  $D_{i'j'}$  and  $\phi_m$  and  $\phi_j$  those which are occupied in  $D_{i'j'}$ , but not in  $D_{ij}$ . We assume that the orbitals  $\phi_p$  in the determinants are listed in order of increasing p and that  $i < k$  and  $m < j$ . We define the numbers  $P_i$  ( $i = 1 - 18$ ) to be the occupation numbers of the states  $\phi_i$  in a given determinant, D, so that  $P_i = 1$  if the state  $\phi_i$  is occupied in D and is zero otherwise. Then we denote by  $S_p$  the sum  $\sum_{i=1}^P P_i$ . Effectively,  $S_p$  gives the position of the orbital  $\phi_p$  in the determinant.

By analogy with equation (7.20) we have

$$\begin{aligned} I_2(ij, i'j') = & -\frac{1}{2\pi} \sum_{j_0 \in S} \int d\underline{r}_{-1} \dots d\underline{r}_{-N+1} D\{\phi_r(1) \dots \phi_i(q) \dots \phi_{j_0}(\ell) \dots \\ & \dots \phi_k(p) \dots \phi_t(N)\} \left( \sum_{n=1}^N \frac{1}{|\underline{r}_n - \underline{r}_{N+1}|} - \frac{1}{|\underline{r} - \underline{r}_{N+1}|} \right) \\ & \times D\{\phi_r^*(1) \dots \phi_m^*(r) \dots \phi_{j_1}^*(N+1) \dots \phi_j^*(S) \dots \phi_t^*(N)\} . \end{aligned}$$

This equation is rather complicated but it does simplify considerably.

The coordinates which are involved in the integrand apart from in the wavefunctions are  $\underline{r}_n$ ,  $\underline{r}_\ell$  and  $\underline{r}_{N+1}$ . Since the orbitals  $\phi_i$ ,  $\phi_k$ ,  $\phi_j$  and  $\phi_m$  occur in only one of the determinants and since the states  $\phi_p$  are orthogonal, it follows that  $\phi_{j_0} = \phi_i$  or  $\phi_k$  and  $\phi_{j_1} = \phi_m$  or  $\phi_j$ .

Also,  $n$  can only take the value  $p$  or  $q$ , according as  $j_0 = i$  or  $k$ .

It can easily be shown that there are two non-vanishing terms in each of the determinants, and we obtain the result that

$$I_2(ij, i'j') = -\frac{1}{2\pi} \iiint \frac{d\underline{r}_p d\underline{r}_i d\underline{r}_{N+1}}{|\underline{r}_p - \underline{r}_{N+1}|} \left\{ (\phi_i(\ell) \phi_k(p) - \phi_i(p) \phi_k(\ell)) \right. \\ \left. \times (\phi_m^{*(N+1)} \phi_j^*(p) - \phi_m^*(p) \phi_j^{*(N+1)}) \right\} (-1)^{s_m - s_k - s_i + s_j} .$$

The multiplicative factor comes from the necessary rearrangement of the rows of the determinants. Since spin must be conserved, there are further restrictions which must be considered. First, the spin of the final state with coordinate  $\underline{r}_{N+1}$  must be spin-up. Second, the initial and final states with position vector  $\underline{r}_p$  must have the same spins. We define the function  $T_{knj}$  by

$$T_{knj} = \int d\underline{r} \int d\underline{R} \frac{\phi_k(\underline{r}) \phi_n^*(\underline{R}) \phi_j^*(\underline{r})}{|\underline{r} - \underline{R}|} \quad (9.16)$$

Then

$$I_2(ij, i'j') = -\frac{1}{2\pi} \left\{ X(i) (T_{kmj} - T_{kjm}) - X(k) (T_{imj} - T_{ijm}) \right\} \\ \times (-1)^{s_m - s_k - s_i - s_j} \quad (9.17)$$

where the X functions are defined by equation (9.8). We have mentioned before that  $X(i)$  vanishes unless  $\phi_i$  is a spin-up s-state. It follows that unless at least one of  $\phi_i$  and  $\phi_k$  is a spin-up s state, then  $I_2$  is zero. Because of the restrictions due to spin, mentioned above,  $T_{kmj}$  is zero unless  $\phi_m$  is a spin-up state, and  $\phi_k$  and  $\phi_j$  have the same spin.

We now consider the function  $T_{kmj}$ . By comparing equation (9.16) with equations (9.12), (9.13) and (9.15), we see that  $T_{kmj}$  is either a  $G_1$ , a  $G_2$  or a  $G_3$  integral. In Table 9.2 we give the combinations of  $k$ ,  $m$  and  $j$  which give a non-zero  $T_{kmj}$ . It should be noted that, for a given horizontal line, if in one column three numbers appear separated by commas, then in any other column in which three numbers appear separated by commas, the corresponding entry must be taken. For example, if  $k = 6$  and  $m = 3$ , then for a non-zero result we must have  $j = 14$ . The combination  $k = 6$ ,  $m = 3$  and  $j = 13$  is not allowed in the table, and so the corresponding T function is zero. The final column gives the resulting type of integral.

We can in this way evaluate the contribution  $I_2(ij, i'j')$  given by equation (9.17) for any pair of determinants  $D_{ij}$  and  $D_{i'j'}$ , which differ by two orbitals.

This completes the analysis necessary to evaluate the matrix element (9.7) of the potential  $V$  with respect to any two allowed determinants. Therefore, since the weight factors  $c_i$  and the constants  $\alpha_{ij}$  are known we can use equation (9.6) to calculate the Born exchange amplitude at zero energy, for the elastic scattering of an electron by an N-electron atom.

We have written a computer program BORN which performs this calculation. It follows the above analysis precisely and so we do not go into further detail here. The program was tested by using it to

calculate  $g_{\beta}(0, 0)$  for the neon atom in its closed shell configuration,  $(1s)^2(2s)^2(2p)^6$ , using the tabulated Clementi (1965) wavefunctions.

In this case the problem reduces to that discussed in §7.3, and the results should agree with those of Table 7.3. This agreement was found.

Table 9.2

The non zero cases of  $T_{kmj}$

<u>k</u>	<u>m</u>	<u>j</u>	<u>Type of Integral</u>
2 or 4 or 12	3 or 11	2 or 4 or 12	$G_1$
2 or 4 or 12	5, 6, 7	8, 9, 10	$G_3$
2 or 4 or 12	5, 6, 7	16, 17, 18	$G_3$
2 or 4 or 12	13, 14, 15	8, 9, 10	$G_3$
2 or 4 or 12	13, 14, 15	16, 17, 18	$G_3$
3 or 11	5, 6, 7	13, 14, 15	$G_3$
3 or 11	13, 14, 15	5, 6, 7	$G_3$
5, 6, 7	3 or 11	13, 14, 15	$G_2$
5, 6, 7	13, 14, 15	3 or 11	$G_3$
13, 14, 15	3 or 11	5, 6, 7	$G_2$
13, 14, 15	5, 6, 7	3 or 11	$G_3$
8, 9, 10	3 or 11	16, 17, 18	$G_2$
8, 9, 10	13, 14, 15	2 or 4 or 12	$G_3$
8, 9, 10	5, 6, 7	2 or 4 or 12	$G_3$
16, 17, 18	3 or 11	8, 9, 10	$G_2$
16, 17, 18	5, 6, 7	2 or 4 or 12	$G_3$
16, 17, 18	13, 14, 15	2 or 4 or 12	$G_3$

CHAPTER X

PRELIMINARY RESULTS

10.1. The Programs

We have a suite of three computer programs which calculate the Born exchange scattering amplitude at zero energy.

(a) An MCHF program.

We have two such programs, one written by Fischer (1969) and the other an unpublished program of Bagus. They calculate a configuration interaction wavefunction, as described in §8.1. The total wavefunction is written in the form (9.3)

$$\Psi = \sum_{i,j} c_i \alpha_{ij} D_{ij} .$$

The  $\alpha_{ij}$  are constants depending on the given configurations and are calculated by Hibbert (1971). The  $D_{ij}$  are Slater determinants. The CI program outputs the weights  $c_i$  and the radial wavefunctions in numerical form.

(b) A Fitting Program.

This fits the numerical wavefunctions calculated by the CI program to a Clementi-type analytic form, equations (8.12) and (8.13). It is described in §8.2.

(c) BORN.

This uses the fitted wavefunctions and the weights  $c_i$  to calculate the Born exchange scattering amplitude  $g_B(0, 0)$  (see equation (9.6)).

The two versions of the CI program were run for the single configuration  $(1s)^2(2s)^2(2p)^6$  of neon and the results for the total energy were compared. The Fischer program predicted a value of -128.5472 a.u. which compares with the Clementi Hartree-Fock (1965) value of -128.5470 a.u. . The Bagus program produced a slightly higher energy of -128.5447 a.u. . However, for the two configuration case which we shall discuss in §10.3 we were unable to obtain convergence of the wavefunctions with the Fischer program. For this reason, and also because it allows more configurations and is believed to be more accurate, we choose to use the Bagus version of the CI program.

#### 10.2. The one-configuration example for neon

We have run the Bagus CI program for the single configuration of neon,  $(1s)^2(2s)^2(2p)^6$ , and have stored the resulting radial wavefunctions on magnetic tape. These orbitals have been fitted to the Clementi-type of analytic form, as described in §8.2. The initial values of the parameters were chosen to be those of the Clementi 5-state function, given in Table 7.2. The best values of  $\chi^2$  which were achieved for the 1s, 2s and 2p orbitals were respectively .033, .42 and .033. The resulting analytic wavefunctions were used in BORN to calculate  $g_B(0, 0)$ . It was found to be 5.072. Comparing with Table 7.3 we see that although this improves slightly on the previous Clementi 5-state value, it is lower than the values from the Clementi 6-state and the Weber et al. wavefunctions. However, we would expect this to be the case, since the total energy predicted by this CI wavefunction is lower than the standard Hartree-Fock value.

### 10.3. A Two-configuration Example

We have considered the two configuration representation of the ground state of the neon atom in which we have the configurations

$$(i) \quad (1s)^2(2s)^2(2p)^6$$

$$(ii) \quad (1s)^2(2s)^2(2p)^4(3s)^2 \quad .$$

We do not expect this second configuration to be important, but it is the simplest one with which to test our suite of programs. The input data required for the CI program has been discussed in §8.1. The only quantities which are not uniquely defined are the initial weights  $c_j$  of the two configurations. There is no systematic way of estimating these, and we have found that the CI programs are very sensitive to the values chosen. We have tried many values to obtain results from the Fischer program but have so far been unsuccessful. We have, however, managed to get convergence in the Bagus program, using the initial weights of .85 and .15 for the configurations (i) and (ii) respectively. The total energy of the neon atom predicted by this choice is -128.5469, which is still slightly higher than the standard Clementi value.

The final weights produced by the program were .999990 and -.004455. The numerical radial wavefunctions for the 1s, 2s, 2p and 3s orbitals were fitted to the analytic forms (8.12) and (8.13). For the 1s, 2s and 2p orbitals the initial parameters were chosen to be the Clementi 5-state values used earlier in the one-configuration example and given in Table 7.2. The parameters for the 3s function were guessed, and convergence of  $\chi^2$  was only obtained after a large number of iterations. The best values of  $\chi^2$  which were obtained for the 1s, 2s,



2p and 3s orbitals were respectively .04, .4, .008 and .37.

The Born exchange amplitude,  $g_B(0, 0)$ , was then calculated using these fitted orbitals and was found to be 5.014, which is slightly worse than in the one-configuration calculation.

However, no real importance can be attached to these preliminary results. The main purpose of this calculation has been to test the suite of programs which we have developed. It is clear that the CI program is very sensitive to the initial choice of the weights  $c_i$ . Also, we expect the second configuration which we have used,  $(1s)^2(2s)^2(2p)^4(3s)^2$  to be unimportant. Much more important will be the configuration  $(1s)^2(2s)^2(2p)^4(3p)^2$ .

#### 10.4. Conclusions

The method of phase shift analysis of experimental data has been successfully applied to electron-helium scattering by Bransden and McDowell (1961). The dispersion relation which was conjectured by Gerjuoy and Krall (1960) has been tested for this case and shown to be consistent within the errors associated with it. We have applied a similar technique to the problem of electron-neon scattering, our aim being to test the dispersion relation. Our initial calculation resulted in a discrepancy in the dispersion relation evaluated at zero energy. There are two possible conclusions which can be drawn from this. First, the conjectured dispersion relation is not valid, or secondly, there are errors in our calculations of the quantities involved in it. This latter point needs further investigation. There are two sources of error in our calculation. There are uncertainties in the adopted values of the total cross-section, because of the lack of direct experimental measurements and the resulting interpolation in the intermediate energy range. Also the Born approximation to the exchange scattering amplitude

$g_B(0, 0)$ , is very sensitive to the ground state wavefunction of the neon atom. The standard Clementi Hartree-Fock functions may not be accurate enough. This last point can be tested by repeating the calculation with a highly-correlated configuration interaction type of wavefunction. We have developed a suite of computer programs to calculate  $g_B(0, 0)$  using a CI wavefunction, but at present this work is in a preliminary stage. Our programs have been tested by considering a two configuration example. There still remains a lot to be done in investigating the importance of such an approach, the most immediate problem being the calculation of the Born exchange amplitude including several configurations in the neon wavefunction. This work is in progress at the present time.

To conclude then, although at the moment there is a discrepancy in the dispersion relation for electron-neon scattering, it is thought likely that this is due to errors in our calculations. Much more experimental data on the total scattering cross-section is required particularly in the intermediate energy range. Also, the Born exchange scattering amplitude must be evaluated using a very accurate ground state neon wavefunction.

APPENDIX A

We consider the J integrals which are defined by equation (5.5)

$$\begin{aligned}
 J_{\ell_4}(l_s, k_0^{\ell_4}; k_4^{\ell_4}, k_3^{\ell_3}) &= \int_0^\infty dr_1 \int_0^\infty dr_2 P(l_s, r_1) P(k_4^{\ell_4}, r_1) P(k_3^{\ell_3}, r_2) \\
 &\quad P(k_0^{\ell_4}, r_2) \beta_{\ell_4}(r_1, r_2) \quad (A.1) \\
 &\equiv J_{\ell_4}(k_4^{\ell_4}, k_3^{\ell_3}).
 \end{aligned}$$

For reasons explained in the text we take  $\ell_4 = 1$ . The appropriate  $\beta$  function is given by Sack (1964):

$$\beta_1(r_1, r_2) = \frac{3}{4} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \log \left( \frac{r_1 + r_2}{|r_1 - r_2|} \right) - \frac{3}{2r_1 r_2} .$$

We write equation (A.1) in the form

$$J_1(k_4^1, k_3^{\ell_3}) = \int_0^\infty P(k_0^1, r_1) P(k_3^{\ell_3}, r_1) g(k_4^1, r_1) dr_1 \quad (A.2)$$

where

$$g(k_4^1, r_1) = - \frac{3}{2r_1} \int_0^\infty \frac{dr_2}{r_2} P(l_s, r_2) P(k_4^1, r_2) + \frac{3}{4} N(r_1)$$

with

$$N(r_1) = \int_0^\infty dr_2 P(l_s, r_2) P(k_4^1, r_2) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \log \left( \frac{r_1 + r_2}{|r_1 - r_2|} \right) .$$

The first integral in  $g$  can be evaluated numerically as it stands, but  $N(r_1)$  has a logarithmic singularity at the origin. We transform  $N(r_1)$

into a form suitable for the application of the Krilov formula.

We have

$$\begin{aligned}
 N(r_1) = & \int_0^\infty dr_2 h(r_2) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \log(r_1+r_2) - \int_0^{r_1} dr_2 h(r_2) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \log|r_1-r_2| \\
 & - \int_{r_1}^{2r_1} dr_2 h(r_2) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \log|r_1-r_2| - \int_{2r_1}^\infty dr_2 h(r_2) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \log|r_1-r_2|
 \end{aligned} \tag{A.3}$$

where  $h(r) = P(1s, r)P(k_4p, r)$ .

The substitutions  $y = \frac{r_1-r_2}{r_1}$ ,  $y = \frac{r_2-r_1}{r_1}$  and  $y = r_2-2r_1$  are made in the second, third and fourth integrals respectively on the r.h.s. of equation (A.3), giving

$$\begin{aligned}
 N(r_1) = & \int_0^\infty h(r_2) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \log(r_1+r_2) - \int_0^1 r_1 dy h(r_1-r_1y) \left( \frac{1}{r_1} + \frac{1}{(r_1-r_1y)^2} \right) \\
 & \times \log(r_1, y) \\
 & - \int_0^1 r_1 dy h(r_1+r_1y) \left( \frac{1}{r_1} + \frac{1}{(r_1+r_1y)^2} \right) \log(r_1y) \\
 & - \int_0^\infty dy h(y+2r_1) \left( \frac{1}{r_1} + \frac{1}{(y+2r_1)^2} \right) \log(y+r_1)
 \end{aligned} \tag{A.4}$$

The second term, Y say, in this expression can be written as the sum of two terms, one involving  $\log r_1$  and the other  $\log y$ :

$$\begin{aligned}
 Y = & r_1 \log r_1 \int_0^1 dy h(r_1-r_1y) \left( \frac{1}{r_1} + \frac{1}{(r_1-r_1y)^2} \right) \\
 & + r_1 \int_0^1 dy h(r_1-r_1y) \left( \frac{1}{r_1} + \frac{1}{(r_1-r_1y)^2} \right) \log y
 \end{aligned}$$

The first term in Y can be simplified by making the substitution  $x = (1-y)r_1$ . That is

$$Y = \log r_1 \int_0^{r_1} dx h(x) \left( \frac{1}{r_1} + \frac{1}{x} \right) + r_1 \int_0^1 \log y dy h(r_1 - r_1 y) \left( \frac{1}{r_1} + \frac{1}{(r_1 - r_1 y)^2} \right).$$

The third term in equation (A.4) can be treated similarly to Y using the substitution  $x = (1 + y)r_1$  and we obtain as the final expression for  $N(r_1)$

$$\begin{aligned} N(r_1) = & \int_0^\infty h(r_2) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \log(r_1 + r_2) dr_2 \\ & - \log r_1 \int_0^{2r_1} dx h(x) \left( \frac{1}{r_1} + \frac{1}{x} \right) \\ & - r_1 \int_0^1 dy \log y \left( \frac{1}{r_1} + \frac{1}{(r_1 - r_1 y)^2} \right) h(r_1 - r_1 y) + \left( \frac{1}{r_1} + \frac{1}{(r_1 + r_1 y)^2} \right) \\ & \hspace{20em} h(r_1 + r_1 y) \\ & - \int_0^\infty dy \left( \frac{1}{r_1} + \frac{1}{(y + 2r_1)^2} \right) \log(y + r_1) h(y + 2r_1) . \end{aligned}$$

In this form all except the third integral in  $N(r_1)$  can be evaluated directly using a Simpson's rule. The remaining integral can be performed by using a 5-point Krilov formula, which for a function  $f(y)$  is

$$\int_0^1 f(y) \log y dy = \sum_{n=1}^5 f(y_n) \omega_n$$

where the weights  $\omega_n$  and the abscissae  $y_n$  are given in Table A.1.

Table A.1

The Krilov Weights and Abscissae

<u>n</u>	<u>weight <math>\omega_n</math></u>	<u>abscissae <math>y_n</math></u>
1	.297893	.029345
2	.349776	.173977
3	.234488	.411703
4	.0989305	.677314
5	.0189116	.894771

Now the function  $P(k_4 p, x)$  occurring in  $h(x)$  has been evaluated and stored at 475 points as described in §2.1. The value of the function  $P(k_4 p, r_1 - r_1 y_n)$  is taken to be the value of  $P(k_4 p, y)$  where  $y$  is the nearest point to  $r_1 - r_1 y_n$  at which the function has been stored. This will not introduce any inaccuracies since the mesh size involved is so small.

A 475-point Simpson's rule was used to evaluate the final integration over  $r$ , in equation (A.2), thus giving the function  $J_1(k_4 l, k_3 l_3)$ .

APPENDIX B

We give here an outline of the method which was first proposed by Bransden et al. (1954), of evaluating the function  $M(\lambda, \mu)$  defined by

$$M(\lambda, \mu) = \int d\underline{r}_1 \int d\underline{r}_2 \frac{e^{ik \cdot (\underline{r}_1 - \underline{r}_2)} e^{-\lambda r_1} e^{-\mu r_2}}{|\underline{r}_1 - \underline{r}_2|} \quad (B.1)$$

We define the function  $\bar{M}(\lambda, \mu)$  by

$$\bar{M}(\lambda, \mu) = \int d\underline{r}_1 \int d\underline{r}_2 \frac{e^{ik \cdot (\underline{r}_1 - \underline{r}_2)} e^{-\lambda r_1} e^{-\mu r_2}}{|\underline{r}_1 - \underline{r}_2| r_1 r_2} \quad (B.2)$$

so that 
$$M(\lambda, \mu) = \frac{\partial^2 \bar{M}(\lambda, \mu)}{\partial \lambda \partial \mu} \quad (B.3)$$

By making use of the two results (see Dwight)

$$\frac{1}{|\underline{r}_1 - \underline{r}_2|} = \frac{2}{\sqrt{\pi}} \int_0^\infty dx e^{-|r_1 - r_2| x} e^{-x^2}$$

$$\frac{e^{-\lambda r_1}}{r_1} = \frac{2}{\sqrt{\pi}} \int_0^\infty dy e^{-(\lambda^2/4y^2 + r_1^2 y^2)}$$

we have

$$\bar{M}(\lambda, \mu) = \frac{8}{\pi^{3/2}} \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz e^{-\left(\frac{\lambda^2}{4y^2} + \frac{\mu^2}{4z^2}\right)} N(x, y, z) \quad (B.4)$$

where

$$N(x, y, z) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} e^{-x^2(r_1^2 + r_2^2 - 2r_1 r_2) - y^2 r_1^2 - z^2 r_2^2}$$

N was evaluated by Bransden et al. and shown to be

$$N(x, y, z) = \frac{\pi^3 e^{-k_0^2/4q}}{(x^2 y^2 + y^2 z^2 + z^2 x^2)^{3/2}} \tag{B.5}$$

with 
$$q = \frac{x^2 y^2 + y^2 z^2 + z^2 x^2}{y^2 + z^2}$$

By making the substitutions  $x = R \cos \theta$ ,  $y = R \sin \theta \sin \phi$ ,  $z = R \sin \theta \cos \phi$ , and combining (B.4) and (B.5) we obtain

$$\bar{M}(\lambda, \mu) = 8\pi^{3/2} \int_0^\infty R^2 dR \int_0^{\pi/2} \sin \theta d\theta \int_0^{\pi/2} \frac{d\phi e^{-\xi/R^2}}{R^6 \sin^3 \theta L^{3/2}}$$

where  $L = \cos^2 \theta + \sin^2 \theta \sin^2 \phi \cos^2 \phi$  (B.6)

and 
$$\xi = \frac{1}{4} \left( \frac{k^2}{L} + \frac{\lambda^2}{\sin^2 \theta \sin^2 \phi} + \frac{\mu^2}{\sin^2 \theta \cos^2 \phi} \right)$$

The integration over R may be carried out using the formula (Watson 1944)

$$\int_0^\infty e^{-\xi/R^2} e^{-2n} dR = \frac{(2n-3)!!}{2(2\xi)^{n-1}} \sqrt{\frac{\pi}{\xi}}, \quad n \geq 2$$

and so 
$$\bar{M}(\lambda, \mu) = 8\pi^{3/2} \int_0^1 d(\cos \theta) \int_0^{\pi/2} d\phi \sqrt{\frac{\pi}{\xi}} \cdot \frac{1}{4\xi \sin^3 \theta L^{3/2}}$$



We write

$$\begin{aligned} \chi &= k^2 \sin^2 \theta \sin^2 \phi \cos^2 \phi + (\lambda^2 \cos^2 \phi + \mu^2 \sin^2 \phi) L \\ &= L.4 \cos^2 \phi \sin^2 \theta \sin^2 \phi. \xi, \end{aligned} \tag{B.7}$$

then

$$\bar{M}(\lambda, \mu) = 16\pi^2 \int_0^1 d(\cos \theta) \int_0^{\pi/2} d\phi \frac{\sin^3 \phi \cos^3 \phi}{\chi^{3/2}}.$$

We next make the substitutions  $y = \cos \theta$  and  $x = \cos 2\phi$  and obtain

$$\bar{M}(\lambda, \mu) = 4\pi^2 \int_0^1 dy \int_{-1}^1 \frac{dx(1-x^2)}{4x^{3/2}}$$

Also, by combining (B.6) and (B.7) we can factor out the  $y$  dependence of  $\chi$  and express it in the form  $A+By^2$  where

$$A = \frac{1}{4}(1-x^2)k^2 + \lambda^2 \left(\frac{1+x}{2}\right) + \mu^2 \left(\frac{1-x}{2}\right) \tag{B.8}$$

and  $B = -\frac{1}{4}(1-x^2)k^2 + (1 - \frac{1}{4}(1-x^2))(\lambda^2 \left(\frac{1+x}{2}\right) + \mu^2 \left(\frac{1-x}{2}\right))$

Thus

$$\bar{M}(\lambda, \mu) = \pi^2 \int_0^1 dy \int_{-1}^1 \frac{dx(1-x^2)}{(A+By^2)^{3/2}}.$$

The integration over  $y$  is now straightforward, and

$$\bar{M}(\lambda, \mu) = \pi^2 \int_{-1}^1 \frac{dx(1-x^2)}{A\sqrt{A+B}}.$$

From equation (B.8),  $A+B = \lambda^2 \left(\frac{1+x}{2}\right) + \mu^2 \left(\frac{1-x}{2}\right) = P^2$ , say. Also

$A = \frac{1}{4}(1-x^2)(k^2+p^2)$  and thus

$$\bar{M}(\lambda, \mu) = \pi^2 \int_{-1}^1 \frac{4 dx}{P(k_o^2 + p^2)}$$

where  $dx = \frac{4p dp}{\lambda^2 - \mu^2}$ . The integration over  $p$  is trivial and we obtain as

the final expression for  $\bar{M}$

$$\bar{M}(\lambda, \mu) = \frac{16\pi^2}{(\lambda^2 - \mu^2)k} \left\{ \tan^{-1}\left(\frac{\lambda}{k}\right) - \tan^{-1}\left(\frac{\mu}{k_o}\right) \right\} .$$

By differentiating with respect to  $\lambda$  and  $\mu$  in turn we obtain the result for  $M(\lambda, \mu)$  given in equation (7.31).

APPENDIX C

In this appendix we give a brief account of the calculation of the function  $M^A(\lambda, \mu)$  which is defined by

$$M^A(\lambda, \mu) = \frac{\partial^2}{\partial \lambda \partial \mu} \left( \frac{48}{k} \int_0^\infty \frac{k^3 dk}{(k^2 + \lambda^2)^2 (k^2 + \mu^2)^2} \log \left| \frac{k+k}{k-k} \right| \right) dk$$

(see equations (7.40) and (7.41)). Clearly

$$M^A(\lambda, \mu) = \frac{2^8 \cdot 3 \lambda \mu}{k} \int_0^\infty \frac{k^3 dk}{(k^2 + \lambda^2)^3 (k^2 + \mu^2)^3} \log \left| \frac{k+k}{k-k} \right|$$

That is

$$M^A(\lambda, \mu) = \frac{3 \cdot 2^8 \lambda \mu}{k} J$$

where

$$J = \int_0^\infty \frac{k^3 \log |k+k| dk}{(k^2 + \lambda^2)^3 (k^2 + \mu^2)^3} - \int_0^\infty \frac{k^3 \log |k-k| dk}{(k^2 + \lambda^2)^3 (k^2 + \mu^2)^3}$$

The second integral has a logarithmic singularity at the origin and so we follow a technique parallel to that used in Appendix A to express it in a form suitable for the application of the Krilov formula. We split the range into three parts, 0 to k, k to 2k and 2k to  $\infty$ , and make the substitutions  $y = \frac{k-K}{k}$ ,  $y = \frac{K-k}{k}$  and  $y = K-2k$  respectively. We then obtain

$$J = \int_0^{\infty} \frac{K^3 \log |K+k| dK}{(K^2 + \lambda^2)^3 (K^2 + \mu^2)^3} - \int_0^1 \frac{k^3 (1-y)^3 \log(ky) k dy}{(k^2 (1-y)^2 + \lambda^2)^3 (k^2 (1-y)^2 + \mu^2)^3}$$

$$- \int_0^1 \frac{k^3 (1+y)^3 \log(ky) k dy}{(k^2 (1+y)^2 + \lambda^2)^3 (k^2 (1+y)^2 + \mu^2)^3} - \int_0^1 \frac{(y+2k)^3 \log(y+k) dy}{((y+2k)^2 + \lambda^2)^3 ((y+2k)^2 + \mu^2)^3}$$

That is

$$J = J_1(0, \infty) - J_2(0, 1) - J_3(0, 1) \quad (C.1)$$

where

$$J_1(0, \infty) = \int_0^{\infty} \frac{K^3 \log |K+k| dK}{(K^2 + \lambda^2)^3 (K^2 + \mu^2)^3} - \int_0^1 \frac{(y+2k)^3 \log(y+k) dy}{((y+2k)^2 + \lambda^2)^3 ((y+2k)^2 + \mu^2)^3} \quad (C.2)$$

$$J_2(0, 1) = k^4 \int_0^1 (g(a) + g(b)) \log k dy \quad (C.3)$$

and

$$J_3(0, 1) = k^4 \int_0^1 (g(a) + g(b)) \log y dy$$

with 
$$g(a) = \frac{(1-y)^3}{(k^2 (1-y)^2 + \lambda^2)^3 (k^2 (1-y)^2 + \mu^2)^3}$$

and 
$$g(b) = \frac{(1+y)^3}{(k^2 (1+y)^2 + \lambda^2)^3 (k^2 (1+y)^2 + \mu^2)^3}$$

The integral  $J_3$  can now be evaluated numerically using the 5-point Krilov formula, given in Appendix A. A ten-point Gauss-Laguerre quadrature is applied to  $J_1$ . We next consider the remaining integral,  $J_2$ , and we make the substitutions  $z = 1 - y$  and  $z = 1 + y$  in the  $g(a)$  and  $g(b)$  parts of  $J_2$ , respectively. Then

$$J_2(0, 1) = k^4 \log k \int_0^2 \frac{z^3 dz}{(k^2 z^2 + \lambda^2)^3 (k^2 z^2 + \mu^2)^3}$$

We make the further substitution  $z = y^2/k^2$  and obtain

$$J_2(0, 1) = \frac{1}{2} \log k \int_0^{4k^2} \frac{x dx}{(x^2 + Bx + c)^3}$$

where  $B = \lambda^2 + \mu^2$  and  $c = \lambda^2 \mu^2$ . This integral is straightforward; there are two cases to consider,  $\lambda = \mu$  and  $\lambda \neq \mu$ . If  $\lambda = \mu$ , we have

$$J_2(0, 1) = \frac{1}{2} \log k \int_0^{4k^2} \frac{x dx}{(x + \lambda^2)^6}$$

and thus, on integrating by parts

$$J_2(0, 1) = \log k \left[ \frac{1}{10\lambda^8} - \frac{(\lambda^2 + 20k^2)}{10(4k^2 + \lambda^2)^5} \right]. \quad (C.4)$$

If  $\lambda \neq \mu$ , the integral is more complicated, but can be evaluated using known results (Dwight) to give

$$\begin{aligned} J_2(0, 1) = & \frac{\log k}{4(\lambda^2 - \mu^2)^2} \left[ \frac{4k^2(\lambda^2 + \mu^2) + 2\lambda^2 \mu^2}{(16k^4 + (\lambda^2 + \mu^2)4k^2 + \lambda^2 \mu^2)^2} \right. \\ & - \frac{3(\lambda^2 + \mu^2)(8k^2 + \lambda^2 + \mu^2)}{(\lambda^2 - \mu^2)^2 (16k^4 + (\lambda^2 + \mu^2)4k^2 + \lambda^2 \mu^2)} - \frac{6(\lambda^2 + \mu^2)}{(\lambda^2 - \mu^2)^3} \log \left| \frac{4k^2 + \mu^2}{4k^2 + \lambda^2} \right| \\ & \left. - \frac{2}{\lambda^2 \mu^2} + \frac{3(\lambda^2 + \mu^2)^2}{\lambda^2 \mu^2 (\lambda^2 - \mu^2)^2} + \frac{6(\lambda^2 + \mu^2)}{(\lambda^2 - \mu^2)^3} \log \left| \frac{\lambda^2}{\mu^2} \right| \right] \quad (C.5) \end{aligned}$$

By combining the results of equations (C.1) - (C.5) we obtain a value for the integral  $J$  and hence for  $M^A(\lambda, \mu)$ .

APPENDIX D

There are six basic types of integral which occur in the evaluation of the Born exchange amplitude for scattering by the neon atom in its ground state as described in §7.3. They are  $P_1$ ,  $P_9$ ,  $P_{11}$ ,  $P_{12}$ ,  $P_{13}$  and  $P_4$ , and they are defined by

$$P_1(\lambda, \mu) = \int d\underline{r} \int d\underline{R} \frac{e^{-\lambda r} e^{-\mu R} e^{i\underline{k} \cdot \underline{r}}}{|\underline{r} - \underline{R}|} R^2 r Y_{10}(\underline{R}) Y_{11}(\underline{R}) Y_{11}^*(\underline{r})$$

$$P_9(\lambda, \mu) = \int d\underline{r} \int d\underline{R} \frac{e^{-\lambda r} e^{-\mu R} e^{i\underline{k} \cdot \underline{r}}}{|\underline{r} - \underline{R}|} r Y_{10}(\hat{\underline{r}})$$

$$P_{11}(\lambda, \mu) = \int d\underline{r} \int d\underline{R} \frac{e^{i\underline{k} \cdot \underline{r}} e^{-\lambda r} e^{-\mu R} R^2 r Y_{10}(\hat{\underline{r}})}{|\underline{r} - \underline{R}|} [4|Y_{11}(\hat{\underline{R}})|^2 + |Y_{10}(\hat{\underline{R}})|^2] \quad (D.1)$$

$$P_{12}(\lambda, \mu) = 2 \int d\underline{r} \int d\underline{R} \frac{e^{i\underline{k} \cdot \underline{r}} e^{-\lambda r} e^{-\mu R}}{|\underline{r} - \underline{R}|} R^2 r Y_{10}(\hat{\underline{R}}) Y_{11}(\hat{\underline{R}}) Y_{11}^*(\hat{\underline{r}})$$

$$P_{13}(\lambda, \mu) = \int d\underline{r} \int d\underline{R} \frac{e^{i\underline{k} \cdot \underline{r}} e^{-\lambda r} e^{-\mu R} R Y_{10}(\hat{\underline{R}})}{|\underline{r} - \underline{R}|}$$

$$P_4(\lambda, \mu) = \int d\underline{r} \int d\underline{R} \frac{e^{-\lambda r} e^{-\mu R} e^{i\underline{k} \cdot \underline{r}}}{|\underline{r} - \underline{R}|} r R \sum_{m=-1}^{+1} Y_{1m}^*(\hat{\underline{r}}) Y_{1m}(\hat{\underline{R}}) \quad (D.3)$$

Each of the other P functions can be expressed as simple derivatives of these with respect to  $\lambda$  and  $\mu$ . We define

$$P_2(\lambda, \mu) = \frac{\partial^2}{\partial \mu^2} P_1(\lambda, \mu), \quad P_3(\lambda, \mu) = \frac{\partial^2}{\partial \lambda \partial \mu} P_1(\lambda, \mu),$$

$$P_5(\lambda, \mu) = -\frac{\partial}{\partial \lambda} P_1(\lambda, \mu), \quad P_6(\lambda, \mu) = -\frac{\partial^3}{\partial \lambda \partial \mu^2} P_1(\lambda, \mu),$$

$$\begin{aligned}
 P_7(\lambda, \mu) &= -\frac{\partial}{\partial \mu} P_1(\lambda, \mu) , & P_{10}(\lambda, \mu) &= \frac{\partial^2}{\partial \mu^2} P_9(\lambda, \mu) , \\
 P_{15}(\lambda, \mu) &= \frac{\partial}{\partial \mu} P_9(\lambda, \mu) , & P_{14}(\lambda, \mu) &= \frac{\partial^2}{\partial \lambda \partial \mu} P_{13}(\lambda, \mu) , \\
 P_{16}(\lambda, \mu) &= \frac{\partial P_{13}(\lambda, \mu)}{\partial \lambda} , & P_{17}(\lambda, \mu) &= \frac{\partial}{\partial \mu} P_{13}(\lambda, \mu) \\
 P_8(\lambda, \mu) &= +\frac{\partial}{\partial \mu} P_4(\lambda, \mu) .
 \end{aligned}$$

Thus if we express the basic P functions in terms of the K and  $K_p$  functions given in Table 7.1, then we can easily obtain expressions for the others by using the recurrence relations (7.26).

The basic integrals  $P_1$ ,  $P_9$  and  $P_{13}$  can be expressed as combinations of K and  $K_p$  functions. In each case, the angular integration over  $\underline{R}$  can be carried out by using the expansion (2.1), leaving a simple integration over the radial coordinate R. We obtain

$$\begin{aligned}
 P_1(\lambda, \mu) &= 4\pi \left[ \frac{2}{\mu^3} K(\lambda, -1) - \frac{1}{\mu^2} K(\lambda+\mu, 0) - \frac{2}{\mu^3} K(\lambda+\mu, -1) \right] \\
 P_9(\lambda, \mu) &= \frac{\sqrt{12\pi}}{i} \left[ \frac{2}{\mu^3} K_p(\lambda, -1) - \frac{1}{\mu^2} K_p(\lambda+\mu, 0) - \frac{2}{\mu^3} K_p(\lambda+\mu, -1) \right] \\
 P_{13}(\lambda, \mu) &= \sqrt{12\pi}(-i) \left[ \frac{8}{\mu^3} K_p(\lambda, -3) - \frac{1}{\mu^2} K_p(\lambda+\mu, 0) - \frac{4}{\mu^3} K_p(\lambda+\mu, -1) \right. \\
 &\quad \left. - \frac{8}{\mu^4} K_p(\lambda+\mu, -2) - \frac{8}{\mu^5} K_p(\lambda+\mu, -3) \right] .
 \end{aligned}$$

The functions  $P_{11}$  and  $P_{12}$  are a little more difficult. However, a simple result can be obtained in the following way. We use the expansion (2.1) and note that  $Y_{10}(\hat{\underline{r}}) = \sqrt{3/4\pi} \cos\theta$  and  $Y_{11}(\hat{\underline{r}}) = \sqrt{3/8\pi} \sin\theta e^{i\phi}$  in the usual spherical polar coordinates. Thus, from equation (D.1) we have



$$P_{11}(\lambda, \mu) = \left(\frac{3}{4\pi}\right)^{3/2} \int d\underline{r} e^{-\lambda r} e^{\frac{i\mathbf{k}\cdot\underline{r}}{r}} r \cos\theta_r \int d\underline{R} e^{-\mu R} R^2 (2\sin^2\theta_k + \cos^2\theta_k) \\ \times \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2^{\ell+1}} \gamma_{\ell}(r, R) Y_{\ell m}^*(\hat{\underline{r}}) Y_{\ell m}(\hat{\underline{R}})$$

where  $\gamma_{\ell}(r, R) = [\min(r, R)]^{\ell} / [\max(r, R)]^{\ell+1}$ . There are two values of  $\ell$  which give a non-zero contribution to  $P_{11}$ , namely  $\ell = 0$  and  $\ell = 2$ .

In each case the angular integration over  $\hat{\underline{R}}$  can be carried out, and we have

$$P_{11}(\lambda, \mu) = \left(\frac{3}{4\pi}\right)^{3/2} \int d\underline{r} e^{-\lambda r} r \cos\theta_r e^{\frac{i\mathbf{k}\cdot\underline{r}}{r}} \int_0^{\infty} R^4 dR e^{-\mu R} \\ \times \left\{ \frac{20\pi}{3} \gamma_0(r, R) - \frac{8\pi}{15} \gamma_2(r, R) \cdot \frac{1}{2} (3\cos^2\theta_r - 1) \right\} \quad (D.4)$$

The expression (D.2) for  $P_{12}(\lambda, \mu)$  can be simplified by noting that  $Y_{10}(\hat{\underline{R}})Y_{11}(\hat{\underline{R}}) = \sqrt{3/20\pi} Y_{21}(\hat{\underline{R}})$ , and thus there is only one contribution from the sum arising from the expansion of  $|\underline{r} - \underline{R}|^{-1}$ , namely for  $\ell = 2$  and  $m = 1$ . Then

$$P_{12}(\lambda, \mu) = -\frac{3}{5} \frac{3}{4\pi} \int d\underline{r} e^{-\lambda r} e^{\frac{i\mathbf{k}\cdot\underline{r}}{r}} r (\cos\theta_r - \cos^3\theta_r) \int_0^{\infty} R^4 dR e^{-\mu R} \\ \times \gamma_2(r, R) \quad (D.5)$$

Equations (D.4) and (D.5) can be added together to give

$$P_{11} + P_{12} = i \sqrt{\frac{3}{4\pi}} \int d\underline{r} e^{\frac{i\mathbf{k}\cdot\underline{r}}{r}} e^{-\lambda r} r \cos\theta_r \int_0^{\infty} R^4 dR e^{-\mu R} \left[ 5\gamma_0(r, R) - \frac{2}{5}\gamma_2(r, R) \right].$$

We now carry out the radial integration over  $R$  and express the result in terms of the  $K_p$  functions given in Table 7.1. We have

$$\begin{aligned}
 P_{11} + P_{12} = & \frac{3}{4\pi}(-i) \left\{ \frac{120}{\mu^5} K_p(\lambda, -1) - \frac{288}{\mu^7} K_p(\lambda, -3) - \frac{3}{\mu^2} K_p(\lambda + \mu, 2) \right. \\
 & - \frac{18}{\mu^3} K_p(\lambda + \mu, 1) - \frac{42}{\mu^4} K_p(\lambda + \mu, 0) + \frac{24}{\mu^5} K_p(\lambda + \mu, -1) \\
 & \left. + \frac{288}{\mu^6} K_p(\lambda + \mu, -2) + \frac{288}{\mu^7} K_p(\lambda + \mu, -3) \right\} .
 \end{aligned}$$

The remaining P function  $P_4$  is defined by equation (D.3). We use the expansion (2.1) to obtain, in the usual notation

$$\begin{aligned}
 P_4(\lambda, \mu) = & \int d\underline{r} \int d\underline{R} e^{-\lambda \underline{r} - \mu \underline{R} + i \underline{k} \cdot \underline{r}} r R \sum_{m=-1}^1 \sum_{\alpha, \beta} \frac{4\pi}{2\alpha+1} Y_\alpha(r, R) \\
 & \times Y_{1m}^*(\hat{\underline{r}}) Y_{1m}(\hat{\underline{R}}) Y_{\alpha\beta}(\hat{\underline{r}}) Y_{\alpha\beta}^*(\hat{\underline{R}}) .
 \end{aligned}$$

The angular  $\underline{R}$  integration yields a factor  $\delta_{\alpha 1} \delta_{\beta m}$ , and so

$$P_4(\lambda, \mu) = \int d\underline{r} e^{-\lambda \underline{r} + i \underline{k} \cdot \underline{r}} r \int_0^\infty R^3 dR e^{-\mu R} Y_1(r, R) \sum_{m=-1}^1 \frac{4\pi}{3} Y_{1m}^*(\hat{\underline{r}}) Y_{1m}(\hat{\underline{r}}) .$$

Now  $|Y_{10}(\hat{\underline{r}})|^2 + 2|Y_{11}(\hat{\underline{r}})|^2 = 3/4\pi$  and therefore

$$P_4(\lambda, \mu) = \int d\underline{r} e^{-\lambda \underline{r}} e^{i \underline{k} \cdot \underline{r}} r \int_0^\infty R^3 e^{-\mu R} \gamma(r, R) .$$

The R integration is straightforward and we obtain

$$\begin{aligned}
 P_4(\lambda, \mu) = & \frac{24}{\mu^5} K(\lambda, -1) - \frac{3}{\mu^2} K(\lambda + \mu, 2) - \frac{12}{\mu^3} K(\lambda + \mu, 1) \\
 & - \frac{24}{\mu^4} K(\lambda + \mu, 0) - \frac{24}{\mu^5} K(\lambda + \mu, -1) .
 \end{aligned}$$

P functions which are higher derivatives of the function  $P_1$  are needed in the evaluation of  $g_B(0, 0)$  for the N-electron atom. We give a list of these, defining them in terms of  $P_1$ . They are easily calculated explicitly by noting the recurrence relation (7.26).

$$P_{39}(\lambda, \mu) = -\frac{\partial^3}{\partial \mu^3} P_1(\lambda, \mu)$$

$$P_{40}(\lambda, \mu) = \frac{\partial^4}{\partial \mu^4} P_1(\lambda, \mu)$$

$$P_{41}(\lambda, \mu) = \frac{\lambda^4}{\partial \lambda \partial \mu^3} P_1(\lambda, \mu)$$

$$P_{42}(\lambda, \mu) = \frac{\lambda^5}{\partial \lambda \partial \mu^4} P_1(\lambda, \mu)$$

$$P_{43}(\lambda, \mu) = \frac{\partial}{\partial \lambda^2 \partial \mu^2} P_1(\lambda, \mu)$$

$$P_{44}(\lambda, \mu) = \frac{\lambda^5}{\partial \lambda^2 \partial \mu^3} P_1(\lambda, \mu)$$

$$P_{45}(\lambda, \mu) = \frac{\lambda^6}{\partial \lambda^2 \partial \mu^4} P_1(\lambda, \mu)$$

$$P_{18}(\lambda, \mu) = \frac{1}{4\pi} \frac{\partial^6}{\partial \mu^6} P_1(\lambda, \mu)$$

$$P_{21}(\lambda, \mu) = -\frac{1}{4\pi} \frac{\partial^7}{\partial \lambda \partial \mu^6} P_1(\lambda, \mu)$$

$$P_{24}(\lambda, \mu) = \frac{1}{4\pi} \frac{\partial^8}{\partial \lambda^2 \partial \mu^6} P_1(\lambda, \mu)$$

APPENDIX E

The function  $P_{25}$  is defined by

$$P_{25}(\lambda, \mu) = \int d\underline{r} \int d\underline{R} e^{-\lambda r - \mu R} \frac{Y_{1m}^*(\hat{\underline{r}}) Y_{1m}(\hat{\underline{R}}) rR}{|\underline{r} - \underline{R}|}$$

It is shown in the text that  $P_{25}$  is independent of  $m$  and vanishes unless  $m = m'$ . Then

$$P_{25}(\lambda, \mu) = \frac{1}{3} \int d\underline{r} e^{-\lambda r} \int_0^\infty R^3 dR Y_1(r, R) e^{-\mu R}$$

The radial integration over  $R$  is trivial and we easily obtain the expression for  $P_{25}$ :

$$P_{25}(\lambda, \mu) = -\frac{1}{2} \frac{K(\lambda + \mu, 2)}{\mu} - \frac{4}{3} \frac{K(\lambda + \mu, 1)}{\mu} - \frac{8}{4} \frac{K(\lambda + \mu, 0)}{\mu} \\ - \frac{8}{5} \frac{K(\lambda + \mu, -1)}{\mu} + \frac{8}{5} \frac{K(\lambda, -1)}{\mu}$$

The various other  $P$  functions which occur in the expansion (9.14) for the function  $G_3$  defined by equation (9.15) can be expressed as derivatives of  $P_{25}$ .

$$P_{26} = -\frac{\partial}{\partial \mu} P_{25}, \quad P_{33} = -\frac{\partial^3}{\partial \lambda^2 \partial \mu} P_{25},$$

$$P_{27} = \frac{\partial^2}{\partial \mu^2} P_{25}, \quad P_{30} = \frac{\partial^4}{\partial \lambda^2 \partial \mu^2} P_{25},$$

$$P_{28} = -\frac{\partial^3}{\partial \mu^3} P_{25}, \quad P_{31} = -\frac{\partial^5}{\partial \lambda^2 \partial \mu^3} P_{25},$$

$$P_{29} = \frac{\partial^4}{\partial \mu^4} P_{25}, \quad P_{32} = \frac{\partial^6}{\partial \lambda^2 \partial \mu^4} P_{25} .$$

Hence, in view of the recurrence relation (7.26) we can easily express these functions as combinations of the K functions given in Table 9.1.

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## Elastic scattering of slow electrons by helium

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**Abstract.** The optical potential model of Pu and Chang is extended to include EPV diagrams. Calculations are carried out for the s, p and d wave phase shifts at energies up to 17 eV. The results for s and p waves are in close agreement with those of other recent calculations and, with a phase shift analysis of experimental data. The d wave results lie between the full polarized orbital and the Green function expansion results. It is shown that third order diagrams are required for an accurate evaluation of the static polarizability, yielding  $\alpha = 1.372 a_0^3$ , and estimates are made of the third order correction to the d wave phase shift, which brings the optical potential values into good agreement with the full polarized orbital results.

### 1. Introduction

Considerable advances have been made recently in understanding the elastic scattering of slow electrons by helium atoms. Theoretical studies by Callaway and his collaborators (LaBahn and Callaway 1966, Callaway *et al* 1968), using variants of the polarized orbital approach, have led to values of the s and p wave phase shifts in good agreement with those derived directly from elastic scattering experiments (Andrick and Bitsch 1972) and from a phase shift analysis of experimental data (Bransden and McDowell 1969, McDowell 1971, Bransden *et al* 1973). These results also agree well with those of an optical potential approach by Pu and Chang (1966) and of a Green function analysis by Yarlagadda *et al* (1972). They are discussed in more detail in a review by Drachman and Temkin (1972), who also discuss the results of a full polarized orbital calculation by Duxler *et al* (1971). However, the d wave ( $l = 2$ ) results obtained in the different variants of the polarized orbital treatment differ considerably and disagree with the values proposed by McDowell (1971) on the basis of a phase shift analysis of experimental data.

Kelly (1967) has pointed out that the optical potential calculation of Pu and Chang (1966) is incomplete, certain second order terms being omitted. Pu and Chang restricted their work to second order in perturbation theory (omitting terms discussed below), considered the s and p wave phase shifts only and allowed only s, p and d intermediate states. In this paper we extend their work to remove these deficiencies, presenting what we believe to be a complete second order calculation.

In § 2 we review the relevant results of Brueckner–Goldstone perturbation theory and give an explicit expression for the optical potential.

In § 3 we present explicit expressions for all the second order contributions to the elastic scattering phase shifts. Our results for the s, p and d wave shifts, correct to second order, are presented in § 4 and are compared with experiment and with the results of

other theoretical models. Third and higher order contributions are discussed in § 5 and our conclusions presented in § 6.

## 2. Theory

The model adopted is that of Pu and Chang (1966), so that only a brief outline of the theory need be presented.

### 2.1. Brueckner–Goldstone perturbation theory

The problem considered is that of scattering of an electron by a neutral atom with  $N$  atomic electrons which interact through two-body potentials. The total hamiltonian for the system is

$$H = \sum_{i=1}^{N+1} T_i + \sum_{i<j}^{N+1} v_{ij} \quad (1)$$

where  $v_{ij}$  is the mutual Coulomb interaction between electrons  $i$  and  $j$  and  $T_i$  is the sum of the kinetic energy of the  $i$ th particle and all the one-body potentials acting on it.

Schrödinger's equation for the system is

$$H\Psi^{(N+1)} = E\Psi^{(N+1)} \quad (2)$$

where  $E$  is the total energy of the system.

The effect of the  $N$  interacting particles can be approximated by a single-particle potential  $V_i$ ; thus, the true state of the system is approximated by an unperturbed state function  $\Psi_0^{(N+1)}$  and hamiltonian  $H_0$ ,

$$H_0 = \sum_{i=1}^{N+1} (T_i + V_i) = \sum_{i=1}^{N+1} H_{0i} \quad (3)$$

with

$$H_{0i}\Psi_0^{(N+1)} = E_0\Psi_0^{(N+1)}. \quad (4)$$

The difference between the total and unperturbed hamiltonians is denoted by  $H'$ ; thus

$$H' = H - H_0 = \sum_{i<j}^{N+1} v_{ij} - \sum_{i=1}^{N+1} V_i. \quad (5)$$

The choice of the one-body potential  $V_i$  is arbitrary; but it is taken to be hermitian, so that the single-particle wavefunctions  $\phi_n$ , which are solutions of

$$H_{0i}\phi_n = (T_i + V_i)\phi_n = \epsilon_n\phi_n \quad (6)$$

form a complete set. The unperturbed ground state of the target  $\Phi_0^{(N)}$ , is the Slater determinant formed from the  $N$  lowest energy solutions of (6) (allowing for spin and orbital angular momenta). The corresponding unperturbed function for the total system  $\Psi_0^{(N+1)}$  is formed by adding a suitable solution of (6) to describe the free electron. We refer to those states  $\phi_m$  which are occupied in  $\Phi_0^{(N)}$  as unexcited states and all other  $\phi_n$  as excited states. An unoccupied unexcited state is called a hole and an occupied excited state is called a particle. The complete set of  $\phi_n$  is used as the basis for a perturbational expansion for the solution  $\Psi^{(N+1)}$  of (2).

When considering a system of identical fermions, the second quantization approach is useful; the creation and annihilation operators for single-particle states satisfy the Fermi–Dirac anticommutation relations, so that the Pauli Exclusion Principle is satisfied. In this formalism, equations (3) and (5) become

$$H_0 = \sum_n \epsilon_n \eta_n^* \eta_n \quad (7)$$

$$H' = \sum_{p,q,m,n} \langle pq|v|mn \rangle \eta_p^* \eta_q^* \eta_m \eta_n - \sum_{p,m} \langle p|V|m \rangle \eta_p^* \eta_m. \quad (8)$$

Here,  $\eta_n^*$ ,  $\eta_n$  are the usual creation and annihilation operators for the states  $\phi_n$  and the matrix elements are given explicitly by

$$\langle pq|v|mn \rangle = \int \int \phi_p^*(\mathbf{r}) \phi_q^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_m(\mathbf{r}) \phi_n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$\langle p|V|m \rangle = \int \phi_p^*(\mathbf{r}) V(\mathbf{r}) \phi_m(\mathbf{r}) d\mathbf{r}.$$

The summation is over distinct matrix elements only.

It is shown by Goldstone (1957) that the true ground state of the atom,  $\Phi^{(N)}$ , is given by

$$\Phi^{(N)} = \lim_{\alpha \rightarrow 0} \frac{U_\alpha(0) \Phi_0^{(N)}}{\langle \Phi_0^{(N)} | U_\alpha(0) | \Phi_0^{(N)} \rangle} \quad (9)$$

where

$$U_\alpha(t) = \sum_{n=0}^{\infty} (-i)^n \int \dots \int_{t > t_1 > t_2 > \dots > t_n} H'(t_1) \dots H'(t_n) dt_1 \dots dt_n \quad (10)$$

and

$$H'(t) = e^{iH_0 t} H' e^{-iH_0 t} e^{\alpha t}. \quad (11)$$

By use of Wick's theorem,  $\Phi^{(N)}$  may be represented by a sum of distinct Feynmann diagrams, in which a 'particle' is represented by a line directed upwards and a 'hole' by a line directed downwards. By Goldstone's factorization theorem, putting  $E'_0 = E_0 - \frac{1}{2}k_0^2$ ,

$$\Phi^{(N)} = \sum_{n=0}^{\infty} \left( \frac{1}{E'_0 - H_0} H' \right)^n \Phi_0^{(N)} \quad (12)$$

where the sum is over linked diagrams only, that is, ones which have no part totally disconnected from the rest of the diagram.

Similarly, the true solution for the entire scattering system is

$$\Psi^{(N+1)} = \sum_{n=0}^{\infty} \left( \frac{1}{E - H_0 + i\epsilon} H' \right)^n \Psi_0^{(N+1)}. \quad (13)$$

It was first shown by Bell and Squires (1959) that, by projecting  $\Psi^{(N+1)}$  on to  $\Phi_0^{(N)}$ , one obtains the true scattering wavefunction  $\chi(k_0)$  for the incident electron.

$$\begin{aligned} \chi(k_0) &= \langle \Phi_0^{(N)} | \Psi^{(N+1)} \rangle \\ &= \sum_{n=0}^{\infty} \left( \frac{1}{E - H_0 + i\epsilon} H' \right)^n \phi_{k_0} \end{aligned} \quad (14)$$

that is,  $\chi$  is the sum of all linked diagrams having a particle line  $k_0$  at the bottom and one particle line at the top.

## 2.2. An explicit expression for the optical potential

In this method the effect of the target atom on the scattering particle is represented by an equivalent one-body potential, the optical potential,  $W_{\text{op}}$ . Then the scattering wavefunction  $\chi(k_0)$  satisfies the one-particle Schrödinger equation

$$(T_{k_0} + V_{k_0} + W_{\text{op}})\chi(k_0) = \epsilon_{k_0}\chi(k_0) \quad (15)$$

where  $V_{k_0}$  is the arbitrary potential  $V_i$  seen by the electron with momentum  $k_0$ . From equations (13) and (14) it can be shown that

$$(E_0 - H_0)\Psi^{(N+1)} = \sum_{n=0}^{\infty} H' \left( \frac{1}{E - H_0 + i\epsilon} QH' \right)^n \chi(k_0)$$

and hence using (15)

$$W_{\text{op}} = \int ds |\phi_s\rangle \langle \Phi_0^{(N)} | \eta_s \sum_{n=0}^{\infty} H' \left( \frac{1}{E - H_0 + i\epsilon} QH' \right)^n \eta_s^* | \Phi_0^{(N)} \rangle \langle \phi_s|.$$

The  $Q$  operator projects on to a sum of states excluding the ground state and hence we consider only linked and proper diagrams, where by 'proper' we mean those linked diagrams which are not linked by a single-particle line at any intermediate stage. As Goldstone points out, this is to be expected physically, for such a single-particle line would mean that the atom was in its ground state at that intermediate stage.

It is also shown by Goldstone that if the one-particle potential  $V_i$  is chosen to be the Hartree-Fock potential  $V_i^{\text{HF}}$ , defined by its matrix elements

$$\langle i | V^{\text{HF}} | j \rangle = \sum_{n=1}^N \{ \langle in | v | jn \rangle - \langle in | v | nj \rangle \} \quad (16)$$

where the summation is over all orbitals of the ground-state atom, then the first order optical potential diagrams cancel exactly. Thus the leading terms in the expansion for the optical potential are second order.

## 3. Second order contributions to the scattering phase shift

With this choice of  $V_i$ , the single particle eigenvalue equation (6) can be written in a more explicit form

$$\left( -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ne^2}{r} + \sum_{i=1}^N \int \phi_i^*(r') \frac{e^2}{|r-r'|} \phi_j(r') dr' \right) \phi_n(r) - \sum_{i=1}^N \delta(m_{s_n}, m_{s_i}) \times \int dr' \phi_i^*(r') \frac{e^2}{|r-r'|} \phi_n(r') \phi_i(r) = \epsilon_n \phi_n(r) \quad (17)$$

where  $m_{s_n}$  is the spin projection of the electron in the state  $\phi_n$ . The Hartree-Fock orbitals for the ground state of the atom are generated by (17). For  $n \in (1, \dots, N)$  one of the direct and exchange terms cancel, so that the state  $n$  sees a potential due to the nucleus and  $(N-1)$  other orbital electrons. For excited states  $\phi_n (n > N)$ , however, no such

cancellation occurs and so the potential contains  $N$  direct terms; thus an excited state  $\phi_n$  sees the field of the nucleus and  $N$  orbital electrons. From the work of Kelly (1963) and Pu and Chang (1966), we expect no bound excited states for the two-electron atom.

The continuum states  $\phi(k_n, l; m, m_s)$  are determined by equation (18) by letting  $\epsilon_n = k_n^2/2m$ . Spherical symmetry is assumed so that

$$\phi(k, l; m, m_s) = \frac{R(kl; r)}{r} Y_{lm}(\theta, \phi) X_s(m_s) \quad (18)$$

in the usual notation. The  $Y_{lm}$  are spherical harmonics and  $X_s(m_s)$  is the spin eigenfunction. The radial function  $R(kl; r)$  satisfies the integro-differential equation

$$\left( -\frac{d^2}{dr^2} + \frac{2m}{\hbar^2}(V_{ia} + V_l) + \frac{l(l+1)}{r^2} \right) R(kl; r) = k^2 R(kl; r) \quad (19)$$

with  $V_{ia} = z/r_i$ . At large distances from the atom, the potential is effectively zero and the  $R$  functions are linear combinations of  $j_l(kr)$  and  $n_l(kr)$ , the spherical Bessel and spherical Neumann functions respectively. As  $r \rightarrow \infty$

$$R(kl; r) \sim kr[\cos\{\delta_0(k, l)\}j_l(kr) - \sin\{\delta_0(k, l)\}n_l(kr)] \underset{kr \rightarrow \infty}{\sim} \cos\{kr + \delta_0(k, l) - \frac{1}{2}l\pi\} \quad (20)$$

where  $\delta_0(k, l)$  is the zero-order scattering phase shift. With this normalization, it is shown by Kelly (1963) that in calculations one may replace the summation over intermediate states  $\phi_k$  by an integration over  $k$  with a factor  $2/\pi$ , that is

$$\sum_k = \frac{2}{\pi} \int dk.$$

It is shown by Pu and Chang (1966), using a variational approach, (and independently by Kelly (1967)) that the correction to the zero-order phase shift is given by

$$\Delta \delta(k_0, l) = \frac{-2m}{\hbar^2 k_0} \int_0^\infty R^*(k_0 l; r) W_{op} R(k_0 l; r) dr. \quad (21)$$

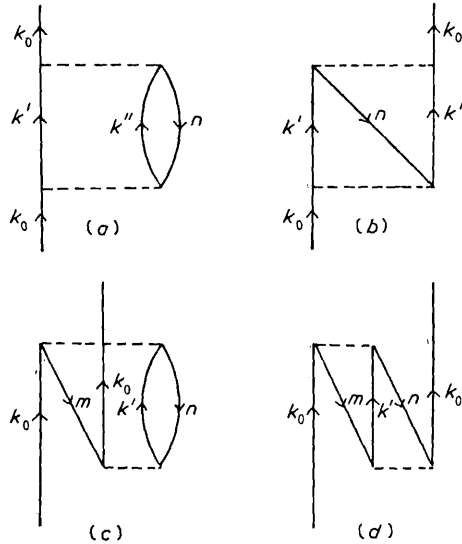
We have seen that the lowest-order contributions to  $\langle k_0 | W_{op} | k_0 \rangle$  come from second-order terms and the corresponding diagrams are shown in figure 1. These diagrams represent correlations between an incoming electron in state  $\phi_{k_0}$  and atomic electrons in states  $\phi_m$  and  $\phi_n$ . Diagrams 1(b) and 1(d) are the exchange diagrams corresponding to 1(a) and 1(c) respectively; 1(c) and 1(d) are exclusion-principle-violating (EPV) diagrams which arise from the linked-cluster factorization. Goldstone (1957) stresses that the Pauli Exclusion Principle is to be ignored when labelling diagrams. These EPV diagrams were omitted in the analysis of Pu and Chang but should be considered in any problem with two or more atomic electrons.

In agreement with Pu and Chang, figures 1(a) and 1(b) contribute respectively

$$\Delta \delta_{(a)}(k_0, l) = -\frac{4}{k_0} \left( \frac{2}{\pi} \right)^2 \sum_{n=1}^N \int_0^\infty dk' \int_0^\infty dk'' \frac{|\langle k_0 n | v | k' k'' \rangle|^2}{2\epsilon_n + k_0^2 - k'^2 - k''^2} \quad (22)$$

$$\Delta \delta_{(b)}(k_0, l) = \frac{4}{k_0} \left( \frac{2}{\pi} \right)^2 \sum_{n=1}^N \int_0^\infty dk' \int_0^\infty dk'' \frac{\delta(m_{s_n}, m_{s_{k_0}}) \langle k_0 n | v | k' k'' \rangle \langle k'' k' | v | k_0 n \rangle}{2\epsilon_n + k_0^2 - k'^2 - k''^2} \quad (23)$$

where only unexcited states are included in the summation over  $n$ .



**Figure 1.** The four second-order diagrams which represent correlations between an incoming electron in state  $\phi_{k_0}$  and atomic electrons in states  $\phi_m$  and  $\phi_n$ . (a) and (b) are the direct and exchange scattering diagrams respectively; (c) and (d) are direct and exchange EPV diagrams.

Similarly we obtain the following contributions from figures 1(c) and 1(d)

$$\Delta \delta_{(c)}(k_0, l) = \frac{4}{k_0} \left( \frac{2}{\pi} \right)^2 \int_0^\infty dk' \sum_{m,n} \delta(m_{s_n}, m_{s_{k_0}}) \frac{|\langle mn|v|k_0 k' \rangle|^2}{\epsilon_m + \epsilon_n - k_0^2 - k'^2} \quad (24)$$

$$\Delta \delta_{(d)}(k_0, l) = -\frac{4}{k_0} \left( \frac{2}{\pi} \right)^2 \int_0^\infty dk' \sum_{m,n} \delta(m_{s_n}, m_{s_m}) \frac{\langle mn|v|k_0 k' \rangle \langle k' k_0|v|mn \rangle}{\epsilon_m + \epsilon_n - k_0^2 - k'^2} \quad (25)$$

where the  $m, n$  summation includes only unexcited states. In equations (22)–(25) the angular momentum indices of the  $k_0, k', k''$  states have been suppressed.

For the case of the helium atom, the states  $m$  and  $n$  are both 1s states. Both orbitals contribute to the direct part (22), whilst only the electron having the same spin as the incident electron contributes to the exchange term (23) and the EPV direct term (24). There is no contribution from the EPV exchange term (25) since the two atomic electrons necessarily have opposite spins.

#### 4. The second order contributions to the phase shifts

Our analysis to this point is identical to that of Pu and Chang (1966) except that

- (i) we include EPV diagrams (1(c) and 1(d));
- (ii) intermediate angular momenta  $l', l'' = 0, 1, 2, 3, 4$  are included, whereas Pu and Chang considered only  $l', l'' = 0, 1, 2$ ;
- (iii) we evaluate the second order correction to the d wave ( $l = 2$ ) phase shift.

We consider each phase shift in turn. For the s wave ( $l = 0$ ) we show in table 1 the results obtained in zero-order (central field exchange approximation), the second-order

correction from non-EPV diagrams, the EPV corrections and the results of Pu and Chang (1966). The EPV corrections are very small and our final second-order results are in close agreement with those of Pu and Chang.

In table 2 we compare our results with those of a parallel Green function method of Yarlagadda *et al* (1972) and the full polarized orbital treatment of Duxler *et al* (1971). The results of the three approaches are in close accord.

**Table 1.** s-wave phase shifts including all second-order contributions

$k_0(\text{au})$	Zero-order	Correction from figures 1(a) and 1(b)	EPV contribution	Our total	Pu and Chang
0.3	2.7045	0.0343	-0.0049	2.7339	2.7391
0.6	2.3111	0.0450	-0.0081	2.3480	2.3555
1.0	1.8900	0.0520	-0.0090	1.9330	1.9412

**Table 2.** Comparison of s-wave phase shifts with those of other theoretical models

$k_0(\text{au})$	This paper	Yarlagadda <i>et al</i>	Duxler <i>et al</i>
0.3	2.7339	—	2.7546
0.6	2.3480	—	2.3719
1.0	1.9330	1.9372	1.9530

Our p wave ( $l = 1$ ) results are given in table 3, where we also give the non-exchange central field approximation results and the Born approximation results using (a) the Hartree-Fock central potential and (b) a polarization potential of the simple form

$$V(r) = -\frac{\alpha}{r^4} (\text{Ryd}) \quad (26)$$

for which the Born phase shift is given analytically by

$$\eta_l(k^2) = \frac{\pi\alpha k^2}{(2l-1)(2l+1)(2l+3)} \quad l \neq 0. \quad (27)$$

The reasonable agreement between the Born phases for the Hartree-Fock potential

**Table 3.** p-wave phase shifts, including a comparison of the relative importance of exchange and polarization

$k_0(\text{au})$	Zero-order —no exchange	1st Born with Hartree-Fock potential	1st Born with polarization potential	Zero-order with exchange	Our total (no EPV)	Our total (+ EPV)	Pu and Chang
0.5	0.0103	0.0091	0.0728	0.0423	0.0757	0.0750	0.0732
0.8	0.0360	0.0311	0.1863	0.1244	0.1830	0.1810	0.1778
1.0	0.0606	0.0517	0.2911	0.1830	0.2505	0.2477	0.2749



and the solutions of (17), neglecting exchange, indicates that our phase shift routine is satisfactory. As expected, exchange is very important, increasing the zero-order phase shift by a factor of between three and four in this energy range. The effects of polarization are represented by diagram 1(a) to second order and of exchange polarization by 1(b). These are significant and give a further large increase in the p wave phase shift at low energies. Again the EPV diagrams give a small ( $<1\%$ ) correction in this order. Our final results are again in close agreement with those of Pu and Chang. The departures from the Born results with potential (26) are small.

Table 4 compares our p wave phase shifts with those of Yarlagadda *et al* (1972) and of Duxler *et al* (1971). The agreement is again close, except with the full polarized orbital result at  $k = 0.5$  au (0.25 Ryd).

Table 4. Comparison of p wave phase shifts with those of other theoretical models

$k_0$ (au)	This paper	Yarlagadda <i>et al</i>	Duxler <i>et al</i>
0.5	0.0750	0.0806	0.0926
0.8	0.1810	—	0.2081
1.0	0.2477	0.2510	0.2749

The main interest of our work was however in obtaining values of the d wave phase shift, since the full polarized orbital results of Duxler *et al* (1971) disagree strongly (see below) with those obtained from a phase shift analysis of experimental data (Bransden and McDowell 1969, McDowell 1971, Bransden *et al* 1973). Our results (table 5 below) follow the same pattern as for the p wave and again agree with those obtained in the Born approximation using the potential given in equation (26). The EPV contributions are small, but both exchange and polarization are important.

Table 5. d wave phase shifts comparing the relative importance of the different second-order contributions

$k_0$ (au)	Zero-order— no exchange	1st Born with Hartree-Fock potential	1st Born with polarization potential	Zero-order— with exchange	Our total (no EPV)	Our total (+EPV)
0.5	0.00006	0.00006	0.01040	0.00061	0.00745	0.00745
0.6	0.00043	0.00042	0.0149	0.00176	0.01149	0.01149
0.7	0.00106	0.00103	0.0203	0.00353	0.01600	0.01600
0.8	0.00200	0.00195	0.0266	0.00609	0.02167	0.02166
0.9	0.00333	0.00323	0.0336	0.00939	0.02779	0.02780
1.0	0.00512	0.00485	0.0416	0.01347	0.03519	0.03516
1.1	0.00728	0.00704	0.0502	0.01824	0.04256	0.04260

In figure 2, our results are compared with the theoretical results of Yarlagadda *et al* (1972) and Duxler *et al* (1971), the phase shift analysis of McDowell (1971) and Bransden and McDowell (1969) and a recent revision of the latter using new experimental measurements (Bransden *et al* 1973). Our results lie intermediate between those of the other theoretical models and are inconsistent (as are those of Yarlagadda *et al* (1972)) with the

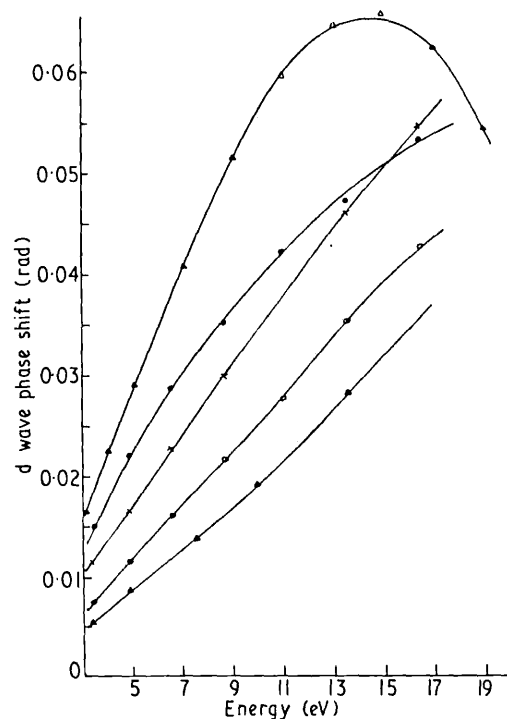


Figure 2. d wave phase shifts.  $\circ$  our results;  $\bullet$  Bransden and McDowell (1969);  $\times$  Duxler *et al* (1971);  $\triangle$  Bransden *et al* (1973);  $\blacktriangle$  Yarlagadda *et al* (1972).

results of the phase shift analysis.† It may well be that the d wave phase shift is not well determined by available experimental data. Nevertheless in view of the discord between the theoretical models for this case, and their accord for the  $l = 0$  and  $l = 1$  cases, it is of interest to attempt to estimate the higher order corrections.

### 5. Estimates of the third-order correction to the d wave phase shift

From tables (3) and (5), we see, choosing  $k = 1.0$  au for convenience, that the polarization correction to the p wave phase shift is approximately 37% of the zero-order exchange result, whereas for the d wave phase shift it is nearly 250% of the zero-order exchange phase shift. We show below that substantial contributions to the polarizability arise from the third-order bubble diagram. Consequently our p wave phase shift may be uncertain by approximately 10%. However it is shown below that the third-order corrections to the d wave phase shift may be as large as 30%.

It is clear that the simple formula (27) gives a good first approximation, but in using it we have adopted the most accurate available value of the polarizability of helium ( $\alpha = 1.385a_0^3$ , Dalgarno and Kingston 1960) and we are comparing with a second order calculation based on the diagrams of figure 1. However, the corresponding second-order contribution to the polarizability does not yield the correct result, there being substantial third-order contributions.

† See also a forthcoming paper by A. L. Sinfailam and R. K. Nesbet (*Phys. Rev.* in the press) whose variational calculation gives a d wave result lying 10% above ours at  $k_0^2 = 1.0$ .

The only second-order polarizability diagram is shown in figure 3(a), in which dotted lines represent interactions with the potential  $U_1$ , given by

$$U_1 = \sum_{i=1}^N r_i P_1(\cos \theta_i) = \sum_{i=1}^N r_i \cos \theta_i.$$

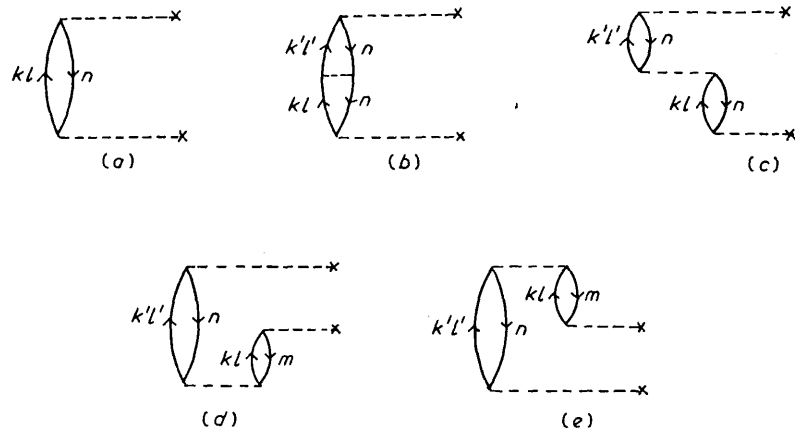


Figure 3. Second and third-order diagrams which contribute to the polarizability of helium.

The contribution  $\alpha_2$  to the polarizability is given explicitly by

$$\alpha_2 = -\frac{8}{\pi} \int_0^\infty dk \frac{|\langle n|r \cos \theta|kp \rangle|^2}{\epsilon_n - \frac{1}{2}k^2} = 0.76531.$$

Thus  $\alpha_2$  gives only 55% of Dalgarno and Kingston's result. There are four third-order contributions to the polarizability (cf Chang (1967)), corresponding to the diagrams shown in figures 3(b), 3(c), 3(d) and 3(e), and the respective contributions are

$$\alpha_{3b} = \frac{16}{\pi^2} \int_0^\infty dk \int_0^\infty dk' \frac{\langle n|r \cos \theta|k'p \rangle \langle k'pn|v|kpn \rangle \langle kp|r \cos \theta|n \rangle}{(\epsilon_n - \frac{1}{2}k'^2)(\epsilon_n - \frac{1}{2}k^2)} = 0.69565$$

$$\alpha_{3c} = -\frac{16}{\pi^2} \int_0^\infty dk \int_0^\infty dk' \frac{\langle n|r \cos \theta|k'p \rangle \langle nk'p|v|kpn \rangle \langle kp|r \cos \theta|n \rangle}{(\epsilon_n - \frac{1}{2}k'^2)(\epsilon_n - \frac{1}{2}k^2)} = -0.13286$$

$$\alpha_{3d} = \alpha_{3e} = -\frac{16}{\pi^2} \int_0^\infty dk \int_0^\infty dk' \frac{\langle n|r \cos \theta|k'p \rangle \langle m|r \cos \theta|kp \rangle \langle k'pkp|v|nm \rangle}{(\epsilon_n - \frac{1}{2}k'^2)(2\epsilon_n - \frac{1}{2}k'^2 - \frac{1}{2}k^2)} = 0.02214.$$

The polarizability including all second and third-order diagrams was found to be  $1.372a_0^3$ , which is in very good agreement with the Dalgarno and Kingston result. This suggests that the third-order contribution to the phase shift might also be non-negligible.

There are in general eightyfour distinct third-order diagrams which contribute to the phase shifts but these can be divided into five classes. Each of these classes subdivides into four groups, corresponding to the four second-order diagrams shown in figure 1. In each class we take the diagram which is an extension of figure 1(a) to be typical of the class and figure 4 shows these five representative diagrams.

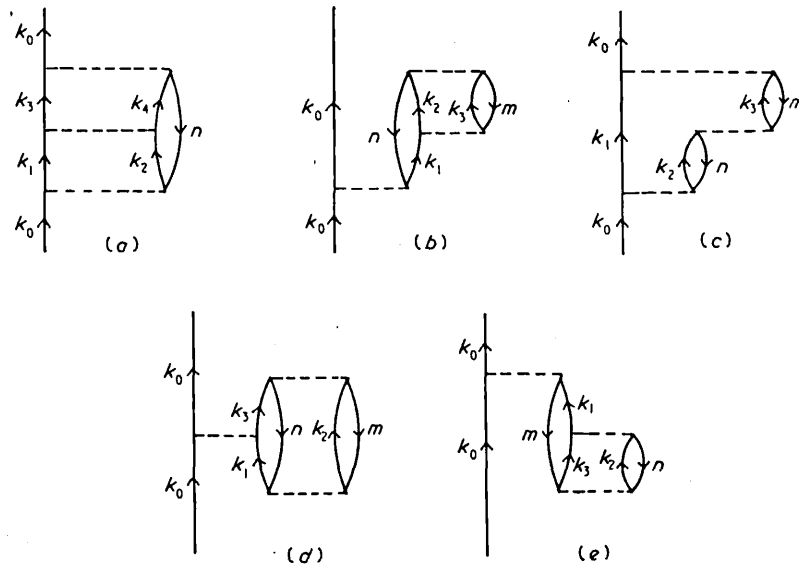
Figure 4(a) is the ladder diagram, the simple extension of the direct scattering diagram, figure 1(a), and we expect this to give the dominant third-order correction to the phase shift. Its contribution, *A*, is given by

$$A = \frac{-2}{k_0} \sum_{k_3, k_4} \frac{\langle k_0 l n | v | k_3 l_3 k_4 l_4 \rangle}{D(k_3, k_4)} \langle k_3 l_3 k_4 l_4 | v | \sum_{k_1, k_2} k_1 l_1 k_2 l_2 \rangle \frac{\langle k_1 l_1 k_2 l_2 | v | k_0 l n \rangle}{D(k_1, k_2)} \quad (28)$$

where

$$D(k_i, k_j) = \epsilon_n + \frac{k_0^2}{2} - \frac{k_i^2}{2} - \frac{k_j^2}{2} \quad (29)$$

and each sum is over the complete set of the continuum states, the solutions of equation



**Figure 4.** The five representative diagrams which give contributions to the third-order correction to the phase shift. (a) is the ladder diagram; (c) is the two-bubble diagram.

(18). The denominator  $D(k_1, k_2)$  is a slowly-varying function of  $k_1, k_2$  in the region of  $k_1, k_2$ -space where  $\langle k_1 l_1 k_2 l_2 | v | k_0 l n \rangle$  is large, so that we can approximate by

$$A = \frac{-2}{k_0 D(k_{10}, k_{20})} \left(\frac{2}{\pi}\right)^2 \int_0^\infty dk_3 \int_0^\infty dk_4 \frac{\langle k_0 l n | v | k_3 l_3 k_4 l_4 \rangle \langle k_3 l_3 k_4 l_4 | v^2 | k_0 l n \rangle}{D(k_3, k_4)} \quad (30)$$

with  $k_{10} = 0.9, k_{20} = 1.1$  when  $k_0 = 1.0$  (see below). This double integral is identical with that of equation (22) except that one of the  $v$  matrix elements is replaced by a  $v^2$  matrix element. That is, in one of the radial integrals, the usual  $\gamma_\lambda(r_1, r_2)$  function arising from the expansion for  $1/|r_1 - r_2|$  is replaced by a  $\beta_\lambda(r_1, r_2)$  function occurring in the expansion for  $1/|r_1 - r_2|^2$ . These  $\beta_\lambda$  coefficients are given explicitly by Sack (1964).

An accurate evaluation of the integral in (22) required a mesh of 1764 pairs of values of  $(k_3, k_4)$ . The replacement of the  $\gamma_\lambda$  coefficients by the  $\beta_\lambda$  causes a large increase in computing time, which was judged prohibitive since an upper bound on the correction factor  $A$  is all that is required.

The dominant contributions to equation (22) and also to  $A$ , because of the factor  $\langle k_0 l m | v | k_3 l_3 k_4 l_4 \rangle$  come from intermediate angular momenta  $l'' = 1, l' = 1$  or  $3$  (that is  $l_4 = 1, l_3 = 1$  or  $3$ ). For fixed  $k_0, l_3$  and  $l_4$  this factor is sharply-peaked at  $k_3 = k_{30}, k_4 = k_{40}$  say. A numerical investigation shows that the other factor,  $\langle k_0 l m | v^2 | k_3 l_3 k_4 l_4 \rangle$ , occurring in the integrand of equation (30) is also sharply peaked at  $k_3 = k_{30}$ , but is slowly-varying with  $k_4$  in this neighbourhood. Thus to a good approximation

$$A = \frac{-2}{k_0 D(k_{10}, k_{20})} \left(\frac{2}{\pi}\right)^2 \int_0^\infty dk_3 \frac{\langle k_3 l_3 k_{40} l_4 | v^2 | k_0 l m \rangle}{D(k_3, k_{40})} \left\{ \int_0^\infty dk_4 \langle k_0 l m | v | k_3 l_3 k_4 l_4 \rangle \right\}.$$

A rough upper bound† is then obtained by supposing that the  $\langle k_3 l_3 k_{40} l_4 | v^2 | k_0 l m \rangle$  matrix element may be replaced by its peak value everywhere in  $k_3$ -space; thus we approximate  $A$  by

$$A^{(u)} = -\frac{2}{k_0} \left(\frac{2}{\pi}\right)^2 \frac{\langle k_{30} l_3 k_{40} l_4 | v^2 | k_0 l m \rangle}{D(k_{10}, k_{20}) D(k_{30}, k_{40})} \int_0^\infty dk_3 \int_0^\infty dk_4 \langle k_0 l m | v | k_3 l_3 k_4 l_4 \rangle.$$

On physical grounds, and from our second-order work, we expect  $k_1$  and  $k_2$  to take values near 0.9 au and 1.1 au respectively when  $k_0 = 1.0$  au. With the corresponding value of  $D(k_1, k_2)$ , we obtain a result for  $A^{(u)}$  of 0.15, which is approximately 40% of the total second-order result for the same value of  $k_0$ . Although this result is an upper bound, we do not think it is a gross over-estimate of the actual contribution of the third-order ladder diagram, figure 4(a), to the d wave phase shift at that energy. That is, in view of the corresponding correction to the polarizability, this third-order diagram and its corresponding exchange and EPV diagrams are not negligible and, in any accurate work using this potential approach, they must be taken into account.

The contribution,  $B$ , of figure 4(c) to the third-order correction to the phase shift is given by

$$B = -\left(\frac{2}{\pi}\right)^3 \int_0^\infty dk_1 \int_0^\infty dk_2 \int_0^\infty dk_3 \frac{\langle m k | v | k_3 k_1 \rangle \langle n k_3 | v | k_2 m \rangle \langle k_1 k_2 | v | k n \rangle}{D(k_1, k_3) D(k_1, k_2)}$$

where the  $D$  functions are defined in equation (29). This was estimated using a method first proposed by Kelly (1963). We considered the ratio of  $B$  to the contribution of the second-order diagram, figure 1(a), using a peaking approximation to fix the values of  $k_1$  and  $k_3$ , and so reduced the number of repeated integrals. Our results for two values of the incident energy,  $k_0$ , are shown in table 6 and it can be seen that the effect of the two-bubble diagram, figure 4(c), is negligible.

The diagrams shown in figures 4(b) and 4(e) each give a contribution  $C$  where

$$C = -\left(\frac{2}{\pi}\right)^3 \frac{2}{k_0} \int_0^\infty dk_1 \int_0^\infty dk_2 \int_0^\infty dk_3 \frac{\langle n m | v | k_2 k_3 \rangle \langle k_2 k_3 | v | n k_1 \rangle \langle k k_1 | v | k m \rangle}{D(k_1, k_2) (2\epsilon_n - \frac{1}{2}k_2^2 - \frac{1}{2}k_3^2)}.$$

We estimated this by using a peaking approximation, because the matrix elements involved are very sharply-peaked, and our results are given in table 7. These figures show that the contribution  $C$  to the third-order correction to the phase shift is also insignificant.

† The  $v^2$  matrix element is negative and the  $v$  matrix element positive throughout the region of interest, while both denominators are negative hence  $A^{(u)} > A$ .

**Table 6.** Ratio of the contribution B of figure 4(c) to that of figure 1(a) for the d wave phase shift

$k_0(\text{au})$	$k_1, k_3$	$l_1, l_3$	Ratio of contributions 4(c) to 1(a)
0.5	0.8, 1.0	1, 1	-0.0336
	0.8, 1.0	1, 3	-0.0318
1.0	0.8, 1.0	1, 1	-0.0416
	0.9, 1.0	1, 1	-0.0398
	0.8, 1.0	1, 3	-0.0394

**Table 7.** The contribution C from figures 4(b) and 4(e) compared with the total second-order result

$k_0(\text{au})$	Contribution C	Total second order result	C as a percentage of total second order
0.5	$0.127 \times 10^{-4}$	$0.352 \times 10^{-1}$	0.04%
1.0	$0.141 \times 10^{-4}$	$0.745 \times 10^{-2}$	0.19%

The correction from the diagram figure 4(d) was not evaluated because of the expense involved in calculating the 'four excited state' matrix elements  $\langle k_1 k_2 | t | k_3 k_4 \rangle$  but, for physical reasons, we expect it to be smaller than that from the ladder diagram, figure 4(a).

## 6. Conclusions

We have seen that for the s and p wave phase shifts there is very good agreement between our second-order optical potential results, those of the Green's function method of Yarlagadda *et al* (1972) and those of the full polarized orbital treatment of Duxler *et al* (1971). Our results for the d wave phase shifts, however, lie intermediate between the other two sets of results, which differ considerably from each other. From our third-order work we can conclude that the ladder diagram gives a significant contribution to the third-order correction to the phase shift. Since this is the dominant contribution, and is positive, we expect the total third-order correction to be positive. This would bring our results close to the Duxler *et al* (1971) results, which are also in better agreement with the phase shift analysis work of Bransden *et al* (1973) than are those of Yarlagadda *et al* (1972). To calculate the third-order contribution more accurately than in this present work would be prohibitively expensive.

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