DISPERSION RELATION ANALYSIS FOR ELECTRON-ATOM SCATTERING AT ZERO ENERGY, ~~AND IN THE FORWARD DIRECTION~~.

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ABSTRACT

The dispersion relations are expressions which relate the real and the imaginary parts of the scattering amplitude. The importance of the dispersion relations in collision theory lies in that they can be used to derive rigorous formulae for quantities directly related to the measured values; and can therefore serve as a criterion for the analysis of experimental data. This is done by connecting an integral over the total cross section with the scattering length, the consistency and accuracy of total cross section measurements can be assessed.

The most extensive application so far, of the dispersion relations has been to the electron scattering by hydrogen (Gerjuoy and Krall, 1960) and helium (Lawson et al. 1966, Bransden and McDowell 1969, 1970). Part of the problem addressed in the following account is that of accurately calculating the Born exchange contribution at zero energy for electron scattering by helium and lithium in the forward direction using various wavefunctions. The corresponding dispersion relations have also been discussed.

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CHAPTER I

INTRODUCTION

In recent years, an important development in the quantum field theory and in the study of collisions of elementary particles is the theory of dispersion relations. The term 'disperson relations' comes, historically, from the observation of Kronig and Kramers (1926, 1927) that in the theory of dispersion of light by atoms, a relation exists between the real and the imaginary parts of the complex index of refraction. It has been found that an extension of the formulation of such general relations to the S—matrix is possible both in ordinary quantum mechanics and in the quantum field theory. These relations will be between the real and the imaginary parts of the scattering amplitude. In the last few years, a considerable amount of literature has grown up on various aspects of this subject, such as the foundation of the dispersion relations, and the application to various systems.

The dispersion relations can prove a useful tool in the analysis of atomic scattering experiments. In the present work we shall confine ourselves to an elementary account of application of dispersion relations appropriate to the elastic scattering of electrons by atoms, and then test the validity of these relations at zero energy.

I.A. Theory

The following account is based on the work of Klein and Zemach (1959).

Let the Schrodinger equation for a particle in the potential field V(r) be

$$(H_o + V(r) - E)\,\psi(\underline{r}) = 0 \qquad (1.1)$$

Equation (1.1) can be transformed into an equivalent integral form

$$\psi(\underline{r}) = \phi(\underline{r}) + \int G_o(\underline{r},\underline{r}')\, V(\underline{r}')\, \psi(\underline{r}')\, \underline{dr}' \qquad (1.2)$$

where $\phi(\underline{r})$ is a particular solution of the homogeneous equation

$$(H_o - E)\,\phi(\underline{r}) = 0, \quad \phi(r) = e^{i\underline{k}.\underline{r}} \tag{1.3}$$

and $G_o(\underline{r},\underline{r}')$ is the Green's function for operator $H_o - E$, i.e.

$$(H_o - E)\,G(\underline{r},\underline{r}') = \delta(\underline{r} - \underline{r}') \tag{1.4}$$

Formally, we can iteratate and obtain a solution of (1.1):

$$\psi(\underline{r}) = \sum_{\ell=0}^{\infty} (-\,G_oV)^{\ell}\phi_i(\underline{r}) \tag{1.5}$$

where $\phi_i(\underline{r})$ represents a free particle incident along $\underline{k}_i = k\underline{n}_i$ with energy $E = \hbar^2k^2/2m$, and

$$G_o(\underline{r},\underline{r}') = \lim_{\varepsilon\to 0} \frac{1}{(E - H_o + i\varepsilon)} \tag{1.6}$$

Equation (1.5) is the Born-Neumann series.

Now, (1.2) and (1.6) can be combined to give

$$\psi(\underline{r}) = \phi_i(\underline{r}) + \frac{1}{(E - H_o + i\varepsilon)} V(r)\,\psi(\underline{r})$$

If $G(\underline{r},\underline{r}')$ is the Green's function for the total Hamiltonian $H_o + V$, i.e.

$$G(\underline{r},\underline{r}') = \lim_{\varepsilon\to 0} \frac{1}{(E - H_o - V + i\varepsilon)} \tag{1.7}$$

then,

$$\psi(\underline{r}) = \phi_i(\underline{r}) + \frac{1}{(E - H_o - V + i\varepsilon)} V(r)\,\psi(\underline{r})$$

Let $\underline{n}_f$ represent the final scattering direction. Then it is well known that:

$$F(\theta,E) = -\frac{\mu}{2\pi} \langle\phi_f|V|\psi\rangle \tag{1.8}$$

is the exact amplitude for scattering of the particle into direction $\underline{n}_f$ making an angle θ with $\underline{n}_i$. The first Born approximation to $F(\theta,E)$ is

$$F_B(\theta,E) = -\frac{\mu}{2\pi} \langle\phi_f|V|\phi_i\rangle \tag{1.9}$$

Then in effect Klein and Zemach showed that with $\underline{n}_f = \underline{n}_i$, the function

$$Q(E) = F(0,E) - F_B(0,E)$$

(i) is an analytic function of E in the complex energy plane with a branch cut along the positive real axis ; and $0 \leq$ any $E \leq 2\pi$.

(ii) has simple poles at the bound states of the system.

(iii) has a branch point at $E = 0$.

(iv) vanishes at large complex E, provided the potential is of bounded. first and second moment.

It follows from Cauchy's Integral theorm that

$$Q(E) = \frac{1}{2\pi i} \int_{C_1} \frac{Q(E')\, dE'}{(E' - E)}$$

$$= \frac{1}{2\pi i} \int_{C_2} \frac{Q(E')\, dE'}{(E' - E)} - \sum_j R_j(E) \tag{1.10}$$

where the contours C_1 and C_2 are given in Fig. 1.A; and R_j are the residues of $Q(E')/(E' - E)$ at the poles $E' = E_j$. The integrals above and below the cut do not cancel. From (1.7) and (1.8), it can be seen that

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

since H_o is real and assumming that V is real as well.

Similarly

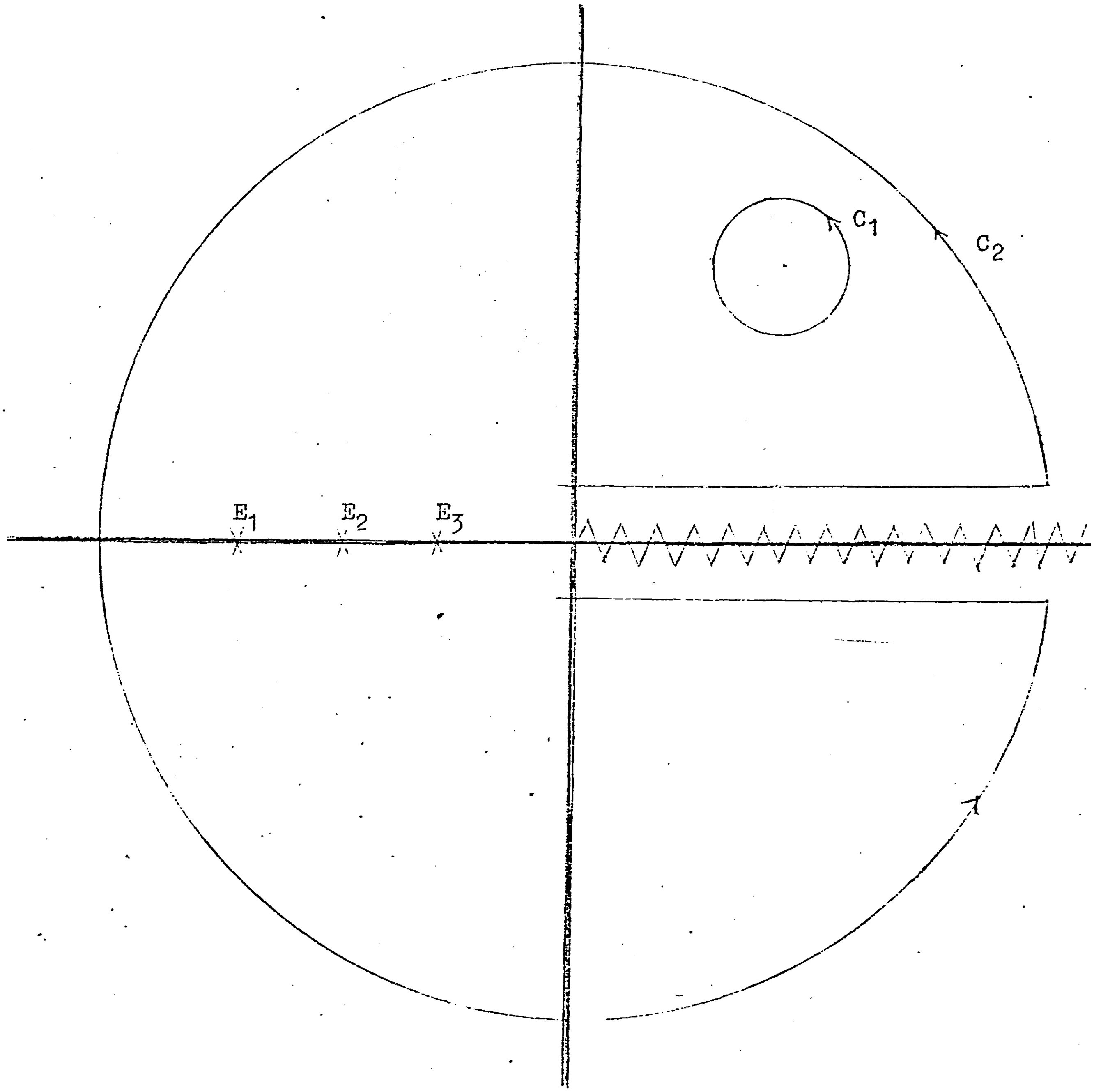

Fig. 1.A Contours of integration in the complex energy plane.

$$F^*_B(0,E) = F_B(0,E^*)$$

Therefore,

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

Since Q(E) vanishes at infinity,

$$\frac{1}{2\pi i}\int_{C_2} \frac{Q(E')\,dE'}{E' - E} = \frac{1}{2\pi i}\int_0^\infty \frac{Q(E' + i\varepsilon)dE'}{E' - E} - \frac{1}{2\pi i}\int_0^\infty \frac{Q(E' - i\varepsilon)}{E' - E}$$

$$= \frac{P}{\pi}\int_0^\infty dE' \, \frac{\mathrm{Im}Q(E')}{E' - E} \tag{1.11}$$

Here P stands for taking the principal value.

From (1.10) and (1.11) and noting that $F_B(0,E)$ is real, we get

$$\mathrm{Re}F(0,E) = F_B(0,E) + \frac{P}{\pi}\int_0^\infty \frac{\mathrm{Im}F(0,E')}{E' - E}\,dE' - \sum_j R_j(E) \tag{1.12}$$

This integral relation between the real and imaginary part of the scattering amplitude is the desired dispersion relation.

By using the 'optical theorem',

$$\mathrm{Im}F(0,E) = \frac{k}{4\pi}\,\sigma_T\,(0,E) \tag{1.13}$$

where σ_T is the total collision cross-section (elastic plus inelastic), we may write (1.12) in the form

$$\mathrm{Re}F\,(0,E) = F_B(0,E) + \frac{P}{4\pi^2}\int k'\,\frac{\sigma_T(0,E')}{E' - E}\,dE' - \sum_j R_j(E) \tag{1.14}$$

I.B. Can we extend this to electron-atom scattering problem?:

E. Gerjuoy and M.A. Krall (1960) suggested that the relation (1.14) would hold for electron-atom scattering provided the Green's function for the total Hamiltonian (1.7):

(a) has poles at the bound states of the system;

(b) has a branch point at $E = 0$ and at every energy E_t corresponding to the threshold of a new inelastic channel;

(c) 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 that $0 \leqq$ any $(E - E_t) < 2\pi$ for every threshold energy E_t;

(d) has the representation $\phi_j(\underline{r})\, \phi_j^*(\underline{r}')/(E - E_j)$ near any bound state pole, where $\phi_j(r)$ satisfies

$$(H - E_j)\phi_j(\underline{r}) = 0.$$

For cases in which no bound states of the electron-atom system exist, the residue term vanishes and we get

$$\mathrm{Re}F(0,E) = F_B(0,E) + \frac{P}{4\pi^2} \int_0^\infty k' \,\frac{\sigma_T(0,E')}{E' - E}\, dE' \qquad (1.15)$$

Equation (1.15) is applicable for electron scattering by rare gases since in such cases no bound states of the system exist.

Because of the identity of the incident and target electrons the amplitude $F(0,E)$ is a combination of direct and exchange amplitudes and for the scattering of electrons by helium we have

$$F(0,E) = f\,(0,E) - g(0,E) \qquad (1.16)$$

where f is the direct and g the exchange amplitude.

CHAPTER II

ELECTRON HELIUM SCATTERING

From Chapter 1 we have a dispersion relation for electron scattering by rare gases:

$$\mathrm{Re}F(0,k^2) = F_B(0,k^2) + \frac{P}{4\pi^2} \int k' \frac{\sigma_T(0,k'^2)}{k'^2 - k^2} \, dk'^2 \tag{2.1}$$

Because of the identity of the incident and the target electrons, the amplitude $F(0,k^2)$ is a combination of direct and exchange amplitudes, and for the scattering of electrons by helium, we have:

$$F(0,k^2) = f(0,k^2) - g(0,k^2) \tag{2.2}$$

where f is the direct and g is the exchange amplitude (Mott and Massey 1965).

Thus the dispersion relation for the forward electron-helium scattering amplitude can be written as

$$\mathrm{Re}F(0,k^2) = f_B(0,k^2) - g_B(0,k^2) + \frac{P}{4\pi^2} \int_0^{\infty} k' \frac{\sigma_T(0,k'^2)}{k'^2 - k^2} \, dk'^2 \tag{2.3}$$

The Born approximation to the direct and the exchange amplitudes, f_B and g_B respectively, are defined as

$$f_B(0,k^2) = -\frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \, \psi_o^2(\underline{r}_1,\underline{r}_2) \left[-\frac{2}{r_3} + \frac{1}{|\underline{r}_1 - \underline{r}_3|} + \frac{1}{|\underline{r}_2 - \underline{r}_3|} \right] \tag{2.4}$$

$$g_B(0,k^2) = -\frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \, \psi_o^*(\underline{r}_2,\underline{r}_3) \, e^{-i\underline{k}_f \cdot \underline{r}_1}$$

$$\left[-\frac{2}{r_3} + \frac{1}{|\underline{r}_1 - \underline{r}_3|} + \frac{1}{|\underline{r}_2 - \underline{r}_3|} \right] \psi_o(\underline{r}_1,\underline{r}_2) \quad e^{i\underline{k}_i \cdot \underline{r}_3} . \tag{2.5}$$

where $\psi_o(\underline{r}_1,\underline{r}_2)$ is the ground state wave function for the helium atom.

By choosing a suitable ground state wave function for the atom, the quantities f_B and g_B can be calculated. Thus we can predict from the dispersion relation (2.3) values of the real part of the forward scattering amplitude $F(0,k^2)$ provided the total cross section $\sigma_T(0,k'^2)$ is known over a sufficiently wide range of energy for the right-hand integral in (2.3) to converge.

In the special case of zero energy, the dispersion relation (2.3) becomes

$$-A = f_B(0,0) - g_B(0,0) + \frac{P}{4\pi^2} \int^{\infty} \frac{\sigma_T(0,k'^2)}{k'} dk'^2 \qquad (2.6)$$

where A is the scattering length defined by

$$-A = \lim_{k\to 0} \mathrm{Re}F(0,k^2)$$

A is usually very accurately known and hence in equation (2.6) we have a means of testing the validity of the dispersion relations for electron-helium scattering.

II.A. The direct scattering amplitude $f_B(0,k^2)$

The function $f_B(0,k^2)$ is independent of k^2. Bransden and McDowell (1969) calculated the $f_B(0,k^2)$ to be 0.7878 using an analytic Hartree-Fock ground state wave function (Green et al. 1954). Pekeris (1959) used a many parameter wave function and got a value of $f_B(0,k^2) = 0.791334$. On the other hand, Kim and Inokuti's (1968) sum rule value for $f_B(0,k^2)$ is 0.79114. In fact, $f_B(0,k^2)$ is relatively insensitive to the particular choice of the ground state wave function.

II.B. The total cross section $\sigma_T(0,k^2)$:

We essentially wish to calculate the value of

$$\frac{1}{4\pi^2}\int_0^\infty \frac{\sigma_T(0,k'^2)}{k'}\,dk^2 \qquad (2.7)$$

where $\sigma_T(0,k'^2)$ is in the units of πa_o^2.

Bransden and Hutt (1975) have calculated the integral (2.7) using the total cross sections given by Golden and Bandel (1965) for the energy region below 20 eV, Normand's (1930) results between the energy range of 20 eV and 100 eV and de Heer's (1974) results from 100 eV to 1000 eV. Assymptotically the following expression was used

$$\sigma_T(0,k) = \frac{1}{k^2}\left(6.18 + 3.011\ \ln k^2 - \frac{178.4}{k^2} - \frac{4875.4}{k^4}\right)$$

which has the same leading terms as the expression of Inokuti and McDowell (1974). Bransden and Hutt (1975) obtained the value for

$$\frac{1}{4\pi^2}\int_0^\infty \frac{\sigma_T(0,k'^2)}{k'}\,dk'^2 = 2.36 \qquad (2.8)$$

II.C. The scattering length A

O'Malley (1963) has reviewed most of the experimental work on electron-helium scattering. He has calculated the scattering length corresponding to each set of results. The lowest value of the scattering length O'Malley reported was 1.06 a_o, extrapolated from the results of an experiment by Füchtbauer et al. (1934). The largest value of the scattering length reported was from the experiments of Gould and Brown (1954) and this was 1.19 a_o. Golden and Bandel (1965) have measured the total scattering cross section at low energies using an electron-beam technique and have extrapolated to zero energy to obtain a scattering length of 1.15 a_o.

From the theoretical point of view, S.K. Houston (1968) has reviewed most of the previous calculations. La Bahn and Callaway (1966) obtained the value 1.1 a_o for the scattering length and this is very close to the value of 1.097 a_o obtained by Houston (1968).

Summarily, we see that various experimental 'results' differ by up to 10%. The theoretical calculations produce a variety of values for the scattering length, ranging from 1.097 a_o to 1.193 a_o — almost as much variation as in the experimental results.

II.D. The Born exchange amplitude $g_B(0,k^2)$

The forward Born exchange amplitude for electron-helium scattering is formally defined as

$$g_B(0,k^2) = -\frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \, \psi_o^*(\underline{r}_2,\underline{r}_3) \, e^{-i\underline{k}_f \cdot \underline{r}_1}$$

$$\left[-\frac{2}{r_3} + \frac{1}{|\underline{r}_1 - \underline{r}_3|} + \frac{1}{|\underline{r}_2 - \underline{r}_3|} \right] \psi_o(\underline{r}_1,\underline{r}_2) \, e^{i\underline{k}_i \cdot \underline{r}_3} \qquad (2.9)$$

in which $\psi_o(\underline{r}_1,\underline{r}_2)$ is an approximate wave function for the ground state of the target, electrons 1 and 2 being bound initially. If we suppose that $\psi_o(\underline{r}_1,\underline{r}_2)$ is an exact ground state wave function then, in analogy with the well known 'length' and 'velocity' representation of electric-dipole transition matrix elements, we can obtain another equivalent form for $g_B(0,k^2)$:

For the final state of the helium atom, the Schrodinger's equation is

$$\left[\frac{1}{2} \nabla_2^{3} + \frac{1}{2} \nabla_3^{2} + \frac{2}{r_2} + \frac{2}{r_3} - \frac{1}{|\underline{r}_2 - \underline{r}_3|} \right] \psi_o(\underline{r}_3,\underline{r}_2) = -E_o \psi_o(\underline{r}_3,\underline{r}_2)$$

where E_o is the ground state energy of the helium atom. Thus,

$$\left[- \frac{2}{r_3} + \frac{1}{|\underline{r}_2 - \underline{r}_3|} \right] \psi_o(\underline{r}_3,\underline{r}_2) = \left[\tfrac{1}{2} \nabla_2^{\,2} + \tfrac{1}{2} \nabla_3^{\,2} + \frac{2}{r_2} + E_o \right] \psi_o(\underline{r}_3,\underline{r}_2) \tag{2.10}$$

We can rewrite (2.9) as

$$g_B(0,k^2) = - \frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; \psi_o^{*}(\underline{r}_3,\underline{r}_2) e^{-i\underline{k}_f \cdot \underline{r}_1} \frac{1}{|\underline{r}_1 - \underline{r}_3|} \psi_o(\underline{r}_1,\underline{r}_2) e^{i\underline{k}_i \cdot \underline{r}_3} \tag{2.11}$$

$$- \frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; \psi_o^{*}(\underline{r}_1,\underline{r}_2) \, e^{-i\underline{k}_i \cdot \underline{r}_3} \left[- \frac{2}{r_3} + \frac{1}{|\underline{r}_2 - \underline{r}_3|} \right] \psi_o(\underline{r}_3,\underline{r}_2) e^{i\underline{k}_f \cdot \underline{r}_1}$$

Substituting (2.10) into (2.11), we get

$$g_B(0,k^2) = - \frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; \psi_o^{*}(\underline{r}_3,\underline{r}_2) e^{-i\underline{k}_i \cdot \underline{r}_1} \frac{1}{|\underline{r}_1 - \underline{r}_3|} \psi_o(\underline{r}_1,\underline{r}_2) \cdot e^{i\underline{k}_i \cdot \underline{r}_3}$$

$$- \frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; \psi_o^{*}(\underline{r}_1,\underline{r}_2) \, e^{-i\underline{k}_i \cdot \underline{r}_3} \left[\tfrac{1}{2} \nabla_2^{\,2} + \tfrac{1}{2} \nabla_3^{\,2} + \frac{2}{r_2} + E_o \right] \psi_o(\underline{r}_3,\underline{r}_2) e^{i\underline{k}_f \cdot \underline{r}_1}$$

Using Hermiticity

$$g_B(0,k^2) = - \frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; \psi_o^{*}(\underline{r}_3,\underline{r}_2) \, e^{-i\underline{k}_f \cdot \underline{r}_1} \left[\tfrac{1}{2} \nabla_2^{\,2} + \tfrac{1}{2} \nabla_3^{\,2} + \frac{2}{r_2} + E_o + \frac{1}{|\underline{r}_1 - \underline{r}_3|} \right] \psi_o(\underline{r}_1,\underline{r}_2) e^{i\underline{k}_i \cdot \underline{r}_3} \tag{2.12}$$

Putting $k^2 = 0$ in (2.9) and (2.12) we get

$$g_B{}^L(0,0) = -\frac{1}{2\pi}\int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3\, \psi_o{}^*(\underline{r}_3,\underline{r}_2)\left[-\frac{2}{r_3} + \frac{1}{|\underline{r}_1 - \underline{r}_3|} + \frac{1}{|\underline{r}_2 - \underline{r}_3|}\right] \psi_o(\underline{r}_1,\underline{r}_2) \qquad (2.14)$$

$$g_B{}^V(0,0) = -\frac{1}{2\pi}\int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3\, \psi_o{}^*(\underline{r}_3,\underline{r}_2)\left[\tfrac{1}{2}\nabla_2{}^2 + \frac{2}{r_2} + E_o + \frac{1}{|\underline{r}_1 - \underline{r}_3|}\right] \psi_o(\underline{r}_1,\underline{r}_2) \qquad (2.15)$$

where subscripts L and V indicate length and velocity respectively. We may anticipate that more reliability may be attributed to the value of $g_B(0,0)$ for which both forms agree. We have therefore calculated these using the following wave functions.

(i) One parameter variational,

$\psi_o = (\underline{r}_1,\underline{r}_2) = e^{-\alpha(r_1 + r_2)}$;

$\alpha = 1.6875$

(ii) and (iii) two parameter open shell,

$\psi_o(\underline{r}_1,\underline{r}_2) = e^{-\alpha r_1 - \beta r_2} + e^{-\beta r_1 - \alpha r_2}$

with

(ii)	$\alpha = 2.14$	$\beta = 1.19$	(Eckhart, 1930)
(iii)	$\alpha = 2.1832$	$\beta = 1.1886$	(Lowdin and Schull, 1951)

(iv) and (v) analytic Hartree-Fock

$\psi_o(\underline{r}_1,\underline{r}_2) = \phi(\underline{r}_1)\,\phi(\underline{r}_2)$; $\phi(\underline{r}) = e^{-\alpha r} + ce^{-\beta r}$

with

(iv) $\alpha = 1.45558$ $\beta = 2\alpha$ $C = 0.6$ (Green et al. 1954)

(v) $\alpha = 1.41$ $\beta = 2.61$ $C = .799$ (Byron and Joachain, 1966)

(vi) two parameter Hylleraas (Baber 1937)

$$\psi_o(\underline{r}_1,\underline{r}_2) = e^{-\alpha(r_1 + r_2)}(1 + Ar_{12})$$

with

$\alpha = 1.849$, $A = 0.364$

(vii) three parameter Hylleraas (Green et al. 1953)

$$\psi_o(\underline{r}_1,\underline{r}_2) = e^{-\alpha(r_1 + r_2)}(1 + A(r_1 - r_2)^2 + Br_{12})$$

with

$\alpha = 1.816$, $A = 0.13$, $B = 0.3$

(viii) six parameter Hylleraas (Stewart and Webb, 1963)

$$\psi_o(\underline{r}_1,\underline{r}_2) = e^{-\alpha(r_1 + r_2)}\Big[1 + C_1\alpha r_{12} + C_2\alpha^2(r_2 - r_1)^2 + C_3\alpha(r_1 + r_2)$$

$$+ C_4\alpha^2(r_1 + r_2)^2 + C_5\alpha^2 r^2_{12}\Big]$$

with

$\alpha = 1.755$, $C_1 = .192094$, $C_2 = .03648$, $C_3 = -.083394$,

$C_4 = .007652$, $C_5 = .012036$.

(ix) six parameter Hylleraas (Lawson et al. 1966)

$$\psi_o(\underline{r}_1,\underline{r}_2) = e^{-\alpha(r_1 + r_2)}(1 + A(r_1 + r_2) + B(r^2_1 + r^2_2) + Cr_1r_2 +$$

$$Dr_1r_2\cos\theta_{12} + Er_{12})$$

with

$\alpha = 1.82$, $A = -0.10083$, $B = 0.12985$ $C = -0.19079$

$D = 0.063598$ $E = 0.3538$

In the evaulation of $g_B(0,0)$ with the above wave functions, the main type of integrals took the form:

$$K(\alpha,n) = \int e^{-\alpha r} \; r^{n} \; d\underline{r} = 4\pi \frac{(n+2)!}{\alpha^{n+3}} \qquad (2.17)$$

$$P(I,\alpha,\beta) = \int d\underline{r}_1 \int d\underline{r}_2 \; \frac{r_1^{n_1} r_2^{n_2} e^{-\alpha r_1 - \beta r_2}}{|\underline{r}_1 - \underline{r}_2|} \; Y_{\ell m}(\Omega_1) Y_{\ell m}^{*}(\Omega_2) \qquad (2.18)$$

where I depends on the values of n_1 and n_2. These P integrals can be expressed in close analytical form and are listed in Appendix A.

However in the analysis with the wave function of the Hylleraas type, an additional integral encountered, which needs a bit of elaboration, was of the type

$$PP(a,b,c) = \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; e^{-ar_1 - br_2 - cr_3} \; \frac{|\underline{r}_1 - \underline{r}_2|\,|\underline{r}_3 - \underline{r}_2|}{|\underline{r}_1 - \underline{r}_3|} \qquad (2.19)$$

We take,

$$|\underline{r}_i - \underline{r}_j| = \sum_{\ell=0}^{\infty} \rho_\ell(\underline{r}_i,\underline{r}_j) \; P_\ell(\mathrm{Cos}\theta_{ij})$$

and

$$\frac{1}{|\underline{r}_i - \underline{r}_j|} = \sum_{\ell=0}^{\infty} \gamma_\ell(\underline{r}_i,\underline{r}_j) \; P_\ell(\mathrm{Cos}\theta_{ij})$$

where

$$\rho_\ell(\underline{r}_i,\underline{r}_j) = r_> \left[\frac{r_<^2}{r_>^2(2\ell+3)} - \frac{1}{(2\ell-1)} \right] \left[\frac{r_<}{r_>} \right]^{\ell}$$

$$\gamma_\ell(r_i,r_j) = \frac{r_<^{\ell}}{r_>^{\ell+1}}$$

$r_<$ denotes the smaller of r_i and r_j

$r_>$ denotes the larger of r_i and r_j

Then

$$PP(a,b,c) = \int \underline{dr}_1 \int \underline{dr}_2 \int \underline{dr}_3 \sum_{\ell_1=o}^{\alpha} \frac{4\pi}{2\ell_1+1} \sum_{m_1=-\ell_1}^{+\ell_1} Y^*_{\ell_1 m_1}(\Omega_1)\; Y_{\ell_1 m_1}(\Omega_2)$$

$$\sum_{\ell_2=o}^{\propto} \frac{4\pi}{2\ell_2+1} \sum_{m_2=\ell_2}^{\ell_2} Y^*_{\ell_2 m_2}(\Omega_2)\; Y_{\ell_2 m_2}(\Omega_3) \times \sum_{\ell_3=0}^{\propto} \frac{4\pi}{(2\ell_3+1)} \sum_{m=-\ell_3}^{\ell_3} Y^*_{\ell_3 m_3}(\Omega_3)$$

$$Y_{\ell_3 m_3}(\Omega_1)\; \rho_{\ell_1}(r_1,r_2)\; \rho_{\ell_2}(r_2,r_3)\; \gamma_{\ell_3}(r_1,r_3) e^{-ar_1-br_2-cr_3}$$

After carrying out the angular integration by using the orthogonality conditions for the Spherical Harmonics, we are left with

$$PP(a,b,c) = \sum_{\ell=o}^{\alpha} \frac{64\pi^3}{(2\ell+1)^2} \int_0^{\propto} dr_1 \int_o^{\propto} dr_2 \int_o^{\propto} dr_3\; r_1^2 r_2^2 r_3^2\; e^{-ar_1-br_2-cr_3}$$

$$\gamma_\ell(r_1,r_3)\; \rho_\ell(r_1,r_2)\; \rho_\ell(r_2,r_3) \qquad (2.20)$$

The above (2.19) type of integral was also encountered by Houston (1968) who found that it converged to sufficient accuracy after only the first two terms of the infinite series. The following is the analysis for including only the first three terms of the infinite series in (2.20):

$$\begin{aligned} PP(a,b,c) = \Big\{ & W1(a,b,c;J1,J2,J3,J4) + W1(a,c,b;J1,J3,J4,J5) \\ & + W1(b,a,c;J6,J3,J1,J4) + W1(b,c,a;J6,J3,J1,J4) \\ & + W1(c,a,b;J1,J3,J4,J5) + W1(c,b,a;J1,J2,J3,J4) \\ + \frac{1}{9}\Big[& W2(a,b,c;J7,J8,J6,J1) + W2(a,c,b;J7,J1,J6,J3) \\ & + W2(b,a,c;J9,J7,J6,J1) + W2(b,c,a;J9,J7,J6,J1) \\ & + W2(c,a,b;J7,J1,J6,J3) + W2(c,b,a;J7,J8,J6,J1)\Big] \\ + \frac{1}{25}\Big[& W3(a,b,c;J10,J9,J11,J7) + W3(a,c,b;J10,J9,J7,J6) \\ & + W3(b,a,c;J12,J9,J10,J7) + W3(b,c,a;J12,J9,J10,J7) \\ & + W3(c,a,b;J10,J9,J7,J6) + W3(c,b,a;J10,J9,J11,J7)\Big] \Big\} 64\pi^3 \end{aligned}$$

where typically,

$$W1(a,b,c;J1,J2,J3,J4) = \frac{J1(a,b,c)}{9} + \frac{J2(a,b,c)}{3} + \frac{J3(a,b,c)}{3} + J4(a,b,c)$$

$$W2(a,b,c;J6,J7,J8,J9) = \frac{J6(a,b,c)}{25} - \frac{J7(a,b,c)}{5} - \frac{J8(a,b,c)}{5} + J9(a,b,c)$$

$$W3(a,b,c;J8,J9,J10,J11) = \frac{J8(a,b,c)}{49} - \frac{J9(a,b,c)}{21} - \frac{J10(a,b,c)}{21} + \frac{J11(a,b,c)}{9}$$

If we let

$$J(n_1,n_2,n_3;a,b,c) = \int_0^\infty r_3^{n_3} e^{-cr_3} \int_0^{r_3} r_2^{n_2} e^{-br_2} \int_0^{r_2} r_1^{n_1} e^{-ar_1}\, dr_1 dr_2 dr_3 \qquad (2.21)$$

Then

$J1(a,b,c) = J(4,3,0;a,b,c)$

$J2(a,b,c) = J(2,5,0;a,b,c)$

$J3(a,b,c) = J(4,1,2;a,b,c)$

$J4(a,b,c) = J(2,3,2;a,b,c)$

$J5(a,b,c) = J(2,1,4;a,b,c)$

$J6(a,b,c,) = J(6,1,0;a,b,c)$

$J7(a,b,c) = J(6,3,-2;a,b,c)$

$J8(a,b,c) = J(4,5,-2;a,b,c)$

$J9(a,b,c) = J(8,1,-2;a,b,c)$

$J10(a,b,c) = J(8,3,-4;a,b,c)$

$J11(a,b,c) = J(6,5,-4;a,b,c)$

$J12(a,b,c) = J(10,1,-4;a,b,c)$

These 'J integrals' are discussed in appendix B.

Moussa et al. (1973) have published a program to calculate the following general integral:

$$I = \frac{1}{64\pi^3} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; e^{-\alpha r_1 \beta r_2 - \gamma r_3} \; r_1^{\,i} r_2^{\,j} r_3^{\,k} \; \frac{r_{23}^{\,m} r_{12}^{\,\ell}}{r_{13}}$$

For the test run, they consider

$\alpha = \beta = \gamma = 2$, $i = 0$, $j = 0$, $k = 0$, $\ell = 1$, $m = 1$ and get

$I = \cdot 045055054$

after taking the first five terms only.

The corresponding value of the integral via our program, after taking the first three terms, is: .045055362

The table 2.B gives the values of $g_B^{\,L}(0,0)$ and $g_B^{\,V}(0,0)$ for various wave functions explained earlier in this chapter.

TABLE 2.B Values of $g_B^{\,L}(0,0)$ and $g_B^{\,V}(0,0)$ for electron-helium scattering

Wave function.	$g_B^{\,L}(0,0)$	$g_B^{\,V}(0,0)$
(i)	3.1478	2.4583
(ii)	4.23	4.62
(iii)	4.21	4.52
(iv)	3.8329	3.7887
(v)	3.9003	3.9312
(vi)	3.319	2.698
(vii)	3.795	3.176
(viii)	3.903	3.295
(ix)	3.831	3.297

From table 2.B we see that the simple one parameter function (i) is clearly inadequate. The average results for $g_B^{\,L}(0,0)$ and $g_B^{\,V}(0,0)$ obtained with the open-shell functions (ii) and (iii) agrees well with the value of 4.309 adopted by Bransden and Hutt (1975) to fit the sum rule (2.6). But the $g_B^{\,L}(0,0)$ and $g_B^{\,V}(0,0)$ values using Hartree-Fock functions (iv) and (v) are in good agreement and strongly suggest a value in the vicinity of 3.9. The results obtained for $g_B^L(0,0)$ with the simple Hylleraas functions ((vi) to (ix)) agree well with the Hartree-Fock values, but these functions give a rather low $g_B^V(0,0)$ values. Lawson et al. (1966) have evaulated the dispersion relation (2.6) using wave functions (iv) and (ix). Our results for $g_B^L(0,0)$ do not agree with the values implied by them. Because of this discrepancy and the failure to converge on the value of 4.309 used by Bransden and Hutt (1975) we shall attempt to use configuration Interaction type of wave functions.

CHAPTER III

CONGIFURATION INTERACTION WAVEFUNCTIONS

In this chapter, we calculate the Born exchange amplitudes for electron-helium scattering as defined in equations (2.14) and (2.15) using the configuration interaction wave functions. Before we do so, we discuss the generation of these configuration interaction wavefunctions.

In the Hartree self-consistent field method of solution of the Schrodinger equation for an N-electron atom, the wave function is a product of N one electron orbitals. The Hartree-Fock method improves on this by having an antisymmetrised determinantal wave function, which stipulates that no two electrons of same spin may occupy the same point of space. But correlation errors are inherent in the Hartree-Fock model. These errors, though small in most cases, are often too large to allow useful prediction of atomic processes. Part of the problem addressed in this chapter is that of finding solutions of the Schrodinger equation with an accuracy beyond that of the Hartree-Fock approximation. The most general method for allowing for the correlation effects, and with which many theoretical calculations are now being made, is the method of configuration interaction (CI). We seek to obtain the ground state representation for Helium using the following ^1S_o configurations:

$$1s^2,\ 2s^2,\ 2p^2,\ 3s^2,\ 3p^2,\ 3d^2.$$

The following account is based on the work of Hibbert (1975). A configuration interaction wave function can be written in the form

$$\psi(LS) = \sum_{i=1}^{m} C_i \Phi_i(\alpha_i LS) \tag{3.1}$$

where each of the configurational wave functions Φ_i is built from one-electron functions whose angular momenta are coupled, in a manner defined by α_i, to form total $\underline{L}$ and $\underline{S}$ common to all configurations in (3.1) and C_i are the associated constants. Thus the functions Φ_i are eigenfunctions of L^2 and S^2. Each orbital is a product of a radial function, a spherical harmonic and a spin function:

$$\phi_{n\ell m_\ell m_s}(\underline{r}) = r^{-1}(P_{n\ell}(r))Y_{\ell m_\ell}(\Omega)\chi(m_s) \tag{3.2}$$

with

$$P_{n\ell}(r) = \sum_{j=1}^{k} a_{jn\ell}\, r^{I_{jn\ell}} \exp(-\alpha_{jn\ell} r) \tag{3.3}$$

choosen ~~orthogonalized~~ to satisfy

$$\int_0^{\infty} P^2_{n\ell}(r)\, dr = 1$$

In general, the Φ_i are linear combinations of determinants, D_{ij}, such that

$$\Phi_i = \sum_{j=1}^{n} \alpha_{ij} D_{ij}$$

and α_{ij} are the associated coefficients.

Thus

$$\Psi = \sum_{i=1}^{m} C_i \sum_{j=1}^{n} \alpha_{ij} D_{ij}$$

If

$$\Psi^{(j)}(\underline{LS}) = \sum_{i=1}^{m} C_i\, \Phi(\alpha_i LS); \quad j = 1,2\ldots m$$

then

$$<\Psi^{(j)}|H|\psi^{(k)}> = E^{(j)}\ \delta_{jk} \qquad (3.4)$$

where H is the ~~N-electron~~ atomic Hamiltonian.

Also

$$E^{(j)} \geqq E^{(j)}_{exact} \quad ij = 1,2,\ldots m. \qquad (3.5)$$

The radial functions are allowed to depend on a number of variational parameters which may be varied to make $E^{(j)}$ a minimum for an appropriate choice of j. Thus the radial functions are analytic where as the multiconfigurational Hartree-Fock radial functions (Fischer 1972, Bagus et a. 1971) are numerical.

If the functions Φ_i are known (i.e. if $P_{n\ell}(r)$ are specified), then the Hamiltonian matrix defined by

$$H_{ij} = <\Phi_i|H|\Phi_j> \qquad (3.6)$$

is evaluated for each state, and is diagonalised. In each case, the coefficients C_i are taken as the components of the eigenvector corresponding to the lowest eigenvalue.

For the purposes of present calculations, we have utilized Hartree-Fock radial functions for the 1s orbital, while the 2s, 2p, 3s, 3p, 3d orbitals which are included for correlation, have been determined by the Hibbert program CIV3 (1975). Table 3.A gives the various parameters for the radial functions.

TABLE 3.A THE CONSTANTS FOR THE RADIAL FUNCTIONS DEFINED BY EQUATION(3.3).

Orbital	Clementi-type* Coefficients	$I_{jn\ell}$	Exponents $\alpha_{jn\ell}$
1s	.78502	1	1.43
	.20284	1	2.4415
	.03693	1	4.0996
	-.00293	1	6.4843
	.00325	1	.7978
2s	3.00255	1	1.26755
	-3.35216	2	1.66475
2p	1.0	2	2.4596
3s	3.95936	1	1.31924
	- .88069	2	1.3022
	-3.4218	3	3.76517
3p	1.07129	2	2.10324
	-1.34918	3	6.18093
3d	1.0	3	3.56856

* The Clementi-type coefficients have to be multiplied by:

$$\frac{(2\alpha_{jn\ell})^{I_{jn\ell}+\frac{1}{2}}}{(2I_{jn\ell})!^{\frac{1}{2}}}$$

$g_B^L(0,0)$ and $g_B^V(0,0)$ have been evaluated using the following wave functions for the ground state $({}^1S_0)$ of helium:

(i) $\Psi = C_1\Phi(1s^2) + C_2\Phi(2s^2) + C_3\Phi(2p^2)$

with

$C_1 = -.99621, \quad C_2 = .06102, \quad C_3 = -.06201$

(ii) $\Psi = C_1\Phi(1s^2) + C_2\Phi(2s^2) + C_3\Phi(3s^2)$

with

$C_1 = 0.99804, \quad C_2 = -.06208, \quad C_3 = -.00768$

(iii) $\Psi = C_1\Phi(1s^2) + C_2\Phi(2s^2) + C_3\Phi(3s^2) + C_4\Phi(3d^2)$

with

$C_1 = -.99795, \quad C_2 = .06188, \quad C_3 = .00761, \quad C_4 = .01462$

(iv) $\Psi = C_1\Phi(1s^2) + C_2\Phi(2p^2) + C_3\Phi(3p^2) + C_4\Phi(3d^2)$

with

$C_1 = .99796, \quad C_2 = .06165, \quad C_3 = .01057, \quad C_4 = -.01254$

(v) $\Psi = C_1\Phi(1s^2) + C_2\Phi(2s^2) + C_3\Phi(2p^2) + C_4\Phi(3s^2) + C_5\Phi(3p^2)$

with

$C_1 = .99625, \quad C_2 = -.05979, \quad C_3 = .00142, \quad C_4 = -.00729, \quad C_5 = .00963$

(vi) $\Psi = C_1\Phi(1s^2) + C_2\Phi(2s^2) + C_3\Phi(2p^2) + C_4\Phi(3s^2) + C_5\Phi(3p^2) + C_6\Phi(3d^2)$

with

$C_1 = .99624, \quad C_2 = -.05966, \quad C_3 = .06036, \quad C_4 = -.00724, \quad C_5 = .00954,$

$C_6 = -.0123$

Let

$\phi_1 = \phi_{1s\alpha} \quad \phi_2 = \phi_{1s\beta}$

$\phi_3 = \phi_{2s\alpha} \quad \phi_4 = \phi_{2s\beta}$

$\phi_5 = \phi_{2p1\alpha} \quad \phi_6 = \phi_{2po\alpha} \quad \phi_7 = \phi_{2p\bar{1}\alpha}$

$\phi_8 = \phi_{2p1\beta} \quad \phi_9 = \phi_{2po\beta} \quad \phi_{10} = \phi_{2p\bar{1}\beta}$

$\phi_{11} = \phi_{3s\alpha} \quad \phi_{12} = \phi_{3s\beta}$

$\phi_{13} = \phi_{3p1\alpha} \quad \phi_{14} = \phi_{3po\alpha} \quad \phi_{15} = \phi_{3p\bar{1}\alpha}$

$\phi_{16} = \phi_{3p1\beta} \quad \phi_{17} = \phi_{3po\beta} \quad \phi_{18} = \phi_{3p\bar{1}\beta}$

$\phi_{19} = \phi_{3d2\alpha} \quad \phi_{20} = \phi_{3d1\alpha} \quad \phi_{21} = \phi_{3do\alpha} \quad \phi_{22} = \phi_{3d\bar{1}\alpha} \quad \phi_{23} = \phi_{3d\bar{2}\alpha}$

$\phi_{24} = \phi_{3d2\beta} \quad \phi_{25} = \phi_{3d1\beta} \quad \phi_{26} = \phi_{3do\beta} \quad \phi_{27} = \phi_{3d\bar{1}\beta} \quad \phi_{28} = \phi_{3d\bar{2}\beta}$

where α denotes spin 'up' and β spin 'down'

Then we note,

$$\Phi(2p,{}^1s_o) = \frac{1}{\sqrt{3}}\left\{ D[\phi_5^{(1)}\phi_{10}^{(2)}] - D[\phi_6^{(1)}\phi_9^{(2)}] + D[\phi_7^{(1)}\phi_8^{(2)}] \right\}$$

and similarly for $\Phi(3p^2,{}^1s_o)$

$$\Phi(3d^2,{}^1s_o) = \frac{1}{\sqrt{5}}\Big\{ D[\phi_{19}^{(1)}\phi_{28}^{(2)}] - D[\phi_{20}^{(1)}\phi_{27}^{(2)}] + D[\phi_{21}^{(1)}\phi_{26}^{(2)}]$$

$$- D[\phi_{22}^{(1)}\phi_{25}^{(2)}] + D[\phi_{23}^{(1)}\phi_{24}^{(2)}] \Big\}$$

III.A. Calculation of $g_B^L(0,0)$

In what follows, we shall show the detailed analysis using the function (vi) since the analysis with other functions would then follow through trivially. We recall from (2.14):

$$g_B^L(0,0) = -\frac{1}{2\pi}\int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3\, \psi_o^*(3,2)\left[-\frac{2}{r_3} + \frac{1}{|\underline{r}_2 - \underline{r}_3|}\,\frac{1}{|r_1 - r_3|}\right]\psi_o(1,2)$$

Let

$$I_1 = \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3\, \psi^*(3,2)\,\frac{1}{|\underline{r}_1 - \underline{r}_3|}\,\psi_o(1,2) \qquad (3.6)$$

Also introduce

$$FF2(i,j,kk) = \int d\underline{r}_1 \int d\underline{r}_3\, \phi_i^*(r_1)\,\frac{1}{|\underline{r}_1 - \underline{r}_3|}\,\phi_j(r_3) \qquad (3.7)$$

where kk = 1 if i and j are 's' orbitals

= 2 'p' "

= 3 'd' "

Note that in equation (3.7) no other combination of i and j is allowed

Suppose

$$\phi_i(r) = \sum_{i=1}^{I0} a_i e^{-\alpha_i r} + \sum_{i=I0+1}^{I1} a_i r e^{-\alpha_i r} + \sum_{i=I1+1}^{I2} a_i r^2 e^{-\alpha_i r} + \sum_{i=I2+1}^{I3} a_i r^3 e^{-\alpha_i r} \qquad (3.8)$$

$$\phi_j(r) = \sum_{j=1}^{J0} b_i e^{-\beta_i r} + \sum_{i=J0+1}^{JI} b_i r e^{-\beta_i r} + \sum_{j=J1+1}^{J2} b_i r^2 e^{-\beta_i r} + \sum_{j=J2+1}^{J3} b_i r^3 e^{-\beta_i r} \qquad (3.9)$$

i.e. $\phi_i(r)$ and $\phi_j(r)$ are representing 's-type' orbital with the associated spherical harmonics ($Y_{oo}(\Omega) = 1/\sqrt{4\pi}$) absorbed in the constants a_i and b_i. I0, I1, I2, I3 and J0, J1, J2, J3 can take any values.

Then

$$FF2(i,j,1) = \sum_{i=1}^{J0} a_i \left[\sum_{j=1}^{J0} b_j\, P(1,\alpha_i,\beta_j) + \sum_{j=J0+1}^{J1} b_j P(2,\alpha_i,\beta_j) + \sum_{j=J1+1}^{J2} b_j P(3,\alpha_i,\beta_j) + \sum_{j=J2+1}^{J3} b_j P(4,\alpha_i,\beta_j) \right]$$

$$+ \sum_{i=J0+1}^{I1} a_i \left[\sum_{j=1}^{J0} b_j P(2,\beta_j,\alpha_i) + \sum^{J1} b_j P(8,\alpha_i,\beta_j) + \sum^{J2} b_j P(9,\alpha_i,\beta_j) + \sum^{J3} b_j P(10,\alpha_i,\beta_j) \right]$$

$$+ \sum_{i=I1+1}^{I2} a_i \left[\sum_{j=1}^{J0} b_j P(3,\beta_j,\alpha_i) + \sum^{J1} b_j P(9,\beta_j,\alpha_i) + \sum^{J2} b_j P(14,\alpha_i,\beta_j) + \sum^{J3} b_j P(15,\alpha_i,\beta_j) \right]$$

$$+ \sum_{i=J2+1}^{I3} a_i \left[\sum_{j=1}^{J0} b_j P(4,\beta_i,\alpha_i) + \sum^{J1} b_j P(10,\beta_j,\alpha_i) + \sum^{J2} b_j P(15,\beta_j,\alpha_i) + \sum^{J3} b_j P(19,\alpha_j,\beta_j) \right]$$

where these 'P(I,α,β)' integrals are defined in appendex A ; and if kk = 2, the integrals P(I,α,β) should be replaced by P(I + 30,α,β); and if kk = 3, the intgrals P(I,α,β) should be replaced by P(I + 60,α,β).

Substituting function vi into (3.6) and considering all the cross-terms, we get

$$I_1 = C^2_1\, FF2(1s,1s,1) + C^2_2 FF2(2s,2s,1) + C^2_3 FF2(2p,2p,2)$$

$$+ C^2_4 FF2(3s,3s,1) + C^2_5 FF2(3p,3p,1) + C^2_6 FF2(3d,3d,3).$$

Let

$$I_2 = \int \underline{dr}_1 \int \underline{dr}_2 \int \underline{dr}_3\, \psi_o(3,2) \frac{1}{|\underline{r}_2 - \underline{r}_3|} \psi_o(1,2) \qquad (3.10)$$

We let

$$GG(i,j,k,kk) = \int \underline{dr}_2 \int \underline{dr}_3 \, \phi_i^*(3) \frac{1}{|\underline{r}_2 - \underline{r}_3|} \phi_j^*(2)\phi_k(2)$$

Suppose, ϕ_k is an 's-type' orbital such that

$$\phi_k(r) = \sum_{k=1}^{K0} c_k e^{-\gamma_i r} + \sum_{k=K0+1}^{K1} C_k r e^{-\gamma_k r} + \sum_{k=K1+1}^{K2} C_K r^2 e^{-\gamma_k r} + \sum_{k=K2+1}^{K3} C_K r^3 e^{-\gamma_k r} \qquad (3.11)$$

Then, using (3.8), (3.9) and (3.11) we have,

$$\begin{aligned}
GG(i,j,k,1) = \sum_{i=1}^{I0} a_i \Bigg\{ & \sum_{j=1}^{J0} b_j \Bigg[\sum_{k=1}^{K0} C_k P(1,\alpha_i,\delta) + \sum_{k=K0+1}^{K1} C_k P(2,\alpha_i,\delta) + \sum_{k=K1+1}^{K2} C_k P(3,\alpha_i,\delta) + \\
& \qquad \sum_{k=K2+1}^{K3} C_k P(4,\alpha_i,\delta) \Bigg] \\
& + \sum_{j=J0+1}^{J1} b_j \Bigg[\sum_{k=1}^{K0} C_k P(2,\alpha_i,\delta) + \sum^{K1} C_k P(3,\alpha_i,\delta) + \sum^{K2} C_k P(4,\alpha_i,\delta) \\
& \qquad + \sum^{K3} C_k P(5,\alpha_i,\delta) \Bigg] \\
& + \sum_{j=J1+1}^{J2} b_j \Bigg[\sum_{k=1}^{K0} C_k P(3,\alpha_i,\delta) + \sum^{K1} C_k P(4,\alpha_i,\delta) + \sum^{K2} C_k P(5,\alpha_i,\delta) \\
& \qquad + \sum^{K3} C_k P(6,\alpha_i,\delta) \Bigg] \\
& + \sum_{j=J2+1}^{J3} b_j \Bigg[\sum_{k=1}^{K0} C_k P(4,\alpha_i,\delta) + \sum^{K1} C_k P(5,\alpha_i,\delta) + \sum^{K2} C_k P(6,\alpha_i,\delta) \\
& \qquad + \sum^{K3} C_k P(7,\alpha_i,\delta) \Bigg] \Bigg\}
\end{aligned}$$

$$+\sum_{i=I0+1}^{I1} a_i \Bigg\{ \sum_{j=1}^{J0} b_j \Bigg[\sum_{k=1}^{K0} C_k P(2,\delta,\alpha_i) + \sum^{K1} C_k P(8,\alpha_i,\delta) + \sum^{K2} C_k P(9,\alpha_i,\delta) + \sum^{K3} C_k P(10,\alpha_i,\delta) \Bigg]$$

$$+\sum^{J1} b_j \Bigg[\sum_{k=1}^{K0} C_k P(8,\alpha_i,\delta) + \sum^{K1} C_k P(9,\alpha_i,\delta) + \sum^{K2} C_k P(10,\alpha_i,\delta) + \sum^{K3} C_k P(11,\alpha_i,\delta) \Bigg]$$

$$+\sum^{J2} b_j \Bigg[\sum_{k=1}^{K0} C_k P(9,\alpha_i,\delta) + \sum^{K1} C_k P(10,\alpha_i,\delta) + \sum^{K2} C_k P(11,\alpha_i,\delta) + \sum^{K3} C_k P(12,\alpha_i,\delta) \Bigg]$$

$$+\sum^{J3} b_j \Bigg[\sum_{k=1}^{K0} C_k P(10,\alpha_i,\delta) + \sum^{K1} C_k P(11,\alpha_i,\delta) + \sum^{K2} C_k P(12,\alpha_i,\delta) + \sum^{K3} C_k P(13,\alpha_i,\delta) \Bigg] \Bigg\}$$

$$+\sum_{i=I1+1}^{I2} a_i \Bigg\{ \sum_{j=1}^{J0} b_j \Bigg[\sum_{k=1}^{K0} C_k P(3,\delta,\alpha_i) + \sum^{K1} C_k P(9,\delta,\alpha_i) + \sum^{K2} C_k P(14,\alpha_i,\delta) + \sum^{K3} C_k P(15,\alpha_i,\delta) \Bigg]$$

$$+\sum^{J1} b_j \Bigg[\sum_{k=1}^{K0} C_k P(9,\delta,\alpha_i) + \sum^{K1} C_k P(14,\alpha_i,\delta) + \sum^{K2} C_k P(15,\alpha_i,\delta) + \sum^{K3} C_k P(16,\alpha_i,\delta) \Bigg]$$

$$+\sum^{J2} b_j \Bigg[\sum_{k=1}^{K0} C_k P(14,\alpha_i,\delta) + \sum^{K1} C_k P(15,\alpha_i,\delta) + \sum^{K2} C_k P(16,\alpha_i,\delta) + \sum^{K3} C_k P(17,\alpha_i,\delta) \Bigg]$$

$$+\sum^{J3} b_j \Bigg[\sum_{k=1}^{K0} C_k P(15,\alpha_i,\delta) + \sum^{K1} C_k P(16,\alpha_i,\delta) + \sum^{K2} C_k P(17,\alpha_i,\delta) + \sum^{K3} C_k P(18,\alpha_i,\delta) \Bigg],$$

$$+\sum_{i=I2+1}^{I3} a_i \Bigg\{ \sum_{j=1}^{J0} b_j \Bigg[\sum_{k=1}^{K0} C_k P(4,\delta,\alpha_i) + \sum^{K1} C_k P(10,\delta,\alpha_i) + \sum^{K2} C_k P(15,\delta,\alpha_i) + \sum^{K3} C_k P(19,\alpha_i,\delta) \Bigg]$$

$$+\sum^{J1} b_j \Bigg[\sum_{k=1}^{K0} C_k P(10,\delta,\alpha_i) + \sum^{K1} C_k P(15,\delta,\alpha_i) + \sum^{K2} C_k P(19,\alpha_i,\delta) + \sum^{K3} C_k P(20,\alpha_i,\delta) \Bigg]$$

$$+\sum^{J2} b_j \Bigg[\sum_{k=1}^{K0} C_k P(15,\delta,\alpha_i) + \sum^{K1} C_k P(19,\alpha_i,\delta) + \sum^{K2} C_k P(20,\alpha_i,\delta) + \sum^{K3} C_k P(21,\alpha_i,\delta) \Bigg]$$

$$+\sum^{J3} b_j \Bigg[\sum_{k=1}^{K0} C_k P(19,\alpha_i,\delta) + \sum^{K1} C_k P(20,\alpha_i,\delta) + \sum^{K2} C_k P(21,\alpha_i,\delta) + \sum^{K3} C_k P(22,\alpha_i,\delta) \Bigg]$$

where $\delta = \beta_j + \gamma_k$.

Also let

$$X(i) = \int \phi_i(r)\underline{dr} \qquad (3.12)$$

$$= \sum_{i=1}^{I0} a_i K(\alpha_i,0) + \sum_{i=I0+1}^{I1} a_i K(\alpha_i,1) + \sum_{i=I1+1}^{I2} a_i K(\alpha_i,2) + \sum_{i=I2+1}^{I3} a_i K(\alpha_i,3)$$

where

$$K(a,n) = \int \underline{dr}\; r^n e^{-ar} = \frac{4\pi(n + 2)!}{a^{(n + 3)}} \qquad (3.13)$$

Then, after considering all the cross terms in (3.10):

$$\begin{aligned}
I_2 = {} & C_1\left[C_1X(1s)\;GG(1s,1s,1s,1) + C_2X(2s)\;GG(1s,1s,2s,1) + C_4X(3s)\;GG(1s,1s,3s,1)\right] \\
& + C_2\left[C_1X(1s)\;GG(2s,2s,1s,1) + C_2X(2s)\;GG(2s,2s,2s,1) + C_4X(3s)\;GG(2s,2s,3s,1)\right] \\
& - \frac{3}{\sqrt{3}}\,C_3\left[C_1X(1s)\;GG(2p,2p,1s,2) + C_2X(2s)\;GG(2p,2p,2s,2) + C_4X(3s)\;GG(2p,2p,3s,2)\right] \\
& + C_4\left[C_1X(1s)\;GG(3s,3s,1s,1) + C_2X(2s)\;GG(3s,3s,2s,1) + C_4X(3s)\;GG(3s,3s,3s,1)\right] \\
& - \frac{3}{\sqrt{3}}\,C_5\left[C_1X(1s)\;GG(3p,3p,1s,2) + C_2X(2s)\;GG(3p,3p,2s,2) + C_4X(3s)\;GG(3p,3p,3s,2)\right] \\
& + \frac{5}{\sqrt{5}}\,C_6\left[C_1X(1s)\;GG(3d,3d,1s,3) + C_2X(2s)\;GG(3d,3d,2s,3) + C_4X(3s)\;GG(3d,3d,3s,3)\right]
\end{aligned}$$

where we have used the following relation (Edmonds, 1957):

$$Y_{\ell -m}(\Omega) = (-1)^m\, Y^{*}_{\ell m}(\Omega) \quad .$$

Let

$$I_3 = \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; \psi^*(3,2) \frac{1}{r_3} \psi(1,2) \qquad (3.14)$$

Define

$$Y(i) = \int \frac{\phi_i(r)}{r} \, d\underline{r} \qquad (3.15)$$

Then using (3.8),

$$Y(i) = \sum_{i=1}^{I0} a_i K(\alpha_i,-1) + \sum_{i=I0+1}^{I1} a_i K(\alpha_i,0) + \sum_{i=I1+1}^{I2} a_i K(\alpha_i,1) + \sum_{i=I2+1}^{I3} \alpha_i K(\alpha_i,2)$$

Remembering the orthogonality of the orbitals, (3.11) gives

$$I_3 = C_1^{\,2}\chi(1sY(1s) + C_2^{\,2}\chi(2s)Y(2s) + C_4^{\,2}\chi(3s)Y(3s)$$

$$\therefore \qquad g_B^{\,L}(0,0) = -\frac{1}{2\pi}\left[I_1 + I_2 - 2I_3\right] \qquad (3.16)$$

III.B. Calculation of $g_B^{\,V}(0,0)$

From (2.15) we recall that

$$g_B^{\,V}(0,0) = -\frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; \psi^*(3,2) \left[\tfrac{1}{2}\nabla_2^{\,2} + \frac{2}{r_2} + E_o + \frac{1}{|\underline{r}_1 - \underline{r}_3|}\right] \psi(1,2)$$

Let

$$I_4 = \int d\underline{r}_1 \int d\underline{r}_2 \int d\underline{r}_3 \; \psi^*(3,2)\nabla_2^{\,2}\psi(1,2) \qquad (3.18)$$

Also let

$$\mathrm{FF1}\,(i,j) = \int \underline{dr}\ \phi_i^*(r)\ \nabla^2\ \phi_j(r) \qquad (3.19)$$

where i and j will always be s-type orbital for present calculations. Using $\phi_j(r)$ from (3.9).

$$\nabla^2\phi_j(r) = \frac{1}{r}\frac{d^2}{dr^2}\, r\ \phi_j(r)$$

$$= \sum_{j=1}^{J0} b_j \left[-2\,\frac{\beta_j}{r} + \beta^2_j \right] e^{-\beta_j r} + \sum_{j=J0+1}^{J1} b_j \left[\frac{2}{r} - 4\,\beta_j + \beta_j^{\,2} r \right] e^{-\beta_j r}$$

$$+ \sum_{j=J1+1}^{J2} b_j \left[6 - 6\beta_j r + \beta_j^{\,2} r^2 \right] e^{-\beta_j r} + \sum_{j=J2+1}^{J3} b_j \left[12r - 8\beta_j r^2 + \beta_j^{\,2} r^3 \right] e^{-\beta_j r}$$

Thus, using $\phi_i(r)$ of (3.8):

$$\mathrm{FF1}(i,j) = \sum_{i=1}^{I0} a_i \left[\sum_{j=1}^{J0} b_j \left(-2\beta_j K(\delta,-1) + \beta^2_j K(\delta,0) \right) + \sum_{j=J0+1}^{J1} b_j \left(2K(\delta,-1) - 4\beta_j K(\delta,0) + \beta_j^{\,2} K(\delta,1) \right) \right.$$

$$\left. + \sum_{j=J1+1}^{J2} b_j \left(6K(\delta,0) - 6\beta_j K(\delta,1) + \beta_j^{\,2} K(\delta,2) \right) + \sum_{j=J2+1}^{J3} b_j \left(12K(\delta,1) - 8\beta_j K(\delta,2) + \beta_j^{\,2} K(\delta,3) \right) \right]$$

$$+\sum_{i=I0+1}^{I1} a_i \left[\sum_{j=1}^{J0} b_j \left(-2\beta_j K(\delta,0) + \beta_j^{\,2} K(\delta,1)\right) + \sum^{J1} b_j \left(2K(\delta,0) - 4\beta_j K(\delta,1) + \beta_j^{\,2} K(\delta,2)\right)\right.$$

$$\left. + \sum^{J2} b_j \left(6K(\delta,1) - 6\beta_j K(\delta,2) + \beta_j^{\,2} K(\delta,3)\right) + \sum^{J3} b_j \left(12K(\delta,2) - 8\beta_j K(\delta,3) + \beta_j^{\,2} K(\delta,4)\right)\right]$$

$$+\sum_{i=I1+1}^{I2} a_i \left[\sum_{j=1}^{J0} b_j \left(-2\beta_j K(\delta,1) + \beta_j^{\,2} K(\delta,2)\right) + \sum^{J1} b_j \left(2K(\delta,1) - 4\beta_j K(\delta,2) + \beta_j^{\,2} K(\delta,3)\right)\right.$$

$$\left. + \sum^{J2} b_j \left(6K(\delta,2) - 6\beta_j K(\delta,3) + \beta_j^{\,2} K(\delta,4)\right) + \sum^{J3} b_j \left(12K(\delta,3) - 8\beta_j K(\delta,4) + \beta_j^{\,2} K(\delta,5)\right)\right]$$

$$+\sum_{i=I2+1}^{I3} a_i \left[\sum_{j=1}^{J0} b_j \left(-2b_j K(\delta,2) + \beta_j^{\,2} K(\delta,3)\right) + \sum^{J1} b_j \left(2K(\delta,2) - 4\beta_j K(\delta,3) + \beta_j^{\,2} K(\delta,4)\right)\right.$$

$$\left. + \sum^{J2} b_j \left(6K(\delta,3) - 6\beta_j K(\delta,4) + \beta_j^{\,2} K(\delta,5)\right) + \sum^{J3} b_j \left(12K(\delta,4) - 8\beta_j K(\delta,5) + \beta_j^{\,2} K(\delta,6)\right)\right]$$

where $\delta = \alpha_i + \beta_j$ and the function $K(\alpha,n)$ is defined by (3.13).

Inspecting all the terms in (3.18) gives us

$$I_4 = C_1X(1s)\left[C_1X(1s)FF1(1s,1s) + C_2X(2s)FF1(1s,2s) + C_4X(3s)FF1(1s,3s)\right]$$

$$+ C_2X(2s)\left[C_1X(1s)FF1(2s,1s) + C_2X(1s)FF1(2s,2s) + C_4X(3s)FF1(2s,3s)\right]$$

$$+ C_4X(3s)\left[C_1X(1s)FF1(3s,1s) + C_2X(2s)FF1(3s,2s) + C_4X(3s)FF1(3s,3s)\right]$$

Let

$$I_5 = \int \underline{dr}_1 \int \underline{dr}_2 \int \underline{dr}_3\ \psi^*(3,2)\,\frac{1}{r_2}\,\psi(1,2) \qquad (3.20)$$

Also let

$$FF3(i,j) = \int \underline{dr}\ \phi_i^*(r)\,\frac{1}{r}\,\phi_j(r) \qquad (3.21)$$

Then using, (3.8) and (3.9):

$$FF3(i,j) = \sum_{i=1}^{I0} a_i\left[\sum_{j=1}^{J0} b_jK(\delta,-1) + \sum_{j=J0+1}^{J1} b_jK(\delta,0) + \sum_{j=J1+1}^{J2} b_jK(\delta,1) + \sum_{j=j2+1}^{J3} b_jK(\delta,2)\right]$$

$$+ \sum_{i=I0+1}^{I1} a_i\left[\sum_{j=1}^{J0} b_jK(\delta,0) + \sum^{J1} b_jK(\delta,1) + \sum^{J2} b_jK(\delta,2) + \sum^{J3} b_jK(\delta,3)\right]$$

$$+ \sum_{i=I1+1}^{I2} a_i\left[\sum_{j=1}^{J0} b_jK(\delta,1) + \sum^{J1} b_jK(\delta,2) + \sum^{J2} b_jK(\delta,3) + \sum^{J3} b_jK(\delta,4)\right]$$

$$+ \sum_{i=I2+1}^{I3} a_i\left[\sum_{j=1}^{J0} b_jK(\delta,2) + \sum^{J1} b_jK(\delta,3) + \sum^{J2} b_jK(\delta,4) + \sum^{J3} b_jK(\delta,5)\right]$$

where $\delta = \alpha_i + \beta_j$.

Thus, (3.20) yields

$$I_5 = C_1X(1s)\left[C_1X(1s)FF3(1s,1s) + C_2X(2s)FF3(1sr,2s) + C_4X(3s)FF3(1s,3s)\right]$$

$$+ C_2X(2s)\left[C_1X(1s)FF3(2s,1s) + C_2X(2s)FF3(2s,2s) + C_4X(3s)FF3(2s,3s)\right]$$

$$+ C_4X(3s)\left[C_1X(1s)FF3(3s,1s) + C_2C(2s)FF3(3s,2s) + C_4X(3s)FF3(3s,3s)\right]$$

Let

$$I_6 = \int \underline{dr}_1 \int \underline{dr}_2 \int \underline{dr}_3\ \psi^*(3,2)\ E_o\ \psi(1,2) \tag{3.22}$$

where, as defined earlier, E_o is the ground state energy of helium with the particular ground state wave function chosen.

Remembering the orthogonality of orbital functions involved, we get:

$$I_6 = E_o\left[c_1^2\ \ X(1s)^{\ 2} + C_2^2\ \ X(2s)^{\ 2} + C_4^2\ \ X(3s)^{\ 2}\right].$$

Thus,

$$g_B^{\ V}(0,0) = -\frac{1}{2\pi}\left[\frac{I_4}{2} + 2I_5 + I_6 + I_1\right] \tag{3.23}$$

We can thus obtain $g_B^{\ L}(0,0)$ and $g_B^{\ V}(0,0)$ values from (3.16) and (3.23) for a wave function of the form (vi). For the other wave functions ((i) to (v)) the above analysis follows straight through by judiciously putting some of the weights (C_1, C_2, C_3, C_4, C_5, C_6) to zero. Table 3.B gives the values for $g_B^{\ L}(0,0)$ and $g_B^{\ V}(0,0)$ using wave functions (1) to (vi).

TABLE 3.B

Wave function	$g_B^L(0,0)$	$g_B^V(0,0)$
(i)	3.9025	3.8749
(ii)	3.8154	3.7223
(iii)	3.8276	3.7442
(iv)	3.9025	4.0725
(v)	3.9012	3.8951
(vi)	3.9205	3.9112

The values for $g_B^L(0,0)$ and $g_B^V(0,0)$ converge to 3.915 ± .005 using the configuration interaction wave functions. This is in excellent agreement with the results using the Hartree-Fock wave functions and the $g_B^L(0,0)$ value from using Hylleraas wave functions. We therefore adopt

$$g_B(0,0) = 3.92 \pm .05$$

as our finally converged result. This value is in contradiction with the value that Bransden et al. (1975) calculated using the sum rule (2.6). This raises grave doubts about the sum rule given by (2.6). We shall pick up this point in later discussion.

CHAPTER IV

ELECTRON-LITHIUM SCATTERING

In this chapter, we will briefly sketch the dispersion relations for electron-lithium scattering. We then proceed to calculate the exchange contribution using various wave functions for the ground state representation of the lithium atom for scattering at zero energy and in the forward direction.

For definiteness, let an electron (coordinate $\underline{r}_4$) of initial momentum $\underline{k}_i$ and energy $k^2/2$ be incident on a Lithium atom in the ground state $\psi_\gamma(\underline{r}_1, \underline{r}_2, \underline{r}_3)$ (subscript γ denotes the spin of the valence electron) of energy E_o. The total energy of the system is denoted by W_o so that for various inelastic scatterings (momentum of the scattered electron = $\underline{k}_f$, atom in state $\psi_\alpha(\underline{r}_1, \underline{r}_2, \underline{r}_3)$ with energy E_f), we have:

$$W_o = \frac{k^2}{2} + E_o = \frac{|\underline{k}_f|^2}{2} + E_f \qquad (4.1)$$

Now, the total hamiltonian H is given by

$$H = H_o' + V'$$

where

$$V'(\underline{r}_4;\underline{r}_1,\underline{r}_2,\underline{r}_3) = -\frac{z}{r_4} + \frac{1}{|\underline{r}_1 - \underline{r}_4|} + \frac{1}{|\underline{r}_2 - \underline{r}_4|} + \frac{1}{|\underline{r}_3 - \underline{r}_4|} \qquad (4.2)$$

and

$$H_o' = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \tfrac{1}{2}\nabla_3^2 - \tfrac{1}{2}\nabla_4^2 - \frac{z}{r_1} - \frac{z}{r_2} - \frac{z}{r_3} + \frac{1}{|\underline{r}_1 - \underline{r}_2|}$$

$$+ \frac{1}{|\underline{r}_1 - \underline{r}_3|} + \frac{1}{|\underline{r}_2 - \underline{r}_3|} \qquad (4.3)$$

such that

$$(H_o' - W_o)\, e^{i\underline{k}_f\cdot\underline{r}_4}\, \psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3) = 0 \qquad (4.4)$$

The Schrodinger equation for the system is

$$(H - W_o)\, \Psi^+(\underline{r}_4,\underline{r}_1,\underline{r}_2,\underline{r}_3) = 0 \qquad (4.5)$$

where

$$\Psi^+(\underline{r}_4,\underline{r}_1,\underline{r}_2,\underline{r}_3) = \psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3) e^{i\underline{k}_f\cdot r_4} + \frac{1}{W_o - H + i\varepsilon}\, V'(\underline{r}_4,\underline{r}_1,\underline{r}_2,\underline{r}_3)\, \Psi^+(\underline{r}_4,\underline{r}_1,\underline{r}_2,\underline{r}_3) \qquad (4.6)$$

Then, the direct scattering amplitude is defined as

$$f(\theta,E) = -\frac{1}{2\pi}\int \underline{dr_1}\int \underline{dr_2}\int \underline{dr_3}\int \underline{dr_4}\, \psi_\alpha^*(\underline{r}_1,\underline{r}_2,\underline{r}_3) e^{-i\underline{k}_f\cdot\underline{r}_4} V'(\underline{r}_4,\underline{r}_1,\underline{r}_2,\underline{r}_3)\, \Psi^+(\underline{r}_4,\underline{r}_1,\underline{r}_2,\underline{r}_3) \qquad (4.7)$$

The Born's approximation to this is

$$f_B(\theta,E) = -\frac{1}{2\pi}\int \underline{dr_1}\int \underline{dr_2}\int \underline{dr_3}\int \underline{dr_4}\, e^{-i\underline{k}_f\cdot\underline{r}_4} \psi_\alpha^*(\underline{r}_1,\underline{r}_2,\underline{r}_3) V'(r_4,r_1,r_2,r_3)\, \psi_\gamma(\underline{r}_1\underline{r}_2\underline{r}_3) e^{i\underline{k}_i\cdot\underline{r}_4}$$

Now consider an exchange collision whereby, in the final state, electron '4' is bound and electron '1' is free. Here, let us go through the steps taken above for a direct collision. The total Hamiltonian of the system is

$$H = H_o'' + V'' \qquad (4.8)$$

where

$$V''(\underline{r}_1;\underline{r}_1,\underline{r}_2,\underline{r}_3) = -\frac{z}{r_1} + \frac{1}{|r_1 - r_4|} + \frac{1}{|\underline{r}_1 - \underline{r}_2|} + \frac{1}{|\underline{r}_1 - \underline{r}_3|} \qquad (4.9)$$

and

$$H_o'' = -\tfrac{1}{2}\nabla_1^{\,2} - \tfrac{1}{2}\nabla_2^{\,2} - \tfrac{1}{2}\nabla_3^{\,2} - \tfrac{1}{2}\nabla_4^{\,2} - \frac{z}{r_1} - \frac{z}{r_2} - \frac{z}{r_3} + \frac{1}{|\underline{r}_4 - \underline{r}_2|}$$

$$+ \frac{1}{|\underline{r}_4 - \underline{r}_3|} + \frac{1}{|\underline{r}_2 - \underline{r}_3|} \qquad (4.10)$$

such that

$$(H_o'' - W_o)e^{i\underline{k}_f\cdot\underline{r}_1}\psi_\alpha(\underline{r}_4,\underline{r}_2,\underline{r}_3) = Q$$

Then the exchange scattering amplitude is defined as

$$g(\theta,E) = -\frac{1}{2\pi}\int\underline{dr}_1\int\underline{dr}_2\int\underline{dr}_3\int\underline{dr}_4\, e^{-i\underline{k}_f\cdot\underline{r}_1}\psi_\alpha^*(\underline{r}_4\underline{r}_2\underline{r}_3)V''(r_1r_4r_2r_3)\Psi^+(\underline{r}_1,\underline{r}_4,\underline{r}_2,\underline{r}_3)$$

$$(4.11)$$

The Born's approximation to this is

$$g_B(\theta,E) = -\frac{1}{2\pi}\int\underline{dr}_1\int\underline{dr}_2\int\underline{dr}_3\int\underline{dr}_4\, e^{-i\underline{k}_f\cdot\underline{r}_1}\psi_\alpha^{\,*}(r_4,r_1,r_3)V''(r_4,r_2,r_3)$$

$$\psi_\gamma(\underline{r}_1\underline{r}_2\underline{r}_3)e^{i\underline{k}_i\cdot\underline{r}_4} \qquad (4.12)$$

In analogy with equation (1.12) from Chapter I, we obtain the following dispersion relations **for the forward** ($\theta = 0$) elastic scattering:

$$\mathrm{Re}f(0,E) = f_B(0,E) + \frac{P}{\pi}\int_0^\infty \frac{\mathbf{Im}\, f(0,E')}{E' - E}\, dE' - \sum_j R_{dj}(E) \qquad (4.14)$$

and

$$\mathrm{Re}g(0,E) = g_B(0,E) + \frac{P}{\pi}\int_0^\infty \frac{\mathrm{Im}g(0,E')}{E'-E}\,dE' - \sum_j R_{ej}(E) \qquad (4.15)$$

where R_{dj}, R_{ej} are the residues of $f(0,E)$ and $g(0,E)$ respectively at their poles due to the bound states.

It is more convenient to work with the scattering amplitudes for the singlet and triplet states scatterings:

$$\begin{aligned} F^+(\theta,E) &= f(\theta,E) + g(\theta,E) \\ F^-(\theta,E) &= f(\theta,E) - g(\theta,E) \end{aligned} \qquad (4.16)$$

On applying the optical theorem relating the forward scattering amplitude to the total cross-section (elastic plus inelastic), we get

$$\begin{aligned} \mathrm{Im}F^+(0,E) &= \frac{k}{4\pi}\,\sigma_+(E) \\ \mathrm{Im}F^-(0,E) &= \frac{k}{4\pi}\,\sigma_-(E) \end{aligned} \qquad (4.17)$$

where $\sigma_+(E)$, $\sigma_-(E)$ are total cross-sections for incident electrons in singlet (+) or triplet (-) spin states relative to the lithium atom in its ground state. From (4.14), (4.15), (4.16) and (4.17) we get,

$$\mathrm{Re}F^+(E,0) = F_B^{\;+}(0,E) + \frac{P}{4\pi^2}\int_0^\infty \frac{\sqrt{E'}\,\sigma_+(E')}{E'-E}\,dE' + R^+(E) \qquad (4.18)$$

$$\mathrm{Re}F^-(E,0) = F_B^{\;-}(0,E) + \frac{P}{4\pi^2}\int_0^\infty \frac{\sqrt{E'}\,\sigma_-(E')}{E'-E}\,dE' + R^-(E)$$

where $R^+(E)$, $R^-(E)$ are residues for singlet and triplet states respectively.

In terms of the total cross-section, $\sigma_T(E)$, for an unpolarised beam of incident electrons,

$$\sigma_T(E) = \tfrac{1}{4}\,\sigma_+(E) + \tfrac{3}{4}\,\sigma_-(E) \quad \text{(Garett, 1965)} \qquad (4.19)$$

From (4.18) and (4.19) we can get

$$\mathrm{Re}\left[\tfrac{1}{4}F^+(0,E) + \tfrac{3}{4}F^-(0,E)\right] = \tfrac{1}{4}F_B{}^+(0,E) + \tfrac{3}{4}F_B{}^-(0,E) + \frac{P}{4\pi^2}\int_0^\infty \frac{\sqrt{E'}\,\sigma_T(E')}{E' - E}\,dE'$$

$$+ \tfrac{1}{4}\,R^+(E) + \tfrac{3}{4}\,R^-(E) \qquad (4.20)$$

or in terms of $f(0,E)$ and $g(0,E)$

$$\mathrm{Re}\left[f(0,E) - \tfrac{1}{2}g(0,E)\right] = f_B(0,E) - \tfrac{1}{2}g_B(0,E) + \frac{P}{4\pi^2}\int_0^\infty \frac{\sqrt{E'}\,\sigma_T(E')}{E' - E}\,dE'$$

$$+ \tfrac{1}{4}\,R^+(E) + \tfrac{3}{4}R^-(E) \qquad (4.21)$$

Although $f_B(0,E)$, $g_B(0,E)$, R^+ and R^- can be calculated in principle, the usefulness of this relation is reduced by the fact that the observed forward scattered intensity is not proportional to $|f(0,E) - \tfrac{1}{2}g(0,E)|^2$ but to

$$\tfrac{1}{4}|f(0,E) + g(0,E)|^2 + \tfrac{3}{4}|f(0,E) - g(0,E)|^2$$

so that a direct consistency check cannot be made between the measured quantities on the right-hand and the left-hand sides of (4.21). At zero incident energy, (4.21) becomes

$$\mathrm{Re}\left[f(0,0) - \tfrac{1}{2}g(0,0)\right] = f_B(0,0) - \tfrac{1}{2}g_B(0,0) + \frac{P}{2\pi^2}\int_0^\infty \sigma_T(k'^2)\,dk' + \tfrac{1}{4}\,R^+(0)$$

$$+ \tfrac{3}{4}\,R^-(0) . \qquad (4.22)$$

Using the relation:

$$\mathrm{Re}\left[f(0,0) \pm g(0,0)\right] = - a^{\pm} \qquad (4.23)$$

we get,

$$\mathrm{Re}\left[f(0,0) - \tfrac{1}{2}g(0,0)\right] = - \tfrac{3}{4}a^{-} - \tfrac{1}{4}a^{+} \qquad (4.24)$$

where $a^{\pm}$ are the zero-energy scattering lengths.

Substituting (4.24) into (4.22), we have

$$- \tfrac{3}{4}a^{-} - \tfrac{1}{4} a^{+} = f_B(0,0) - \tfrac{1}{2}g_B(0,0) + \frac{P}{2\pi^2} \int_0^{\infty} \sigma_T(k'^2)dk' + \tfrac{1}{4}R^{+}(0)$$
$$+ \tfrac{3}{4}R^{-}(0) \qquad (4.25)$$

The expression (4.25) can be used to test the validity of the dispersion relations for electron lithium scattering. M.R.C. McDowell and his co-workers have calculated the principal value integral and the direct scattering amplitude $f_B(0,0)$; while the residue contribution is in the process of being calculated. The scattering lengths, $a^{\pm}$, have been calculated by Garrett (1965) and can also be obtained from the work of Burke et al. (1969).

IV.A. Calculation of the exchange contribution $(-\frac{1}{2}g_B(0,0))$:

Let us define,

$$T_{\alpha\beta\gamma\delta} = \langle\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4)|V_f|\mathcal{A}\psi_\gamma(\underline{r}_1\underline{r}_2\underline{r}_3)U_\delta(\underline{r}_4)\rangle \qquad (4.26)$$

where $\mathcal{A}$ is an antisymmetrizer, and $U_\beta(\underline{r})$ $(= e^{i\underline{k}.\underline{r}})$ represents a free electron with spin β.

Thus,

$$T_{\alpha\beta\gamma\delta} = -\ 3\ \langle\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4)|V_f|\psi_\gamma(\underline{r}_2,\underline{r}_3,\underline{r}_4)U_\delta(\underline{r}_1)\rangle$$

$$+ \langle\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(r_4)|V_f|\psi_\gamma(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\delta(\underline{r}_4)\rangle$$

$$= P_{\alpha\beta\gamma\delta} - 3\,q_{\alpha\beta\gamma\delta} \qquad (4.27)$$

For singlet scattering,

$$F^+(0,E) = \tfrac{1}{2}\langle\left[\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4) - \psi_\beta(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\alpha(\underline{r}_4)\right]|V_f|\mathcal{A}\left[\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4)\right.$$

$$\left. - \psi_\beta(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\alpha(\underline{r}_4)\right]\rangle$$

$$= T_{\alpha\beta\alpha\beta} - T_{\alpha\beta\beta\alpha} \qquad (4.28)$$

where, and from now on, α,β denote spin 'up' and spin 'down' respectively. For triplet scattering,

$$F^-(0,E) = \tfrac{1}{2}\langle\left[\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4) + \psi_\beta(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\alpha(\underline{r}_4)\right]|V_f|\mathcal{A}\left[\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4)\right.$$

$$\left. + \psi_\beta(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\alpha(\underline{r}_4)\right]\rangle$$

$$= T_{\alpha\beta\alpha\beta} + T_{\alpha\beta\beta\alpha} \qquad (4.29)$$

Thus, $\tfrac{1}{2}g_B(0,0) = \tfrac{1}{4}\left[-3\,q_{\alpha\beta\alpha\beta} + 3q_{\alpha\beta\beta\alpha} + 3(-3q_{\alpha\beta\alpha\beta} - 3q_{\alpha\beta\beta\alpha})\right]$

$$= \tfrac{1}{4}\left[-12q_{\alpha\beta\alpha\beta} - 6q_{\alpha\beta\beta\alpha}\right] \qquad (4.30)$$

For the purposes of the present calculations, we shall use determinantal wave functions for the ground state representation of lithium atoms. Let

$$\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3) = \frac{1}{\sqrt{6}}\Big[\phi_{1s\alpha}(r_1)\Big(\phi_{1s\beta}(r_2)\phi_{2s\alpha}(r_3) - \phi_{1s\beta}(r_3)\phi_{2s\alpha}(r_2)\Big)$$
$$- \phi_{1s\alpha}(r_2)\Big(\phi_{1s\beta}(r_1)\phi_{2s\alpha}(r_3) - \phi_{1s\beta}(r_3)\phi_{2s\alpha}(r_1)\Big)$$
$$+ \phi_{1s\alpha}(r_3)\Big(\phi_{1s\beta}(r_2)\phi_{2s\alpha}(r_1) - \phi_{1s\beta}(r_1)\phi_{2s\alpha}(r_2)\Big)\Big] \qquad (4.31)$$

and

$$\psi_\beta(\underline{r}_2,\underline{r}_3,\underline{r}_4) = \frac{1}{\sqrt{6}}\Big[\phi_{1s\alpha}(r_2)\Big(\phi_{1s\beta}(r_3)\phi_{2s\beta}(r_4) - \phi_{1s\beta}(r_4)\phi_{2s\beta}(r_3)\Big)$$
$$- \phi_{1s\alpha}(r_3)\Big(\phi_{1s\beta}(r_2)\phi_{2s\beta}(r_4) - \phi_{1s\beta}(r_4)\phi_{2s\beta}(r_2)\Big)$$
$$+ \phi_{1s\alpha}(r_4)\Big(\phi_{1s\beta}(r_3)\phi_{2s\beta}(r_2) \quad \phi_{1s\beta}(r_2)\phi_{2s\beta}(r_3)\Big)\Big] \qquad (4.32)$$

Now

$$q^{L}_{\alpha\beta\alpha\beta}(0,E) = \langle\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4)|V''|\psi_\alpha(\underline{r}_2,\underline{r}_3,\underline{r}_4)U_\beta(\underline{r}_1)\rangle$$

where subscript 'L' denotes the length form with:

$$V'' = -\frac{Z}{r_4} + \frac{1}{|\underline{r}_1 - \underline{r}_4|} + \frac{1}{|\underline{r}_2 - \underline{r}_4|} + \frac{1}{|\underline{r}_3 - \underline{r}_4|} \qquad (4.33)$$

In analogy with the analysis for helium in Chapter II that led us to the formulation of $g_B^{V}(0,0)$, we can obtain

$$q^{V}_{\alpha\beta\alpha\beta}(0,E) = \langle\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4)|V''|\psi_\alpha(\underline{r}_2,\underline{r}_3,\underline{r}_4)U_\beta(\underline{r}_1)\rangle$$

where subscript 'V' denotes the velocity form, and

$$V''' = \tfrac{1}{2}\nabla_2^{\,2} + \tfrac{1}{2}\nabla_3^{\,2} + \frac{z}{r_2} + \frac{z}{r_3} + E_o - \frac{1}{|\underline{r}_2 - \underline{r}_3|} + \frac{1}{|\underline{r}_1 - \underline{r}_4|} \qquad (4.34)$$

Similarly, we can define $q^L_{\alpha\beta\beta\alpha}(0,E)$ and $q^V_{\alpha\beta\beta\alpha}(0,E)$:

$$q^L_{\alpha\beta\beta\alpha}(0,E) = \langle\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4)|V''|\psi_\beta(\underline{r}_2,\underline{r}_3,\underline{r}_4)U_\alpha(\underline{r}_1)\rangle \qquad (4.35)$$

and

$$q^V_{\alpha\beta\beta\alpha}(0,E) = \langle\psi_\alpha(\underline{r}_1,\underline{r}_2,\underline{r}_3)U_\beta(\underline{r}_4)|V'''|\psi_\beta(\underline{r}_2,\underline{r}_3,\underline{r}_4)U_\alpha(\underline{r}_1)\rangle \qquad (4.36)$$

We can now proceed with the evaluation of the exchange contributions. We shall use some of the functions (FF2, GG, etc) defined and used in Chapter III. Using (4.31) and (4.32) we get:

$$q^L_{\alpha\beta\alpha\beta}(0,E) = \frac{1}{6}\langle\left[\phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_4)\phi_{2s\alpha}(r_2) - \phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_4)\phi_{2s\alpha}(r_3)\right]U_\beta(r_1)|V''|$$

$$\left[\phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_1)\phi_{2s\alpha}(r_2) - \phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_1)\phi_{2s\alpha}(r_3)\right]U_\beta(r_4)\rangle$$

For zero energy, i.e. $U_\beta(r) = 1$,

$$q^L_{\alpha\beta\alpha\beta}(0,0) = \frac{1}{3}\left[K - L\right] \qquad (4.37)$$

where

$$K = \langle\phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_4)\phi_{2s\alpha}(r_2)|V''|\phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_1)\phi_{2s\alpha}(r_2)\rangle$$

$$= FF2(1s\beta,1s\beta,1) + \left[GG(1s\beta,2s\alpha,2s\alpha,1) + GG(1s\beta,1s\alpha,1s\alpha,1)\right]X(1s\beta)$$

$$- Z.X(1s\beta)Y(1s\beta)$$

and

$$L = <\phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_4)\phi_{2s\alpha}(r_3)|V''|\phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_1)\phi_{2s\alpha}(r_2)>$$

=0. remembering that the orbitals ϕ's are orthonormal.

$$q^{L}_{\alpha\beta\beta\alpha}(0,E) = \frac{1}{6} <\Big[\phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_3)\phi_{2s\beta}(r_4) - \phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_4)\phi_{2s\beta}(r_3)$$

$$+ \phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_4)\phi_{2s\beta}(r_2)$$

$$- \phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_2)\phi_{2s\beta}(r_4)\Big] U_\alpha(r_1)|V''|\Big[\phi_{1s\alpha}(r_1)\phi_{1s\beta}(r_2)\phi_{2s\alpha}(r_3)$$

$$- \phi_{1s\alpha}(r_1)\phi_{1s\beta}(r_3)\phi_{2s\alpha}(r_2) + \phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_3)\phi_{2s\alpha}(r_1)$$

$$- \phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_2)\phi_{2s\alpha}(r_1)\Big] U_\beta(r_4)> \qquad (4.38)$$

For zero energy,

$$q^{L}_{\alpha\beta\beta\alpha}(0,0) = \frac{1}{3}\Big[L - M + N - 0\Big] \qquad (4.39)$$

where

$$M = <\phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_2)\phi_{2s\beta}(r_4)|V''|\phi_{1s\alpha}(r_1)\phi_{1s\beta}(r_2)\phi_{2s\alpha}(r_3)>$$

= GG(2sβ,1sα,2sα,1) X(1sβ)

$$N = <\phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_3)\phi_{2s\beta}(r_4)|V''|\phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_3)\phi_{2s\alpha}(r_1)>$$

= FF2(2sβ,2sα,1) + [GG(2sβ,1sα,1sα,1) + GG(2sβ,1sβ,1sβ,1)] X(2sα)

- ZX(2sα). Y(2sβ).

and

$$O = \langle\phi_{1s\alpha}(2)\phi_{2s\beta}(3)\phi_{1s\beta}(4)|V''|\phi_{1s\alpha}(2)\phi_{1s\beta}(3)\phi_{2s\alpha}(1)\rangle$$

$$= GG(1s\beta,2s\beta,1s\beta,1)\ X(2s\alpha)$$

From (4.30), (4.37) and (4.39) we get

$$\tfrac{1}{2}g_B^L(0,0) = -K + \tfrac{1}{2}\left[M + L - N + O\right] \qquad (4.40)$$

On substituting V''' from (4.34) into (4.36), we get,

$$q^V_{\alpha\beta\alpha\beta}(0,0) = \frac{1}{3}\left[K' - L'\right] \qquad (4.41)$$

where

$$K' = \langle\phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_4)\phi_{2s\alpha}(r_2)|V'''|\phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_1)\phi_{2s\alpha}(r_2)\rangle$$

and

$$L' = \langle\phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_4)\phi_{2s\alpha}(r_3)|V'''|\phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_1)\phi_{2s\alpha}(r_2)\rangle$$

Before going any further, let us define another function:

$$FF5(i,j,k,\ell,kk) = \int d\underline{r}_1 \int d\underline{r}_2 \frac{\phi_i^*(r_1)\phi_j^*(r_1)\phi_k(r_2)\phi_\ell(r_2)}{|\underline{r}_1 - \underline{r}_2|} \qquad (4.42)$$

Let us define the following s-type orbital:

$$\phi_\ell(r) = \sum_{\ell=0}^{L0} d_\ell e^{-\delta_\ell r} + \sum_{\ell=L0+1}^{L1} d_\ell r e^{-\delta_\ell r} + \sum_{\ell=L1+1}^{L2} d_\ell r^2 e^{-\delta_\ell r} + \sum_{\ell=L2+1}^{L3} d_\ell r^3 e^{-\delta_\ell r}$$

Then, using the orbitals $\phi_i(r)$, $\phi_j(r)$ and $\phi_k(r)$ as defined by equations (3.8), (3.9) and (3.11) respectively, we get:

$$
\begin{aligned}
\mathrm{FF5}(i,j,k,\ell,1) = \sum_{i=1}^{I0} a_i \Bigg\{ \sum_{j=1}^{J0} b_j \Bigg[\sum_{k=1}^{K0} c_k \Bigg(& \sum_{c=1}^{L0} d_\ell P(1,s,t) + \sum^{L1} d_\ell P(2,s,t) + \sum^{L2} d_\ell P(3,s,t) \\
& + \sum^{L3} d_\ell P(4,s,t) \Bigg) \\
+ \sum_{k}^{K1} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(2,s,t) + \sum^{L1} d_\ell P(3,s,t) + \sum^{L2} d_\ell P(4,s,t) + \sum^{L3} d_\ell P(5,s,t) \Bigg) \\
+ \sum^{K2} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(3,s,t) + \sum^{L1} d_\ell P(4,s,t) + \sum^{L2} d_\ell P(5,s,t) + \sum^{L3} d_\ell P(6,s,t) \Bigg) \\
+ \sum^{K3} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(4,s,t) + \sum^{L1} d_\ell P(5,s,t) + \sum^{L2} d_\ell P(6,s,t) + \sum^{L3} d_\ell P(7,s,t) \Bigg) \Bigg] \\
+ \sum_{j=J0+1}^{J1} b_j \Bigg[\sum_{k=1}^{K0} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(2,t,s) + \sum^{L1} d_\ell P(8,s,t) + \sum^{L2} d_\ell P(9,s,t) + \sum^{L3} d_\ell P(10,s,t) \Bigg) \\
+ \sum^{K1} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(8,s,t) + \sum^{L1} d_\ell P(9,s,t) + \sum^{L2} d_\ell P(10,s,t) + \sum^{L3} d_\ell P(11,s,t) \Bigg) \\
+ \sum^{K2} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(9,s,t) + \sum^{L1} d_\ell P(10,s,t) + \sum^{L2} d_\ell P(11,s,t) + \sum^{L3} d_\ell P(12,s,t) \Bigg) \\
+ \sum^{K3} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(10,s,t) + \sum^{L1} d_\ell P(11,s,t) + \sum^{L2} d_\ell P(12,s,t) + \sum^{L3} d_\ell P(13,s,t) \Bigg) \Bigg] \\
+ \sum_{j=J1+1}^{J2} b_j \Bigg[\sum_{k=1}^{K0} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(3,t,s) + \sum^{L1} d_\ell P(9,t,s) + \sum^{L2} d_\ell P(14,s,t) + \sum^{L3} d_\ell P(15,s,t) \Bigg) \\
\sum^{K1} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(9,t,s) + \sum^{L1} d_\ell P(14,s,t) + \sum^{L2} d_\ell P(15,s,t) + \sum^{L3} d_\ell P(16,s,t) \Bigg) \\
+ \sum^{K2} c_k \Bigg(& \sum_{\ell=1} d_\ell P(14,s,t) + \sum^{L1} d_\ell P(15,s,t) + \sum^{L2} d_\ell P(16,s,t) + \sum^{L3} d_\ell P(17,s,t) \Bigg) \\
+ \sum^{K3} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(15,s,t) + \sum^{L1} d_\ell P(16,s,t) + \sum^{L2} d_\ell P(17,s,t) + \sum^{L3} d_\ell P(18,s,t) \Bigg) \Bigg] \\
+ \sum_{j=J2+1}^{J3} b_j \Bigg[\sum_{k=1}^{K0} c_k \Bigg(& \sum_{\ell=1}^{L0} d_\ell P(4,t,s) + \sum^{L1} d_\ell P(10,t,s) + \sum^{L2} d_\ell P(15,t,s) + \sum^{L3} d_\ell P(19,s,t) \Bigg)
\end{aligned}
$$

$$+ \sum^{K1} c_k \Bigg(\sum_{\ell=1}^{L0} d_\ell P(10,t,s) + \sum^{L1} d_\ell P(15,t,s) + \sum^{L2} d_\ell P(19,s,t) + \sum^{L3} d_\ell P(20,s,t) \Bigg)$$

$$+ \sum^{K2} c_k \Bigg(\sum_{\ell=1}^{L0} d_\ell P(15,t,s) + \sum^{L1} d_\ell P(19,s,t) + \sum^{L2} d_\ell P(20,s,t) + \sum^{L3} d_\ell P(21,s,t) \Bigg)$$

$$+ \sum^{K3} c_k \Bigg(\sum_{\ell=1}^{L0} d_\ell P(19,s,t) + \sum^{L1} d_\ell P(20,s,t) + \sum^{L2} d_\ell P(21,s,t) + \sum^{L3} d_\ell P(22,s,t) \Bigg) \Bigg] \Bigg\}$$

$$+ \sum_{i=I0+1}^{I1} a_i \Bigg\{ \sum_{j=1}^{J0} b_j \Bigg[\sum_{k=1}^{K0} c_k \Bigg(\sum_{\ell=1}^{L0} d_\ell P(2,t,s) + \sum_{\ell=L0+1}^{L1} d_\ell P(8,s,t) + \sum^{L2} d_\ell P(9,s,t) + \sum^{L3} d_\ell P(10,s,t) \Bigg)$$

$$+ \sum_{k=K0+1}^{K1} \Bigg(\sum_{\ell=1}^{L0} d_\ell P(8,s,t) + \sum^{L1} d_\ell P(9,s,t) + \sum^{L2} d_\ell P(10,s,t) + \sum^{L3} d_\ell P(11,s,t) \Bigg)$$

$$+ \sum^{K2} c_k \Bigg(\sum_{\ell=1}^{L0} d_\ell P(9,s,t) + \sum^{L1} d_\ell P(10,s,t) + \sum^{L2} d_\ell P(11,s,t) + \sum^{L3} d_\ell P(12,s,t) \Bigg)$$

$$+ \sum^{K3} c_k \Bigg(\sum_{\ell=1}^{L0} d_\ell P(10,s,t) + \sum^{L1} d_\ell P(11,s,t) + \sum^{L2} d_\ell P(12,s,t) + \sum^{L3} d_\ell P(13,s,t) \Bigg) \Bigg]$$

$$+ \sum_{j=J0+1}^{J1} b_j \Bigg[\sum_{k=1}^{K0} c_k \Bigg(\sum^{L0} d_\ell P(3,t,s) + \sum^{L1} d_\ell P(9,t,s) + \sum^{L2} d_\ell P(14,s,t) + \sum^{L3} d_\ell P(15,s,t) \Bigg)$$

$$+ \sum^{K1} c_k \Bigg(\sum^{L0} d_\ell P(9,t,s) + \sum^{L1} d_\ell P(14,s,t) + \sum^{L2} d_\ell P(15,s,t) + \sum^{L3} d_\ell P(16,s,t) \Bigg)$$

$$+ \sum^{K2} c_k \Bigg(\sum^{L0} d_\ell P(14,s,t) + \sum^{L1} d_\ell P(15,s,t) + \sum^{L2} d_\ell P(16,s,t) + \sum^{L3} d_\ell P(17,s,t) \Bigg)$$

$$+ \sum^{K3} c_k \Bigg(\sum^{L0} d_\ell P(15,s,t) + \sum^{L1} d_\ell P(16,s,t) + \sum^{L2} d_\ell P(17,s,t) + \sum^{L3} d_\ell P(18,s,t) \Bigg) \Bigg]$$

$$\sum_{j=J1+1}^{J2} b_j \Bigg[\sum_{k=1}^{K0} c_k \Bigg(\sum_{\ell=1}^{L0} d_\ell P(4,t,s) + \sum^{L1} d_\ell P(10,t,s) + \sum^{L2} d_\ell P(15,t,s,) + \sum^{L3} d_\ell P(19,s,t) \Bigg)$$

$$+ \sum^{K1} c_k \Bigg(\sum_{\ell=1}^{L0} d_\ell P(10,t,s) + \sum^{L1} d_\ell P(15,t,s) + \sum^{L2} d_\ell P(19,s,t) + \sum^{L3} d_\ell P(20,s,t) \Bigg)$$

$$+ \sum^{K2} c_k \Bigg(\sum_{\ell}^{L0} d_\ell P(15,t,s) + \sum^{L1} d_\ell P(19,s,t) + \sum^{L2} d_\ell P(20,s,t) + \sum^{L3} d_\ell P(21,s,t) \Bigg)$$

$$+ \sum^{K3} c_k \Bigg(\sum_{\ell}^{L0} d_\ell P(19,s,t) + \sum^{L1} d_\ell P(20,s,t) + \sum^{L2} d_\ell P(21,s,t) + \sum^{L3} d_\ell P(22,s,t) \Bigg) \Bigg]$$

$$+\sum_{j=J2+1}^{J3} b_j \left[\sum_{k=1}^{K0} c_k \left(\sum_{\ell=1}^{L0} d_\ell P(5,t,s) + \sum^{L1} d_\ell P(11,t,s) + \sum^{L2} d_\ell P(16,t,s) + \sum^{L3} d_\ell P(20,t,s) \right) \right.$$

$$+\sum^{K1} c_k \left(\sum^{L0} d_\ell P(11,t,s) + \sum^{L1} d_\ell P(16,t,s) + \sum^{L2} d_\ell P(20,t,s) + \sum^{L3} d_\ell P(23,s,t) \right)$$

$$+\sum^{K2} c_k \left(\sum^{L0} d_\ell P(16,t,s) + \sum^{L1} d_\ell P(20,t,s) + \sum^{L2} d_\ell P(23,s,t) + \sum^{L3} d_\ell P(24,s,t) \right)$$

$$\left. +\sum^{K3} c_k \left(\sum^{L0} d_\ell P(20,t,s) + \sum^{L1} d_\ell P(23,s,t) + \sum^{L2} d_\ell P(24,s,t) + \sum^{L3} d_\ell P(25,s,t) \right) \right] \Bigg\}$$

$$+\sum_{i=I1+1}^{I2} a_i \left\{ \sum_{j=1}^{J0} b_j \left[\sum_{k=1}^{K0} c_k \left(\sum_{\ell=1}^{L0} d_\ell P(3,t,s) + \sum^{L1} d_\ell P(9,t,s) + \sum^{L2} d_\ell P(14,s,t) + \sum^{L3} d_\ell P(15,s,t) \right) \right. \right.$$

$$+\sum^{K1} c_k \left(\sum^{L0} d_\ell P(9,t,s) + \sum^{L1} d_\ell P(14,s,t) + \sum^{L2} d_\ell P(15,s,t) + \sum^{L3} d_\ell P(16,s,t) \right)$$

$$+\sum^{K2} c_k \left(\sum^{L0} d_\ell P(14,s,t) + \sum^{L1} d_\ell P(15,s,t) + \sum^{L2} d_\ell P(16,s,t) + \sum^{L3} d_\ell P(17,s,t) \right)$$

$$\left. +\sum^{K3} c_k \left(\sum^{L0} d_\ell P(15,s,t) + \sum^{L1} d_\ell P(16,s,t) + \sum^{L2} d_\ell P(17,s,t) + \sum^{L3} d_\ell P(18,s,t) \right) \right]$$

$$+\sum_{j=J0+1}^{J1} b_j \left[\sum_{k=1}^{K0} c_k \left(\sum_{\ell=1}^{L0} d_\ell P(4,t,s) + \sum^{L1} d_\ell P(10,t,s) + \sum^{L2} d_\ell P(15,t,s) + \sum^{L3} d_\ell P(19,s,t) \right) \right.$$

$$+\sum^{K1} c_k \left(\sum^{L0} d_\ell P(10,t,s) + \sum^{L1} d_\ell P(15,t,s) + \sum^{L2} d_\ell P(19,s,t) + \sum^{L3} d_\ell P(20,s,t) \right)$$

$$+\sum^{K2} c_k \left(\sum^{L0} d_\ell P(15,t,s) + \sum^{L1} d_\ell P(19,s,t) + \sum^{L2} d_\ell P(20,s,t) + \sum^{L3} d_\ell P(21,s,t) \right)$$

$$\left. +\sum^{K3} c_k \left(\sum^{L0} d_\ell P(19,s,t) + \sum^{L1} d_\ell P(20,s,t) + \sum^{L2} d_\ell P(21,s,t) + \sum^{L3} d_\ell P(22,s,t) \right) \right]$$

$$+\sum_{j=J1+1}^{J2} b_j \left[\sum_{k=1}^{K0} c_k \left(\sum_{\ell=1}^{L0} d_\ell P(5,t,s) + \sum^{L1} d_\ell P(11,t,s) + \sum^{L2} d_\ell P(16,t,s) + \sum^{L3} d_\ell P(20,t,s) \right) \right.$$

$$+\sum^{K1} c_k \left(\sum^{L0} d_\ell P(11,t,s) + \sum^{L1} d_\ell P(16,t,s) + \sum^{L2} d_\ell P(20,t,s) + \sum^{L3} d_\ell P(23,s,t) \right)$$

$$+\sum^{K2} c_k \left(\sum^{L0} d_\ell P(16,t,s) + \sum^{L1} d_\ell P(20,t,s) + \sum^{L2} d_\ell P(23,s,t) + \sum^{L3} d_\ell P(24,s,t) \right)$$

$$+ \sum^{K3} c_k \left(\sum^{L0} d_\ell P(20,t,s) + \sum^{L1} d_\ell P(23,s,t) + \sum^{L2} d_\ell P(24,s,t) + \sum^{L3} d_\ell P(25,s,t) \right) \Bigg]$$

$$+ \sum_{j=J2+1}^{J3} b_j \Bigg[\sum_{k=1}^{K0} c_k \left(\sum_{\ell=1}^{L0} d_\ell P(\ 6,t,s) + \sum^{L1} d_\ell P(12,t,s) + \sum^{L2} d_\ell P(17,t,s) + \sum^{L3} d_\ell P(21,t,s) \right)$$

$$+ \sum^{K1} c_k \left(\sum^{L0} d_\ell P(12,t,s) + \sum^{L1} d_\ell P(17,t,s) + \sum^{L2} d_\ell P(21,t,s) + \sum^{L3} d_\ell P(24,t,s) \right)$$

$$+ \sum^{K2} c_k \left(\sum^{L0} d_\ell P(17,t,s) + \sum^{L1} d_\ell P(21,t,s) + \sum^{L2} d_\ell P(24,t,s) + \sum^{L3} d_\ell P(26,s,t) \right)$$

$$+ \sum^{K3} c_k \left(\sum^{L0} d_\ell P(21,t,s) + \sum^{L1} d_\ell P(24,t,s) + \sum^{L2} d_\ell P(26,s,t) + \sum^{L3} d_\ell P(27,s,t) \right) \Bigg] \Bigg\}$$

$$+ \sum_{i=I2+1}^{I3} a_i \Bigg\{ \sum_{j=1}^{J0} b_j \Bigg[\sum_{k=1}^{K0} c_k \left(\sum_{\ell=1}^{L0} d_\ell P(\ 4,t,s) + \sum^{L1} d_\ell P(10,t,s) + \sum^{L2} d_\ell P(15,t,s) + \sum^{L3} d_\ell P(19,s,t) \right)$$

$$+ \sum^{K1} c_k \left(\sum^{L0} d_\ell P(10,t,s) + \sum^{L1} d_\ell P(15,t,s) + \sum^{L2} d_\ell P(19,s,t) + \sum^{L3} d_\ell P(20,s,t) \right)$$

$$+ \sum^{K2} c_k \left(\sum^{L0} d_\ell P(15,t,s) + \sum^{L1} d_\ell P(19,s,t) + \sum^{L2} d_\ell P(20,s,t) + \sum^{L3} d_\ell P(21,s,t) \right)$$

$$+ \sum^{K3} c_k \left(\sum^{L0} d_\ell P(19,s,t) + \sum^{L1} d_\ell P(20,s,t) + \sum^{L2} d_\ell P(21,s,t) + \sum^{L3} d_\ell P(22,s,t) \right) \Bigg]$$

$$+ \sum_{j=J0+1}^{J1} b_j \Bigg[\sum_{k=1}^{K0} c_k \left(\sum_{\ell=1}^{L0} d_\ell P(\ 5,t,s) + \sum^{L1} d_\ell P(11,t,s) + \sum^{L2} d_\ell P(16,t,s) + \sum^{L3} d_\ell P(20,t,s) \right)$$

$$+ \sum^{K1} c_k \left(\sum^{L0} d_\ell P(11,t,s) + \sum^{L1} d_\ell P(16,t,s) + \sum^{L2} d_\ell P(20,t,s) + \sum^{L3} d_\ell P(23,s,t) \right)$$

$$+ \sum^{K2} c_k \left(\sum^{L0} d_\ell P(16,t,s) + \sum^{L1} d_\ell P(20,t,s) + \sum^{L2} d_\ell P(23,s,t) + \sum^{L3} d_\ell P(24,s,t) \right)$$

$$+ \sum^{K3} c_k \left(\sum^{L0} d_\ell P(20,t,s) + \sum^{L1} d_\ell P(23,s,t) + \sum^{L2} d_\ell P(24,s,t) + \sum^{L3} d_\ell P(25,s,t) \right) \Bigg]$$

$$+ \sum_{j=J1+1}^{J2} b_j \Bigg| \sum_{k=1}^{K0} c_k \left(\sum_{\ell=1}^{L0} d_\ell P(\ 5,t,s) + \sum^{L1} d_\ell P(12,t,s) + \sum^{L2} d_\ell P(17,t,s) + \sum^{L3} d_\ell P(21,t,s) \right)$$

$$+ \sum^{K1} c_k \left(\sum_{\ell=1}^{L0} d_\ell P(12,t,s) + \sum^{L1} d_\ell P(17,t,s) + \sum^{L2} d_\ell P(21,t,s) + \sum^{L3} d_\ell P(24,t,s) \right)$$

$$+\sum^{K2} c_k \Bigg(\sum_{\ell}^{L0} d_\ell P(17,t,s) + \sum^{L1} d_\ell P(21,t,s) + \sum^{L2} d_\ell P(24,t,s) + \sum^{L3} d_\ell P(26,s,t) \Bigg)$$

$$+\sum^{K3} c_k \Bigg(\sum^{L0} d_\ell P(21,t,s) + \sum^{L1} d_\ell P(24,t,s) + \sum^{L2} d_\ell P(26,s,t) + \sum^{L3} d_\ell P(27,s,t) \Bigg)\Bigg]$$

$$+\sum_{j=J2+1}^{J3} b_j \Bigg[\sum^{K0} c_k \Bigg(\sum^{L0} d_\ell P(7,t,s) + \sum^{L1} d_\ell P(13,t,s) + \sum^{L2} d_\ell P(18,t,s) + \sum^{L3} d_\ell P(22,t,s) \Bigg)$$

$$+\sum^{K1} c_k \Bigg(\sum_{\ell=1}^{L0} d_\ell P(13,t,s) + \sum^{L1} d_\ell P(18,t,s) + \sum^{L2} d_\ell P(22,t,s) + \sum^{L3} d_\ell P(25,t,s) \Bigg)$$

$$+\sum^{K2} c_k \Bigg(\sum^{L0} d_\ell P(18,t,s) + \sum^{L1} d_\ell P(22,t,s) + \sum^{L2} d_\ell P(25,t,s) + \sum^{L3} d_\ell P(27,t,s) \Bigg)$$

$$+\sum^{K3} c_k \Bigg(\sum^{L0} d_\ell P(22,t,s) + \sum^{L1} d_\ell P(25,t,s) + \sum^{L2} d_\ell P(27,t,s) + \sum^{L3} d_\ell P(28,s,t) \Bigg)\Bigg]\Bigg\}$$

where $s = \alpha_i + \beta_j$

$t = \gamma_k + \delta_\ell$

If $kk = 2$, the functions $P(I,a,b)$ should be replaced by $P(I + 30,a,b)$.

If $kk = 3$, the functions $P(I,a,b)$ should be replaced by $P(I + 60,a,b)$.

Thus,

$$K' = FF2(1s\beta,1s\beta,1) + \Big\{ \tfrac{1}{2}\Big[FF1(2s\alpha,2s\alpha) + FF1(1s\alpha,1s\alpha)\Big] - FF5(1s\alpha,1s\alpha,2s\alpha,2s\alpha,1)$$

$$+ Z\Big[FF3(2s\alpha,2s\alpha) + FF3(1s\alpha,1s\alpha)\Big] + E_o\Big\} \Big[X(1s\beta)\Big]^2$$

and

$$L' = - FF5(1s\alpha,2s\alpha,2s\alpha,1s\alpha,1) \Big[X(1s\beta)\Big]^2$$

Thus the substitution of V''' for V'' in (4.38) gives us,

$$q^{V}_{\alpha\beta\beta\alpha}(0,0) = \frac{1}{3}\Big[L' - M' + N' - O'\Big] \qquad (4.43)$$

where

$$M' = \langle \phi_{1s\alpha}(r_3)\phi_{1s\beta}(r_2)\phi_{2s\beta}(r_4)|V'''|\phi_{1s\alpha}(r_1)\phi_{1s\beta}(r_2)\phi_{2s\alpha}(r_3)\rangle$$

$$= \left[\tfrac{1}{2}FF1(1s\alpha,2s\alpha) + Z\ FF3(1s\alpha,2s\alpha) - FF5(1s\beta,1s\beta,1s\alpha,2s\alpha,1)\right] X(2s\beta) \cdot X(1s\alpha)$$

$$N' = \langle \phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_3)\phi_{2s\beta}(r_4)|V'''|\phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_3)\phi_{2s\alpha}(r_1)\rangle$$

$$= FF2(2s\beta,2s\alpha,1) + \left\{\tfrac{1}{2}\left[FF1(1s\alpha,1s\alpha) + FF1(1s\beta,1s\beta)\right] - FF5(1s\alpha,1s\alpha,1s\beta,\right.$$

$$\left. 1s\beta,1) + Z\left[FF3(1s\alpha,1s\alpha) + FF3(1s\beta,1s\beta)\right] + E_o\right\} X(2s\beta)\ X(2s\alpha)$$

$$O' = \langle \phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_4)\phi_{2s\beta}(r_3)|V'|\phi_{1s\alpha}(r_2)\phi_{1s\beta}(r_3)\phi_{2s\alpha}(r_1)$$

$$= \left[\tfrac{1}{2}FF1(2s\beta,1s\beta) + Z\ FF3(2s\beta,1s\beta) - FF5(1s\alpha,1s\alpha,2s\beta,1s\beta)\right] X(1s\beta)\ \ X(2s\alpha)$$

Thus from (4.30), (4.41) and (4.43) we get

$$\tfrac{1}{2}g_B^V(0,0) = -K' + \tfrac{1}{2}\left[M' + L' - N' + O'\right] \qquad (4.44)$$

We have calculated $\frac{1}{2}g_B^L(0,0)$ and $\frac{1}{2}g_B^V(0,0)$ using the following orbitals

(i) Walters (1972) functions:

$$\phi_{1s}(r) = ae^{-\alpha r}\frac{1}{\sqrt{4\pi}}, \quad a = 2.5031, \quad \alpha = 2.7.$$

$$\phi_{2s}(r) = \left[b_1 e^{-\beta_1 r} + b_2 r e^{-\beta_2 r}\right]\frac{1}{\sqrt{4\pi}}$$

with

$$b_1 = -.4221, \quad b_2 = .1125, \quad \beta_1 = 2.7, \quad \beta_2 = .65.$$

(ii) Clementi (1965) functions

$$\phi_{1s}(r) = \left[\sum_{i=1}^{2} a_i e^{-\alpha_i r} + \sum_{i=3}^{6} a_i r e^{-\alpha_i r} \right] \frac{1}{\sqrt{4\pi}}$$

$$\phi_{2s}(r) = \left[\sum_{i=1}^{2} b_i e^{-\beta_i r} + \sum_{i=3}^{6} b_i r e^{-\beta_i r} \right] \frac{1}{\sqrt{4\pi}}$$

The exponents α_i, β_i and the constants a_i, b_i are given in table 4.A.

TABLE 4.A

Parameters for the Clementi wave functions

Coefficients a_i	Exponents α_i	Coefficients b_i	Exponents β_i
7.01385	2.4803	-1.12702	2.4803
2.25307	4.7071	- .32353	4.7071
- .00001	.35	.00017	.35
.00045	.66	.40005	.66
- .00166	1.0	.10481	1.0
.04290	1.735	- .41041	1.735

(iii) Unrestricted Hartree-Fock functions (Sachs, 1960):

$$\phi_{1s\alpha}(r) = \left[\sum_{i=1}^{3} a_i e^{-\alpha_i r} + \sum_{i=4}^{6} a_i r e^{-\alpha_i r} + \sum_{i=7}^{9} a_i r^2 e^{-\alpha_i r} + \sum_{i=10}^{12} a_i r^3 e^{-\alpha_i r} \right] \frac{1}{\sqrt{4\pi}}$$

$$\phi_{1s\beta}(r) = \left[\sum_{i=1}^{3} b_i e^{-\alpha_i r} + \sum_{i=4}^{6} b_i r e^{-\alpha_i r} + \sum_{i=7}^{9} b_i r^2 e^{-\alpha_i r} + \sum_{i=10}^{12} b_i r^3 e^{-\alpha_i r} \right] \frac{1}{\sqrt{4\pi}}$$

$$\phi_{2s}(r) = \left[\sum_{i=1}^{3} c_i e^{-\alpha_i r} + \sum_{i=4}^{6} c_i r e^{-\alpha_i r} + \sum_{i=7}^{9} c_i r^2 e^{-\alpha_i r} + \sum_{i=10}^{10} c_i r^3 e^{-\alpha_i r} \right] \frac{1}{\sqrt{4\pi}}$$

The constants a_i, b_i, c_i and the exponents α_i are given in table 4.B.

TABLE 4.B

Parameters for the unrestricted Hartree-Fock Orbitals

Exponents α_i	Coefficients a_i	Coefficients b_i	Coefficients c_i
2.4	.00000	.00000	- .00000
.67	.01992	.03090	- .01716
4.5	9.26388	9.21155	1.45220
2.4	4.07237	3.93295	1.52511
.67	- .00756	- .01175	- .45448
4.5	9.72431	9.76453	1.13549
2.4	- .92616	- .78585	- .32631
.67	.00093	.00146	.00647
4.5	6.22345	6.36217	.36335
2.4	.03890	- .00246	.19382
.67	- .00004	- .00006	- .00059
4.5	3.35241	3.51640	.22202

Table 4.C gives the results for $\frac{1}{2}g_B^L(0,0)$ and $\frac{1}{2}g_B^V(0,0)$ using these wave functions

TABLE 4.C

Values for the exchange contribution for electron-Lithium scattering

Wave function	$\frac{1}{2}g_B^L(0,0)$	$\frac{1}{2}g_B^V(0,0)$
(i)	71.5556	91.2054
(ii)	69.3754	69.3537
(iii)	69.5283	69.8365

The agreement between the length and the velocity values for the exchange contributions using the Hartree-Fock functions suggests this value to be in the vicinity of 69. We note here that the exchange contribution is not very strongly dependent on the choice of the wave function for length form. We cannot as yet, test the sum rule given by the expression (4.25) because the residue contribution is still in the process of calculation.

CHAPTER V

DISCUSSION

V.A. The Programs

For the calculation of the exchange contribution, we introduced functions FF1, FF2, FF3, FF5, GG, X and Y in chapters III and IV. The analysis given for these functions is based on the assumption that the radial part of the orbitals take the following form:

$$R_{n\ell}(r) = \sum_{i=1}^{I0} a_i e^{-\alpha_i r} + \sum_{i=I0+1}^{I1} a_i r e^{-\alpha_i r} + \sum_{i=I1+1}^{I2} a_i r^2 e^{-\alpha_i r} + \sum_{i=I2+1}^{I3} a_i r^3 e^{-\alpha_i r} \qquad (5.1)$$

The functions FF1, FF2 etc. have been coded with the following flexibilities:

(a) performs calculations as long as the input radial functions are any part of (5.1) e.g. we can have

$$R_{n\ell}(r) = \sum_{i=1}^{I0} a_i e^{-\alpha_i r} + \sum_{i=I0+1}^{I1} a_i r e^{-\alpha_i r} + \sum_{i=I1+1}^{I3} a_i r^3 e^{-\alpha_i r}$$

(b) I0, I1, I2 and I3 can take any value.

These two generalities have enabled us to carry out the calculations for Helium and Lithium using different wavefunctions with relative ease.

As for the future, we may wish to study the dispersion relations for electron scattering by Neon and Argon. Margaret Knowles (Thesis, 1973) has calculated $g_B(0,0)$ for electron-neon scattering to be $5.16 \pm .16$ using Hartree-Fock wavefunctions whereas Bransden and Hutt (1975) require this value to be 8.21 if the sum rule is to be satisfied. Because of this inconsistancy, a desire has been expressed to repeat the calculation of

$g_B(0,0)$ for neon with configuration interaction wavefunctions. For these added reasons, another general program, RINA, has been constructed to evaluate $g_B(0,0)$ ('length' form only) for electron scattering by helium, neon and argon. The configuration interaction wavefunctions have been chosen to have the following form (as in Chapter III):

$$\psi = \sum_{i=1}^{n} C_i \, \Phi_i \tag{5.2}$$

with

$$\Phi_j = \sum_{j}^{m} \alpha_{ij} \, D_{ij} \tag{5.3}$$

where C_i are the weights for the configurations,
D_{ij} are the determinants
and α_{ij} are their associated coefficients.

The only restrictions on the choice of the configurations for the excited states are that the highest orbital that can be included is the 3d-type and that any two determinants should either be identically occupied or differ in occupation by two orbitals. (However, the program can be easily modified to perform more sophisticated calculations).

For the testing of this program, the results for $g_B^L(0,0)$ for electron-helium scattering using the CI wavefunction of Chapter III have been reproduced. Also, the results for $g_B(0,0)$ for electron-neon scattering using the Hartree-Fock wavefunctions are in agreement with those obtained by Margaret Knowles (1973).

V.B. Helium

The dispersion relation for electron-helium scattering at zero energy and in the forward direction may be written (as in equation (2.6) of Chapter II) as

$$- A = f_B(0,0) - g_B(0,0) + \frac{P}{4\pi^2} \int \sigma_T(k'^2)\, dk'^2 \qquad (5.4)$$

The direct Born scattering amplitude, $f_B(0,0)$, may be considered to be known very accurately and takes the value 0.7913. The principal value integral term involves a knowledge of the total cross section at all energies and has been calculated by Bransden and Hutt (1975) to be 2.36. Taking the value of the scattering length, A, to be 1.15, Bransden and Hutt (1975) require the value of $g_B(0,0)$ to be 4.30 to satisfy the sum rule (5.4). The Born exchange amplitude, $g_B(0,0)$, has been calculated (see Chapters II and III) using various wavefunctions for helium including the configuration interaction wavefunctions. We believe that we have finally converged to the value of

$$g_B(0,0) = 3.92 \pm .05$$

Because of this inconsistancy with the relation (5.4) for the value of $g_B(0,0)$, we cannot but conclude that either the sum rule given by equation (5.4) needs to be modified or that the cross-sections adopted for the evaulation of the principle value integral are inaccurate. Thus, before we can make progress with any real confidence, more closely determined and consistent total cross sections with fully analysed errors are required.

V.C. Lithium

We cannot, as yet, test the sum-rule for electron-lithium scattering as given by equation (4.25) of Chapter IV because the contribution from the residue term is still in the process of calculation. The exchange term has been calculated using three different wavefunctions. The closeness of the 'length' and the 'velocity' values for the exchange term calculated with Hartee-Fock wavefunctions suggests this value to be in the vicinity of 69.5. However, if greater accuracy is required, the calculations ought to be repeated with the configuration interaction wavefunctions.

APPENDIX A

In this section, we give details of the integrals P(I,a,b) introduced in chapter II and are extensively used in chapters III and IV. These P(I,a,b) integrals are of the following three basic class of integrals:

$$R1 = \int d\underline{r}_1 \int d\underline{r}_2 \, \frac{r_1^n \, r_2^m}{|\underline{r}_1 - \underline{r}_2|} \, e^{-ar_1 - br_2} \qquad (A.1)$$

$$R2 = \int d\underline{r}_1 \int d\underline{r}_2 \, \frac{r_1^n \, r_2^m}{|\underline{r}_1 - \underline{r}_2} \, e^{-ar_1 - br_2} \, Y_{1m}^{*}(\Omega_1) \, Y_{1m}(\Omega_2) \qquad (A.2)$$

$$R3 = \int d\underline{r}_1 \int d\underline{r}_2 \, \frac{r_1^n \, r_2^m}{|\underline{r}_1 - \underline{r}_2|} \, e^{-ar_1 - br_2} \, Y_{2m}^{*}(\Omega_1) \, Y_{2m}(\Omega_2) \qquad (A,3)$$

The tables A.A, A.B, A.C give the P(I,a,b) integrals corresponding to the integrals given by R1, R2 and R3 respectively. The function k(a,n) used in the tables is defined by equation (3.13) of chapter III.

TABLE A.A

The P(I, a,b) integrals that are of the type R1

n	m	I	P(I,a,b)	
0	0,....,6	1,....7	See Expression	(I)
1	1,...,6	8,...13	" "	(II)
2	2,...,6	14,...18	" "	(III)
3	3,...6	19,...22	" "	(IV)
4	4,...,6	23,...25	" "	(V)
5	5,6	26,27	" "	(VI)
6	6	28	" "	(VII)

TABLE A.B

The P(I, a,b) integrals that are of the type R2.

n	m	I	P(I,a,b)	
0	0,...,6	31,...37	See Expression	(VIII)
1	1,...,6	38,..,43	" "	(IX)
2	2,...,6	44,..,48	" "	(X)
3	3,...,6	49,..,52	" "	(XI)
4	4,...,6	52,..,55	" "	(XII)
5	5,6	56,57	" "	(XIII)
6	6	58	" "	(XIV)

TABLE A.C.

The P(I, a,b) integrals that are of the type R3

n	m	I	P(I,a,b)
1	1,...6	68,...,73	See Expression (XV)
2	2,...6	74,...,78	" " (XVI)
3	3,...6	79,...,82	" " (XVII)

(I) $$4\pi\left[-\frac{k}{a^2}(c,I-1)-\frac{2}{a^3}k(c,I-2)+\frac{2}{a^3}k(b,I-2)\right]$$

(II) $$4\pi\left[-\frac{k}{a^2}(c,I-6)-\frac{4}{a^3}k(c,I-7)-\frac{6}{a^4}k(c,I-8)+\frac{6}{a^4}k(b,I-8)\right]$$

(III) $$4\pi\left[-\frac{k}{a^2}(c,I-10)-\frac{6}{a^3}k(c,I-11)-\frac{18}{a^4}k(c,I-12)-\frac{24}{a^5}k(c,I-13)+\frac{24}{a^5}k(b,I-13)\right]$$

(IV) $$4\pi\left[-\frac{k}{a^2}(c,I-13)-\frac{8}{a^3}k(c,I-14)-\frac{36}{a^4}k(c,I-15)-\frac{96}{a^5}k(c,I-16)-\frac{120}{a^6}k(c,I-17)\right.$$
$$\left.+\frac{120}{a^6}k(b,I-17)\right]$$

(V) $$4\pi\left[-\frac{k}{a^2}(c,I-15)-\frac{10}{a^3}k(c,I-16)-\frac{60}{a^4}k(c,I-17)-\frac{240}{a^5}k(c,I-18)-\frac{600}{a^6}k(c,I-19)\right.$$
$$\left.-\frac{720}{a^7}k(c,I-20)+\frac{720}{a^7}k(b,I-20)\right]$$

(VI) $$4\pi\left[-\frac{k}{a^2}(c,I-16)-\frac{12}{a^3}k(c,I-17)-\frac{90}{a^7}k(c,I-18)-\frac{480}{a^5}k(c,I-19)-\frac{1800}{a^6}k(c,I-20)\right.$$
$$\left.-\frac{4320}{a^7}k(c,I-21)-\frac{5040}{a^8}k(c,I-22)+\frac{5040}{a^8}k(b,I-22)\right]$$

(VII) $$4\pi\left[-\frac{k}{a^2}(c,I-16)-\frac{14}{a^3}k(c,I-17)-\frac{126}{a^4}k(c,I-18)-\frac{840}{a^5}k(c,I-19)\right.$$
$$-\frac{4200}{a^6}k(c,I-20)-\frac{15120}{a^7}k(c,I-21)-\frac{35280}{a^8}k(c,I-22)$$
$$\left.-\frac{40320}{a^9}\Big(k(c,I-23)-k(b,I-23)\Big)\right]$$

(VIII) $- \frac{k}{a^2}(c,I-31) - \frac{2}{a^3}k(c,I-32) - \frac{2}{a^4}k(c,I-33) + \frac{2}{a^4}k(b,I-33)$

(IX) $- \frac{k}{a^2}(c,I-36) - \frac{4}{a^3}k(c,I-37) - \frac{8}{a^4}k(c,I-38) - \frac{8}{a^5}k(c,I-39) + \frac{8}{a^5}k(b,I-39)$.

(X) $- \frac{k}{a^2}(c,I-40) - \frac{6}{a^3}k(c,I-41) - \frac{20}{a^4}k(c,I-42) - \frac{40}{a^5}k(c,I-43) - \frac{40}{a^6}k(c,I-44)$

$+ \frac{40}{a^6}k(b,I-44)$

(XI) $- \frac{k}{a^2}(c,I-43) - \frac{8}{a^3}k(c,I-44) - \frac{38}{a^4}k(c,I-45) - \frac{120}{a^5}k(c,I-46) - \frac{240}{a^6}k(c,I-47)$

$- \frac{240}{7}k(c,I-48) + \frac{240}{7}k(b,I-48)$

(XII) $- \frac{k}{a^2}(c,I-45) - \frac{10}{a^3}k(c,I-46) - \frac{62}{a^4}k(c,I-47) - \frac{272}{a^5}k(c,I-48) - \frac{840}{a^6}k(c,I-49)$

$- \frac{1680}{a^7}k(c,I-50) - \frac{1680}{a^7}\left(k(c,I-51) - k(b,I-51)\right)$

(XIII) $- \frac{k}{a^2}(c,I-46) - \frac{10}{a^3}k(c,I-47) - \frac{92}{a^4}k(c,I-48) - \frac{520}{a^5}k(c,I-49) - \frac{2200}{a^6}k(c,I-50)$

$- \frac{6720}{a^7}k(c,I-51) - \frac{13440}{a^8}k(c,I-52) - \frac{13440}{a^9}\left(k(c,I-53) - k(b,I-53)\right)$

(XIV) $$-\frac{k}{a^2}(c,I-46) - \frac{14}{a^3}k(c,I-47) - \frac{128}{a^4}k(c,I-48) - \frac{888}{a^5}k(c,I-49) - \frac{4800}{a^6}k(c,I-50)$$

$$-\frac{19920}{a^7}k(c,I-51) - \frac{60480}{a^8}k(c,I-52) - \frac{120960}{a^9}k(c,I-53)$$

$$-\frac{120960}{a^{10}}\left(k(c,I-54) - k(b,I-54)\right)$$

(XV) $$-\frac{k}{a^2}(c,I-66) - \frac{4}{a^3}k(c,I-67) - \frac{12}{a^4}k(c,I-68) - \frac{24}{a^5}k(c,I-69) - \frac{24}{a^6}k(c,I-70)$$

$$+\frac{24}{a^6}k(b,I-70)$$

(XVI) $$-\frac{k}{a^2}(c,I-70) - \frac{6}{a^3}k(c,I-71) - \frac{24}{a^4}k(c,I-72) - \frac{72}{a^5}k(c,I-73) - \frac{144}{a^6}k(c,I-74)$$

$$-\frac{144}{a^7}k(c,I-75) + \frac{144}{a^7}k(b,I-75)$$

(XVII) $$-\frac{k}{a^2}(c,I-73) - \frac{8}{a^3}k(c,I-74) - \frac{42}{a^4}k(c,I-75) - \frac{168}{a^5}k(c,I-76) - \frac{504}{a^6}k(c,I-77)$$

$$-\frac{1008}{a^7}k(c,I-78) - \frac{1008}{a^8}k(c,I-79) + \frac{1008}{a^8}k(b,I-79)$$

where $c = a+b$

APPENDIX B

From (2.21) in chapter II, we have

$$J(n_1,n_2,n_3;a,b,c) = \int_0^{\alpha} r_3^{n_3} e^{-cr_3} \int_0^{r_3} r_2^{n_2} e^{-br_2} \int_0^{r_2} r_1^{n_1} e^{-ar_1} \, dr_1 \, dr_2 \, dr_3$$

a) Consider $n_1 \geqq 0$, $n_2 \geqq 0$, $n_3 \geqq 0$:

Then

$$J(n_1,n_2,n_3;a,b,c) = \int_0^{\alpha} r_3^{n_3} e^{-cr_3} \int_0^{r_3} r_2^{n_2} e^{-br_2} \int_0^{r_2} r_1^{n_1} e^{-ar_1} \, dr_1 \, dr_2 \, dr_3$$

$$= \int_0^{\alpha} r_3^{n_3} e^{-cr_3} \int_0^{r_3} r_2^{n_2} e^{-br_2} \left[\frac{n_1!}{a^{n_1+1}} - \sum_{k=0}^{n_1} \frac{n_1!}{a^{n_1+1-k}} \frac{r_2^k \, e^{-ar_2}}{k!} \right] dr_2 \, dr_3$$

$$= \int_0^{\alpha} r_3^{n_3} e^{-cr_3} \left\{ \frac{n_1!}{a^{n_1+1}} \left[\frac{n_2!}{b^{n_2+1}} - \sum_{j=0}^{n_2} \frac{n_2!}{b^{n_2+1-j}} \frac{r_3^j}{j!} e^{-br_3} \right] \right.$$

$$+ \sum_{k=0}^{n_1} \sum_{j=0}^{n_2+k} \frac{n_1!}{a^{n_1+1-k}} \frac{(n_2+k)!}{k!} \frac{r_3^j}{j!} \frac{e^{-(a+b)r_3}}{(a+b)^{n_2+k+1-j}}$$

$$\left. - \sum_{k=0}^{n_1} \frac{n_1!}{a^{n_1+1-k}} \frac{(n_2+k)!}{(a+b)^{n_2+k+1}} \right\} dr_3$$

$$= \frac{n_1!}{a^{n_1+1}} \left[\frac{n_2!}{b^{n_2+1}} \frac{n_3}{c^{n_3+1}} - \sum_{j=0}^{n_2} \frac{n_2!}{b^{n_2+1-j}} \frac{(n_3+j)!}{(b+c)^{n_3+j+1}} \frac{1}{j!} \right]$$

$$+ \sum_{k=0}^{n_1} \sum_{j=0}^{n_2+k} \frac{n_1!}{a^{n_1+1-k}} \frac{(n_2+k)!}{k!} \frac{1}{j!(a+b)^{n_2+k+1-j}} \frac{(n_3+j)!}{(a+b+c)^{n_3+j+1}}$$

$$- \sum_{k=0}^{n_1} \frac{n_1!}{a^{n_1+1-k}} \frac{(n_2+k)!}{(a+b)^{n_2+k+1}} \frac{n_3!}{c^{n_3+1}}$$

b) $n_1 \geqq 0, \quad n_2 \geqq 1, \quad n_3 = -2.$

Let

$$I,(c,b) = \int_0^{\alpha} \frac{e^{-cr_3}}{r_3^2} \int_0^{r_3} r_2 e^{-br_2} dr_2 dr_3 = \frac{1}{b^2} \left[b + c\ln \left(\frac{c}{c+b} \right) \right]$$

Then

$$J(n_1,n_2,-2;a,b,c) = \int_0^{\alpha} \frac{e^{-cr_3}}{r_3^2} \int_0^{r_3} r_2^{n_2} e^{-br_2} \int_0^{r_1} r_1^{n_1} e^{-ar_1} dr_1 dr_2 dr_3$$

$$= \int_0^{\alpha} \frac{e^{-cr_3}}{r_3^2} \left\{ \frac{n_1!}{a^{n_1+1}} \left[- \sum_{j=2}^{n_2} \frac{n_2!}{b^{n_2+1-j}} \frac{r_3^j}{j!} e^{-br_3} + \frac{n_2!}{\beta^{n_2-1}} \int_0^{r_3} r_2 e^{-br_2} dr_2 \right] + \left[\sum_{k=0}^{n_1} \frac{n_1!}{a^{n_1+1-k}} \frac{1}{k!} \left(\sum_{j=2}^{n_2+k} \frac{r_3^j (n_2+k)!}{(a+b)^{n_2+k+1-j}} \frac{1}{j!} - \frac{(n_2+k)!}{(a+b)^{n_2+k-1}} \int_0^{r_3} r_2 e^{-(a+b)r_2} dr_2 \right) \right] \right\} dr_3$$

$$= \frac{n_1!}{a^{n_1+1}} \left[- \sum_{j=2}^{n_2} \frac{n_2!}{n^{n_2+1-j}} \frac{(j-2)!}{j!} \frac{1}{(b+c)^{j-1}} + \frac{n_2!}{b^{n_2-1}} I_1(C,b) \right]$$

$$+ \sum_{k=0}^{n_1} \frac{n_1!}{a^{n_1+1-k}} \frac{(n_2+k)!}{k!} \left[\sum_{j=2}^{n_2+k} \frac{(j-2)!}{j!} \frac{1}{(a+b)^{n_2+k+1-j}(a+b+c)^{j-1}} - \frac{I_1(c,a+b)}{(a+b)^{n_2+k-1}} \right]$$

c) $n_1 \geqq 0, \quad n_2 \geqq 3, \quad n_3 = -4$

Let

$$I_2(c,b) = \int_0^{\alpha} \frac{e^{-cr_3}}{r_3^4} \int_0^{r_3} r_2^3 \, e^{-br_2} \, dr_2 \, dr_3$$

$$= \frac{1}{3b} - \frac{c}{2b^2} + \frac{c^2}{b^3} + \frac{c^3}{b^4} \ \ell n \left[\frac{c}{c+b}\right]$$

Then following (b),

$$J(n_1,n_2,-4;a,b,c) = \int_0^\infty \frac{e^{-cr_3}}{r_3^4} \int_0^{r_3} r_2^{n_2} e^{-br_2} \int_0^{r_2} r_1^{n_1} e^{-ar_1}\, dr_1 dr_2 dr_3$$

$$= \frac{n_1!}{a^{n_1+1}} \left[- \sum_{j=4}^{n_2} \frac{n_2!}{b^{n_2+1-j}} \frac{(j-4)!}{j!(b+c)^{j-3}} + \frac{n_2!}{3!\, b^{n_2-3}} I_2(c,b) \right]$$

$$+ \sum_{k=0}^{n_1} \frac{n_1!}{a^{n_1+1-k}} \frac{(n_2+k)!}{k!} \left[\sum_{j=4}^{n_2+k} \frac{(j-4)!}{j!(a+b)^{n_2+k+1-j}(a+b+c)^{j-3}} - \frac{I_2(c,a+b)}{3!(b+a)^{n_2+k-3}} \right]$$

d) $n_1 \geqq 1$, $n_2 = 1$, $n_3 = -4$

We let

$$I_3(c,b) = \int_0^1 dy\, y\,\ell n(c + by)$$

$$= \tfrac{1}{2}\ell n(c + by) + \frac{c^2}{2b^2}\, \ell n \left(\frac{c}{c+b}\right) - \tfrac{1}{4} + \frac{c}{2b}$$

and

$$I_4(c,b) = \int_0^1 dy\, y^2 \ell n(c + by)$$

$$= \frac{1}{3}\, \ell n(c+b) + \frac{c^3}{3b^3}\, \ell n \left(\frac{c+b}{c}\right) - \frac{1}{9} + \frac{c}{6b} + \frac{c^2}{3b^2}$$

Then,

$$J(1,1,-4;a,b,c) \equiv \int_0^{\infty} \frac{e^{-cr_3}}{r_3^4} \int_0^{r_3} r_2 e^{-br_2} \int_0^{r_2} r_1 e^{-ar_1} \, dr_1 dr_2 dr_3$$

$$= \frac{1}{3a} - \frac{c}{a^2} \left[I_3(c,a+b) - I_3(c,b) \right]$$

$$- \frac{b}{a^2} \left[I_4(c,a+b) - I_4(c,b) \right]$$

After careful evaluation, we obtain for

$$J(n_1,1,-4;a,b,c) \equiv \int_0^{\alpha} \frac{e^{-cr_3}}{r_3^4} \int_0^{r_3} r_2 e^{-br_2} \int_0^{r_2} r_1^{n_1} e^{-ar_1} \, dr_1 dr_2 dr_3$$

$$= \frac{n_1!}{a^{n_1-1}} \, J(1,1,-4;a,b,c)$$

$$+ \sum_{k=2}^{n_1} \frac{n_1!.}{a^{n_1+1-k}} \, \frac{(n_2+k)!}{k!} \left[\sum_{j=4}^{n_2+k} \frac{(j-4)!}{j!} \, \frac{1}{(a+b)^{n_2+k+1-j}} \right.$$

$$\left. \times \frac{1}{(a+b+c)^{j-3}} - \frac{I_2(c,a+b)}{3!(a+b)^{n_2+k-3}} \right]$$

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