SCATTERING OF POSITRONS BY HELIUM ATOMS AND THE USE OF A GRAPHICAL DISPLAY DEVICE

by

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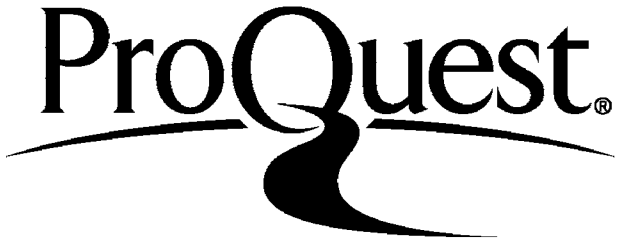

ABSTRACT

The scattering of slow positrons by Helium atoms is of particular interest now that positron beam experiments are being performed. The purpose of this thesis is to carry out an examination of past theoretical investigations of the problem as well as to explore various approximation schemes for describing the problem within the framework of the close-coupling method, where the total wave function is expanded in terms of the eigenstates of the target Hamiltonian and of the Positronium system. The numerical techniques associated with solving the ensuing coupled integro-differential equations are described in detail. A novel use of a graphical display device as an aid to debugging the computer code is illustrated. The theoretical approximations include (1) allowing for all partial waves (2) taking into account the 2P states of both Positronium and Helium (3) the addition of correlation terms (a means of allowing for short-range effects.)

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CHAPTER I

REVIEW OF POSITRON ATOM SCATTERING PROCESSES

The problem of scattering of positrons by atoms has received increasing attention since the advent of sophisticated theoretical treatments of electron-atom scattering and the feasibility of performing positron beam experiments. The physical differences between positron interactions and electron interactions of an atomic system can be exploited to produce more information about the contribution of particular processes of interest. Unlike the electron problem, in the positron case the projectile is distinguishable from the target atom electrons and no allowance for exchange terms is required. However, if Positronium formation is taken into account in describing the collision processes, then rearrangement terms appear which in effect replace the exchange terms of the electron problem. Because of lack of symmetry, these rearrangement terms are more difficult to handle than exchange terms.

The main problem in theoretical calculations is to provide an adequate representation of the target atom state during the collision process. The mean static field of the atom, which would attract an electron, repels a positron, but the induced dipole moment of the atom (polarization of the atom) is attractive in both cases. If Positronium is formed, then it will also be polarized by the positive ion remaining. The various approximation methods formulated to account for

these physical processes are described in the sections following.

One of the first experiments was that of Marder, Hughes, Wu and Bennett[1] who studied the enhancement of Positronium formation by a static electric field. The positron energy can be divided into four regions determined by the atomic ionization energy E_{Ion}, the first excited state energy of the atom E_{Exc} and the threshold energy for Positronium formation E_{Thr} as shown in Figure 1.1 which is a schematic diagram for positron Helium scattering processes.

If $E_{Exc} > E_{Thr}$ then the energy region $(E_{Exc} - E_{Thr})$ is known as the "Ore gap"[2] and is the energy region in which Positronium is most likely to form. For positron energy $< E_{Thr}$ only elastic scattering will occur while in the region $(E_{Ion} - E_{Exc})$ Positronium formation competes with atomic excitation. Finally for positron energy $> E_{Ion}$ Positronium will be formed but with energy such that it is likely to dissociate through further collisions. If we assume that there is a uniform distribution of positron kinetic energy after the last inelastic collision we can estimate the fraction P of positrons forming Positronium as follows:

$$\frac{E_{Exc} - E_{Thr}}{E_{Exc}} < P < \frac{E_{Ion} - E_{Thr}}{E_{Ion}}$$

For Helium this inequality becomes:

$$.10 < P < .28$$

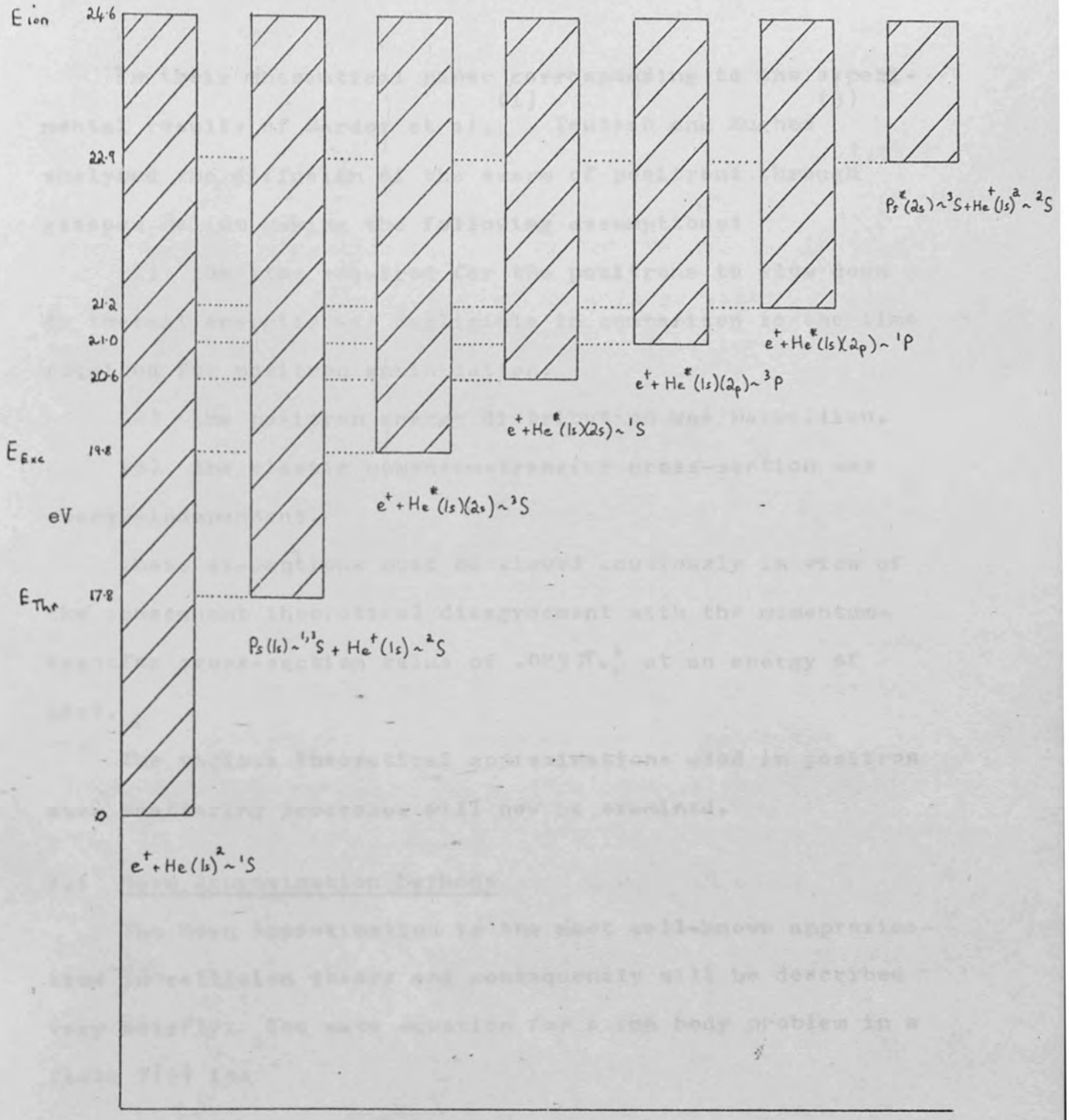


Figure 1.1 A schematic diagram of the energy levels for positron Helium scattering

In their theoretical paper corresponding to the experimental results of Marder et al.[1] Teutsch and Hughes[3] analysed the diffusion of the swarm of positrons through gaseous Helium making the following assumptions:

(1) the time required for the positrons to slow down to thermal energies was negligible in comparison to the time required for positron annihilation.

(2) the positron energy distribution was Maxwellian.

(3) the elastic momentum-transfer cross-section was energy-independent.

These assumptions must be viewed cautiously in view of the consequent theoretical disagreement with the momentum-transfer cross-section value of $.023\pi a_o^2$ at an energy of 18eV.

The various theoretical approximations used in positron atom scattering processes will now be examined.

1.1 Born Approximation Methods

The Born Approximation is the most well-known approximation in collision theory and consequently will be described very briefly. The wave equation for a one body problem in a field V(r) is:

$$\left[\nabla^2 + k^2\right] \psi(r) = V(r)\psi(r) \qquad 1.1a$$

where k^2 is the incident energy of the particle. The asymptotic form of ψ is:

$$\psi \underset{r\to\infty}{\sim} e^{i\underline{k}\cdot\underline{r}} + \frac{e}{r}^{ikr} f(\theta) \qquad 1.1b$$

where $f(\theta)$ is the scattering amplitude. We now assume that the particle wave is not affected to a large extent by the scattering centre so that we may replace $\psi(r)$ on the right hand side of equation (1.1a) by the unperturbed wave function $e^{i\underline{k}\cdot\underline{r}}$. The first Born Approximation is given by:

$$\left[\nabla^2 + k^2\right] \psi_1(r) = V(r) e^{i\underline{k}\cdot\underline{r}} \qquad 1.2$$

This can be solved to give ψ_1 and thus a first approximation to the scattering amplitude $f_1(\theta)$. If $\psi_1(r)$ is now substituted in the right hand side of equation (1.1a) then a second approximation $\psi_2(r)$ and scattering amplitude $f_2(r)$ are obtained which will be the second Born approximation. Thus we are obtaining $\psi(r)$ by iteration as follows:

$$\psi(r) = \sum_{n=0}^{\infty} \psi_n(r) \qquad 1.3$$

where $$\left[\nabla^2 + k^2\right] \psi_n(r) = V(r)\psi_{n-1}(r) \qquad 1.4a$$

$$\psi_0(r) = e^{i\underline{k}\cdot\underline{r}} \qquad 1.4b$$

and $$\psi_n(r) \underset{r\to\infty}{\sim} e^{i\underline{k}\cdot\underline{r}} \cdot \delta_{n0} + \frac{e}{r}^{ikr} \cdot f_n(\theta) \qquad 1.4c$$

It can be seen that this method depends on the interaction

between the particle and the scatterer being small and is thus more applicable to fast collisions than slow. In slow collisions between positrons and atoms the charge distribution of the atomic electrons is distorted to such an extent that the 1st Born approximation cannot be expected to give reliable results.

(a) Positron Hydrogen Collisions.

Massey and Mohr [4] used the 1st Born approximation to calculate cross-sections for formation of Ortho-Positronium in the ground state. The potential energy V of a positron in the mean field of a Hydrogen atom is given by:

$$V(r_p) = 2\int |\psi_0(r)|^2 \left[\frac{1}{r_p} - \frac{1}{|\underline{r}-\underline{r}_p|}\right] d\underline{r} = 2e^{-2r_p}\left(1+\frac{1}{r_p}\right) \qquad 1.5$$

where $\psi_0(r) = \pi^{-\frac{1}{2}} e^{-r}$ is the normalized ground state Hydrogen function in atomic units and $\underline{r}_p$ is the position vector of the positron with respect to the proton.

Since $V(r_p)$ is positive and therefore a repulsive potential, it will distort the incoming positron wave. Massey and Mohr [4] therefore used a distorted wave approximation to try to take this into account. That is, the plane wave approximation in the Born formula is replaced by the function:

$$e^{i\underline{k}\cdot\underline{r}_p} + \frac{1}{kr_p}\left[f_0(r_p) - \sin kr_p\right] \qquad 1.6a$$

where $$f_0(r_p) = e^{-0.4i}\left[\sin(kr_p - 0.4) + e^{-1.6r_p}\sin 0.4\right] \qquad 1.6b$$

and ρ_0 is an empirical approximation to the Mean Static Field solution (see Section 1.4) for $k^2 = 1$. The resulting cross-section was a factor of 1/2 smaller than the Born result.

1.2 Variational Methods.

The Kohn variational method is described in detail in Chapter II and consequently only a brief outline of the basic variational procedures will be given here. For simplicity we consider the case of a single particle with zero orbital angular momentum scattered by a spherical potential V(r).

The wave function $\psi(r)$ describing the scattering of the particle satisfies the following equation:

$$\left[L - V(r)\right] \psi(r) = 0 \qquad 1.7$$

where $L = \frac{d^2}{dr^2} + k^2$

$\psi(r)$ is subject to the following boundary conditions:

$$\psi(r) = 0 \quad \text{at} \quad r = 0 \qquad 1.8a$$

$$\psi(r) \underset{r\to\infty}{\sim} A\sin(kr+\eta) \qquad 1.8b$$

Consider the integral I given by:

$$I = \int \psi(r) \left[L - V(r)\right] \psi(r)\, dr \qquad 1.9$$

Because of equation (1.7) $I=0$. Now consider a small arbitrary variation $\delta\psi$ in ψ such that:

$$\delta\psi(r) = 0 \quad \text{at} \quad r = 0 \tag{1.10a}$$

$$\delta\psi(r) \underset{r\to\infty}{\sim} \delta A \sin(kr+\eta) + A\cos(kr+\eta).\delta\eta \tag{1.10b}$$

Using the fact that $I=0$ the variation δI in I is given by:

$$\delta I = \int_0^\infty [\psi(r)+\delta\psi(r)][L-V(r)][\psi(r)+\delta\psi(r)]dr$$

$$\doteqdot -A^2 k.\delta\eta \tag{1.11}$$

The expression (1.11) was obtained by using equations (1.10) and is correct to the first order in $\delta\psi$.

(a) <u>The Kohn and Hulthen's Methods</u>.

Taking $A = \sec\eta$ we obtain the following:

$$\psi(r) \underset{r\to\infty}{\sim} \sin kr + \tan\eta.\cos kr \tag{1.12}$$

and $$\delta[I + k\tan\eta] = 0 \tag{1.13}$$

Let us consider a trial wave function ψ_t containing parameters $c_1, \cdots\cdots, c_n$ and satisfying equations (1.8a) and (1.12) but not (1.7). Writing $\tan\eta_t = R_t$ we have the following:

$$\delta I_t = \sum_{j=1}^{n} \frac{\partial I_t}{\partial c_j}.\delta c_j + \frac{\partial I_t}{\partial R_t}.\delta R_t$$

Thus equation (1.13) is satisfied if:

$$\frac{\partial I_t}{\partial c_j} = 0 \quad \text{for} \quad j = 1, \ldots, n \qquad 1.14a$$

$$\frac{\partial I_t}{\partial R_t} = -k \qquad 1.14b$$

Equations (1.14) define Kohn's variational method. Referring to equation (1.13) we may write:

$$I_t + kR_t = kR$$

Therefore, to the second order in $\delta\psi$ the best approximation to the exact R is given by:

$$R = k^{-1} I_t + R_t \qquad 1.15$$

We may use a further condition, namely:

$$\frac{\partial I_t}{\partial A} = 0$$

which requires $I_t = 0$ 1.16

Equations (1.14a) and (1.16) define Hulthen's variational method.

(b) Schwinger's Variational Method.

The important difference between this method and the previous two is that the trial function is not required to have a particular normalization such as is defined by equation (1.12). We consider equation (1.7) where the trial wave function $\psi_t(r)$ satisfies the following boundary conditions:

$$\psi_t(r) = 0 \text{ at } r = 0 \qquad 1.17a$$

$$\psi_t(r) \underset{r\to\infty}{\sim} B\sin kr + C\cos kr \qquad 1.17b$$

Therefore the phase shift η_t is defined by:

$$\tan\eta_t = \frac{C}{B} \qquad 1.18$$

ψ_t satisfies the following integral equation:

$$\psi_t(r) = B\sin kr + \int_0^\infty G(r,r')\,V(r')\,\psi_t(r')\,dr' \qquad 1.19a$$

where
$$G(r,r') = -k^{-1}\sin kr\cos kr' \quad \text{if} \quad r \le r'$$
$$= -k^{-1}\cos kr\sin kr' \quad \text{if} \quad r \ge r' \qquad 1.19b$$

Since $$\psi_t(r) = B\sin kr + \int_0^r G(r,r')V(r')\psi_t(r')dr' + \int_r^\infty G(r,r')\,V(r')\psi_t(r')dr'$$

$$\underset{r\to\infty}{\sim} B\sin kr - k^{-1}\cos kr\int_0^\infty \sin kr'\,V(r')\,\psi_t(r')\,dr'$$

comparing this to equation (1.17b) we obtain:

$$C = -k^{-1}\int_0^\infty \sin kr'\, V(r')\,\psi_t(r')\,dr' \qquad 1.20$$

Now consider the integral I_t in the following form:

$$I_t = \int \psi_t(r)\left[L-V(r)\right]\left[B\sin kr + \int_0^\infty G(r,r')\,V(r')\,\psi_t(r')\,dr'\right] dr \qquad 1.21$$

and choose the variational approximation to $\tan\eta$ such that $I_t = 0$. Using the fact that the Green's functions G satisfies:

$$L\,G(r,r') = \delta(r-r')$$

we have that:

$$\left[L-V(r)\right]\left[B\sin kr + \int_0^\infty G(r,r')\,V(r')\,\psi_t(r')\,dr'\right] = V(r)\,\psi_b(r)$$
$$- V(r)\left[B\sin kr + \int_0^\infty G(r,r')\,V(r')\,\psi_t(r')\,dr'\right] \qquad 1.22$$

Substituting equations (1.18), (1.20) and (1.22) into (1.21) gives the following expression for $\cot\eta_t$:

$$k^{-1}\cot\eta_t \doteq \frac{\int_0^\infty\int_0^\infty \psi_t(r)\,V(r)\,G(r,r')\,V(r')\,\psi_t(r')\,dr'dr - \int_0^\infty \psi_t(r)\,V(r)\,\psi_t(r)\,dr}{\left[\int_0^\infty \psi(r)\,V(r)\sin kr\,dr\right]^2} \qquad 1.23$$

This defines the Schwinger variational formula. If we choose $\psi_t(r) = \sin kr$ we obtain:

$$\tan\eta_t = \frac{\tan^2\eta_B^{(1)}}{\tan\eta_B^{(1)} - \tan\eta_B^{(2)}} \qquad 1.24$$

where $\eta_B^{(1)}$ and $\eta_B^{(2)}$ are the first and second iterated Born phase shifts respectively.

(c) Positron Hydrogen Collisions.

One of the first variational calculations was that of Massey and Moussa[5] who calculated zero-order phase shifts using two types of wave functions. The first function contained no allowance for distortion of the positron wave and was of the form used by Massey and Moiseiwitsch[6] for electron Hydrogen scattering:

$$F_1(r_p) = \frac{1}{r_p}\left[\sin kr_p + \left\{a + be^{-r_p}\right\}\left(1 - e^{-r_p}\right)\cos kr_p\right] \qquad 1.25$$

Again following Massey and Moiseiwitsch[6] terms dependent on $\rho = |\underline{r}_1 - \underline{r}_p|$ were added to F_1 where $\underline{r}_1$ and $\underline{r}_p$ are the positron vectors of the electron and positron relative to the proton respectively. The second function F_2 was

$$F_2(r_p, \rho) = \frac{1}{r_p}\left[\sin kr_p + \left\{a + (b + c\rho)e^{-r_p}\right\}\left(1 - e^{-r_p}\right)\cos kr_p\right] \qquad 1.26$$

Both Kohn's and Hulthen's methods were used but no appreciable difference in the phase shifts was found in using F_1 and F_2, see Table 1-1.

Rather than considering distortion of the incoming positron wave, Moussa[7] considered distortion of the Hydrogen atom by the presence of the colliding positron. The total trial wave function Ψ was chosen as:

$$\Psi(r_1, r_p) = \psi_0(r_1) F(r_p) + \varphi_0(r_1, r_p)$$

where ψ_0 is the ground state Hydrogen function and:

$$\varphi_0(r_1, r_p) = \omega(\rho) G(\sigma)$$

where $\underset{\sim}{\rho} = \underset{\sim}{r}_1 - \underset{\sim}{r}_p$ and $\underset{\sim}{\sigma} = \frac{1}{2}(\underset{\sim}{r}_1 + \underset{\sim}{r}_p)$, $\omega(\rho)$ is the ground state Positronium function and G was chosen as:

$$G(\sigma) = Ce^{-K\sigma}$$

where $\frac{1}{2}K^2 = (k^2 - \frac{1}{2})$

and $\frac{1}{2}K^2$ is the kinetic energy of the Positronium in rydbergs. Moussa[7] applied the Kohn and Hulthen methods with a, b and c as the variational parameters for the single energy $k^2 = .25$ and s-wave scattering only. The elastic scattering cross-section was reduced when φ_0 was included in the trial wave

TABLE 1-1

Phase shifts for L=0 scattering of positrons by Hydrogen atoms. Row (a) static approximation; row (b) 2-parameter variational; row (c) 3-parameter variational including a term depending on the Positronium coordinate; row (d) extensive variational.

ka_o	0.1	0.2	0.3	0.4	0.5	0.6	Reference
(a)	.	-.084	.	.	-.203	.	5
(b)	.	-.114	.	.	-.264	.	5
(c)	.	-.098	.	.	-.251	.	5
(d)	+.151	+.188	+.168	+.120	+.062	+.007	11

function but not by a sufficient amount to give any agreement with the experimental results of Marder et al.[1] The form chosen for G is unlikelyto be adequate for non-asymptotic distances which could account for the relatively small change in the cross-section value.

Extending the calculations for obtaining equation (1.24) to the scattering amplitude defined in equation (1.1b) it can be shown that if f_{B1} and f_{B2} are the scattering amplitudes obtained from the first and second Born approximation respectively, then the best approximation for the true scattering amplitude f that can be obtained from f_{B1} and f_{B2} is given by:

$$f = \frac{f_{B1}^2}{f_{B1} - f_{B2}} \qquad 1.27$$

Using this method Moiseiwitsch[8] gained agreement with Massey and Moussa[5] and an extension of the approximation f_{B2} by a method due to Newstein[9] to allow for polarization, resulted in a decrease in the cross-sections.

Moiseiwitsch and Williams[10] used a simplification of the second Born approximation and Schwinger's method to calculate differential cross-sections for elastic scattering. The positron energy considered was greater than 200 eV so allowance for excited states of the atom was included.

Schwartz[11] calculated the elastic scattering for zero angular momentum using the Kohn variational method and the following type of trial wave function:

$$\psi_t(r_1, r_\rho) = \varphi(r_1, r_\rho) + \sum_{\ell,m,n \geq 0} C_{\ell mn} e^{-K\rho} \rho^{\ell} r_1^{m} r_\rho^{n} \qquad 1.28a$$

where φ is of the form:

$$e^{-r_1}\left[\frac{\sin k r_\rho}{k r_\rho} + \tan\delta \cdot \frac{\cos k r_\rho}{k r_\rho} \left(1 - e^{-\frac{K}{2} r_\rho}\right) \right] \qquad 1.28b$$

and $\underset{\sim}{\rho} = \underset{\sim}{r}_1 - \underset{\sim}{r}_\rho$, $\underset{\sim}{s} = \frac{1}{2}(\underset{\sim}{r}_1 + \underset{\sim}{r}_\rho)$. K is a variable scale parameter adjusted to aid convergence. The ensuing phase shifts are displayed in Table 1-1.

(d) Positron Helium Collisions.

Moiseiwitsch and Williams [10] applied the same methods to positron Helium scattering, for energies greater than 300 eV, as for positron Hydrogen scattering. The two methods gave little agreement and at small angles the differential cross-sections differed by a factor of three.

1.3 Bounds on the Scattering Length.

According to effective range theory, for short-range central potential scattering, $k \cot \delta_0$ (where δ_0 is the s-wave phase shift) can be expanded in powers of k^2 as follows:

$$k \cot \delta_0 = -\frac{1}{a} + k^2 \cdot \frac{r_0}{2} + O(k^4) \qquad 1.29a$$

where a is the scattering length and r_0 the effective range. Alternatively we may define a as follows:

$$a = \underset{k\to 0}{\text{Limit}} \left[-\frac{\tan \delta_0}{k} \right] \qquad 1.29b$$

Up to this point there has been no criterion to judge whether the addition of more variational parameters would produce improved phase shifts. Spruch and Rosenberg [12] generalised the results of Kato [13] to show that the Kohn variational method provides an upper bound on tbe scattering length. We first of all consider the case of zero energy scattering in a static central potential V(r). Referring to equation (1.15) the exact expression for R is:

$$R = R_t + k^{-1} I_t - k^{-1} \int_0^\infty \delta\psi(r) \left[\lambda - V(r) \right] \delta\psi(r) . dr \qquad 1.30$$

where $\psi(r)$ satisfies equation (1.12).

If we consider equation (1.30) in the limit as $k \to 0$ we obtain the following:

$$a = a_t + I_t - \int_0^\infty \delta\psi(r) \, \mathcal{D}(r) \, \delta\psi(r) . dr \qquad 1.31$$

where $\mathcal{D}(r) \equiv \frac{d^2}{dr^2} - V(r)$

$$\psi(0) = 0 \qquad 1.32a$$

$$\psi(r) \underset{r\to\infty}{\sim} r - a \qquad 1.32b$$

and a is the true scattering length. The normalization of $\psi(r)$ in the zero-energy limit has been changed by a factor of k. Estimating the size of the integral term on the right hand side of equation (1.31) will give us some measure of the error incurred in the variational calculations. Spruch and Rosenberg[14] showed that if the potential V(r) could not support a bound state then:

$$-\int_0^\infty \delta\psi(r)\, D(r)\, \delta\psi(r)\, dr \leq 0 \qquad 1.33$$

Therefore equation (1.31) reduces to:

$$a \leq a_t + I_t \qquad 1.34$$

That is, any choice of parameters in the trial function will yield an upper bound on the scattering length so the choice leading to the smallest values of $(a_t + I_t)$ will provide the best approximation to the true scattering length.

In the one-dimensional problem Kato[12] calculated upper and lower bounds on the error term in equation (1.30). By considering the associated eigenvalue equation:

$$\mathcal{L}\varphi_n(r) + \mu_n \cdot \rho(r)\varphi_n(r) = 0 \qquad 1.35$$

where $\mathcal{L} = L - V(r)$, ρ is a non-negative weight function and φ_n satisfies the same boundary conditions as $\delta\psi_t$, it can be seen that there exists an infinite set of discrete eigenvalues. If we denote the smallest positive eigenvalue by α

and the smallest (in magnitude) negative eigenvalue by $-\beta$ then:

$$-\frac{1}{\beta} \leq \frac{1}{\mu_n} \leq \frac{1}{\alpha} \qquad \text{for all n} \qquad 1.36$$

Since $\psi_t = \psi + \delta\psi$ where $\mathcal{L}\psi = 0$

we use equation (1.36) and the fact that:

$$\mathcal{L}\psi_t = \mathcal{L}\delta\psi$$

to obtain the following expression:

$$-\frac{1}{\beta}\int_0^\infty \left[\mathcal{L}\psi_t\right]^2 \frac{dr}{\rho(r)} \leq \int_0^\infty \delta\psi\,\mathcal{L}\,\delta\psi\,dr \leq \frac{1}{\alpha}\int_0^\infty \left[\mathcal{L}\psi_t\right]^2 \frac{dr}{\rho(r)}$$

Spruch and Rosenberg[12] generalized this to the scattering of a particle by a compound system. Providing the following conditions hold, namely:

(1) the eigenfunctions φ_n of the associated problem form a complete set.

(2) Levinson's theorem generalized to a many-body system is valid. That is: when the exclusion principle is not in effect, the phase shift for zero energy scattering is $n\pi$ where n is the number of bound states of the system.

(3) no three-body bound state exists for the positron Helium system.

then the scattering length obtained from Kohn's variational method for positron-Hydrogen is an upper bound to the true scattering length.

(a) Positron Hydrogen Collisions.

Spruch and Rosenberg [12] considered two types of trial wave functions. The first F_1 corresponds to the Mean Static Field approximation:

$$F_1(r_1, r_p) = \varphi_0(r_1) f(r_p)$$

where $\varphi_0(r_1) = \pi^{-\frac{1}{2}} e^{-r_1}$ is the ground state Hydrogen function and:

$$f(r_p) = 0 \quad \text{at} \quad r_p = 0$$

$$f(r_p) \underset{r_p \to \infty}{\sim} a_1 - r_p$$

where a_1 is the scattering length in the Mean Static Field Approximation. a_1 was found to be positive and was an upper bound on the scattering length for the true problem.

The second type of function F_2 contained terms in ρ to allow for polarization of the Hydrogen atom:

$$F_2(r_1, r_p, \rho) = \pi^{-\frac{1}{2}}\left[A e^{-r_1}(1 - e^{-r_p}) - r_p\left(e^{-r_1} - B e^{-q r_p - s r_1} - C e^{-t\rho - u r_1}\right)\right]$$

The parameters q, s, t and v are varied and the linear parameters determined variationally to give the least value of the scattering length. This produced an upper bound of $-1.356a_0$ showing that the positron is attracted to the Hydrogen atom at low energies. The addition of a further term $\pi^{-\frac{1}{2}} D r_1 e^{-\frac{\beta}{4}-2r_1}$ similar to the first excited state of Positronium reduced the upper bound to $-1.397a_0$ which can be compared to Schwartz's[11] variational result of $-2.1a_0$.

Allison, McIntyre and Moiseiwitsch[15] calculated the scattering length for elastic collisions using the Kohn and Hulthen variational principles. The total wave function $\Psi(\underline{r}_1, \underline{r}_p)$ for total angular momentum zero was chosen as:

$$\Psi(\underline{r}_1, \underline{r}_p) = \varphi_0(r_1)\left\{1 + \gamma f(\underline{r}_1, \underline{r}_p)\right\} F(r_1)$$

where

$$f(\underline{r}_1, \underline{r}_p) = r_p^{-2}\left(1-e^{-\delta r_p}\right)^3\left(\tfrac{1}{2}r_1^2 + r_1\right)\cos\theta_{1p}$$

and

$$F(r_p) = r_p^{-1}\left[(\alpha + \beta e^{-r_p})(1-e^{-r_p}) - r_p\right]$$

and α, β, γ and δ are arbitrary parameters. f contains allowance for the polarization of the Hydrogen atom (see Section 1.5) and F obeys the following asymptotic boundary condition:

$$r_p F(r_p) \underset{r_p \to \infty}{\sim} \alpha - r_p$$

hence the calculated scattering length is α. Varying the parameters β, γ and δ in the variational methods, the best value of the scattering length was $-.785a_0$ which is greater than Spruch and Rosenberg's [12] upper bound result. A probable cause of error in Alison et al's choice of wave function is the omission of any allowance for virtual Positronium formation.

Houston and Moiseiwitsch [16] used Kohn's variational method to calculate scattering lengths. By considering the function F_2 defined by equation (1.26) in the limit of zero energy but replacing the exponential terms by $e^{-\alpha r_p}$ and $e^{-\beta r_p}$ respectively, a negative scattering length $-.466a_0$ was obtained. This is less accurate than Schwartz's [11] since only linear dependence on the positronium coordinate was accounted for.

A further trial function similar to Schwartz's [11] defined by equations (1.28) in the zero-energy limit was used by Houston et al.[16]:

$$\psi_t(r_1, r_p) = \chi(r_1, r_p, \rho)\phi_0(r_1)$$

where $$\chi(r_1, r_p, \rho) = \frac{1}{r_p}\left[a\left\{1 - e^{-\gamma r_p}\right\} - r_p\right] + e^{-\alpha r_p - \beta r_1}\sum_{i=1}^{N} a_i r_p^{\ell} r_1^{m} \rho^{n} \qquad 1.37$$

and ϕ_0 is the ground state Hydrogen function. Calculations were performed for N=4, 10, 20 and 35 corresponding to all possible values satisfying $\ell+m+n \leq 1$, 2, 3 and 4 respectively with $\ell, m, n \geq 0$. Optimal values of α, β and γ were calculated for the N=4 case and these were used for the remaining cases.

The lowest scattering length of $-1.89a_0$ was obtained for N=35. Allowance for Positronium formation was made by including a further term:

$$a_{N+1}\, e^{-\beta\rho-\gamma r_1}$$

This reduced the lowest scattering length to $-1.92a_0$.

(b) Positron Helium Collisions.

Allison et al.[15] applied the Kohn and Hulthen variational methods to positron Helium scattering where the total wave function $\Psi(\underline{r}_1, \underline{r}_2, \underline{r}_\rho)$ for zero orbital angular momentum was chosen as:

$$\Psi(\underline{r}_1, \underline{r}_2, \underline{r}_\rho) = \psi_0(r_1, r_2)\left[1 + \gamma f(\underline{r}_1, \underline{r}_2, \underline{r}_\rho)\right] F(r_\rho)$$

where $$f(\underline{r}_1, \underline{r}_2, \underline{r}_\rho) = \frac{1}{r_\rho^2}\left\{1 - e^{-\delta^2 r_\rho}\right\}\left\{\cos\theta_{1\rho}\left(\beta_0 r_1 + \beta_1 r_1^2\right) + \cos\theta_{2\rho}\left(\beta_0 r_2 + \beta_1 r_2^2\right)\right\}$$

and $F(r_\rho)$ is the same as in the positron Hydrogen case. The Helium ground state function ψ_0 is the 3-parameter approximation to the Hartree-Fock function given by Green, Mulder, Lewis and Woll:[17]

$$\psi_0(r_1, r_2) = u(r_1)\,u(r_2) \qquad 1.38a$$

where $$u(r) = \frac{N}{\sqrt{4\pi}}\left[e^{-Ar} + Ce^{-Br}\right] \qquad 1.38b$$

and A, B, C and N are defined in Chapter II. The constants β_0 and β_1 were chosen so that for large r_p, $\psi_0 f$ was the first order correction to ψ_0 arising from the dipole term of the perturbation due to the positron, see Section 1.5.

As in the Hydrogen case, the scattering length for positron Helium was negative, equaling $-.16a_0$ in the Kohn method and $-.10a_0$ in the Hulthen method. Since the Helium atomic function is approximate no rigorous bounds can be applied in this case.

Houston et al.[16] extended their variational method to Helium using an analogous trial wave function:

$$\psi_b(r_1, r_2, r_p) = \psi_0(r_1, r_2)\, f(r_1, r_2, r_p, \rho_1, \rho_2)$$

where ψ_0 is defined in equation (1.39) and:

$$f(r_1, r_2, r_p, \rho_1, \rho_2) = \frac{1}{r_p}\left[a(1-e^{-\gamma r_p}) - r_p\right] + e^{-\alpha r_p}\sum_{i=1}^{N} a_i(1+P_{12})\left\{e^{-\beta r_1}\chi(r_1, r_p, \rho_1)\right\}$$

and χ is defined by equation (1.37). P_{12} is the operator interchanging all coordinates 1 and 2 and $\underset{\sim}{\rho}_i = \underset{\sim}{r}_i - \underset{\sim}{r}_p$ for i=1 and 2. Calculations for N=4, 10 and 20 were performed, the smallest scattering length of $-.398a_0$ being obtained for maximum N.

1.4 Partial Wave Theory and the Close Coupling Approximation.

We expand the total wave function Ψ in terms of the eigenstates of the target Hamiltonian. For simplicity we will consider the case of positron Hydrogen scattering, without allowance for Positronium formation.

$$\Psi(\underline{r}_1, \underline{r}_p) = \sum_n \varphi_n(\underline{r}_1) F_n(\underline{r}_p) \qquad 1.39$$

where φ_n is the nth state Hydrogen function satisfying:

$$\left[-\nabla^2 - \frac{2}{r} - E_n\right] \varphi_n(\underline{r}) = 0 \qquad 1.40a$$

where $$\varphi_n(\underline{r}) = \sum_{\ell m} \frac{R_{n\ell}(r)}{r} Y_{\ell m}(\hat{r}) \qquad 1.40b$$

F_n satisfies the following boundary conditions:

$$F_n(\underline{r}_p) = 0 \quad \text{at}$$

$$F_n(r_p) \underset{r_p \to \infty}{\sim} e^{i\underline{k}_0 \cdot \underline{r}_p} + \frac{e}{r_p}^{ik_n r_p} f_n(\theta_p)$$

where $k_n^2 = E - E_n$ and E is the total energy of the system. We are considering the positron with energy k_0^2 incident on the atom in its ground state of energy E_0.

The Schroedinger wave equation is:

$$\left[-(\nabla_1^2 + \nabla_p^2) - \frac{2}{r_1} + \frac{2}{r_p} - \frac{2}{\rho} - E\right] \Psi(\underline{r}_1, \underline{r}_p) = 0 \qquad 1.41$$

Premultiplying by $\varphi_n^*(\underline{r}_1)$, integrating with respect to $\underline{r}_1$, and using equation (1.39) we obtain:

$$\left[\nabla_\rho^2 + k_n^2\right] F_n(r_\rho) = \sum_{n'} V_{nn'} F_{n'}(r_\rho) \qquad 1.42a$$

where $$V_{nn'} = 2\int \varphi_n^*(r_1)\left[\frac{1}{r_\rho} - \frac{1}{\rho}\right]\varphi_{n'}(r_1)\,dr_1 \qquad 1.42b$$

To solve these numerically we expand F_n in terms of the spherical harmonics as follows:

$$F_n(r_\rho) = \sum_{\ell m} \frac{f_{n\ell m}(r_\rho)}{r_\rho} Y_{\ell m}(\hat{r}_\rho) \qquad 1.43$$

Therefore substitution of equation (1.43) into (1.42a) yields the following system of an infinite number of coupled second-order differential equations:

$$\left[\frac{d^2}{dr^2} + k_n^2 - \frac{\ell(\ell+1)}{r^2}\right] f_{n\ell m}(r) = r\int d\hat{r}\, Y_{\ell m}^*(\hat{r}) \sum_{n'} V_{nn'} F_{n'}(r) \qquad 1.44$$

(a) Polarization Potential

Consider a positron incident on a Hydrogen atom in its ground state. The positron energy k_0^2 being insufficient to excite the atom we have:

$$k_0^2 \geq 0$$
$$k_\nu^2 < 0 \qquad \text{for } \nu \neq 1 \qquad 1.45$$

where $k_v^2 = E - E_v$ and E is the total energy of the system. E_v is defined in equation (1.40a). From equations (1.45) we obtain:

$$F_0(r) \underset{r\to\infty}{\sim} e^{i\underline{k}_0\cdot\underline{r}} + \frac{e}{r}^{ik_0 r} f_0(\theta_0, \varphi_0) \qquad 1.46$$

$$r F_v(r) \underset{r\to\infty}{\sim} 0 \quad \text{for}$$

Since the $F_v(r)$ for v≠1 are bound state functions decaying exponentially, for large r_p the right hand side of equation (1.42a) will be replaced by a single diagonal potential term $V_p(r_p) F_0(r_p)$. Castillejo, Percival and Seaton [18] showed that:

$$F_v(r_p) \underset{r_p\to\infty}{\sim} -\frac{1}{2} \cdot \frac{V_{v0}(r_p) F_0(r_p)}{k_0^2 - k_v^2} + O\left(\frac{1}{r_p^3}\right)$$

and hence, substituting n=0 in equation (1.42a) we obtain:

$$\left[\nabla_p^2 + k_0^2\right] F_1(r_p) \sim -\frac{1}{2}\left[\sum_{n'\neq 0} \frac{V_{on'}(r_p) V_{n'0}(r_p)}{(k_0^2 - k_{n'}^2)}\right] F_0(r_p) + O\left(\frac{1}{r_p^5}\right)$$

Therefore the polarization potential $V_p(r_p)$ is given by:

$$V_p(r_p) = -\frac{1}{2} \sum_{n'\neq 0} \frac{\left|V_{n'0}(r_p)\right|^2}{(k_0^2 - k_{n'}^2)} \qquad 1.47$$

Substituting equation (1.43) into (1.47) and using equation (1.42b) we obtain:

$$V_{n'0}(r_p) = 2\int \sum_{\ell m} f_{n'\ell}(r') \left[\frac{1}{r} - \frac{1}{|\underline{r}-\underline{r}'|}\right] f_{00}(r') Y_{\ell m}(\hat{r}') Y_{00}(\hat{r}')\, d\hat{r}'\, dr'$$

Using the addition formula for spherical harmonics (see equation 2.12) this reduces to:

$$V_{n'0}(r_p) = 2\sum_{\ell m} \int_0^\infty f_{n'\ell}(r') f_{00}(r') \left[\frac{\delta_{\ell 0}\delta_{m0}}{r_p} - \sqrt{4\pi}\frac{r_<^\ell}{r_>^{\ell+1}} Y_{\ell m}(\hat{r})\right] dr'$$

$$\underset{r_p\to\infty}{\sim} -2\sum_{\ell m} \frac{\sqrt{4\pi}}{2\ell+1} \frac{Y_{\ell m}(\hat{r}_p)}{r_p^{\ell+1}} \int_0^\infty f_{n'\ell}(r') f_{00}(r') r'^{\ell} dr'$$

where $r_< = r$, $r_> = r'$ if $r \le r'$

$r_< = r'$, $r_> = r$ if $r \ge r'$

Thus:

$$V_p(r_p) \underset{r_p\to\infty}{\sim} 2\sum_{\ell, n'\neq 0} \frac{|A_{n'\ell}|^2}{(2\ell+1) r_p^{2\ell+2} (k_0^2 - k_{n'}^2)}$$

where $$A_{n'\ell} = \int_0^\infty f_{n'\ell}(r') f_{00}(r') r'^{\ell} dr'$$

Because of the factor of $r_p^{-2\ell-2}$ in $V_p(r)$ the largest contribution asymptotically will arise from the smallest ℓ value. Considering $\ell=0$ for Hydrogen, $A_{n'0} = 0$ because of the orthogonality of the Hydrogen radial functions. Therefore the dominant term is the $\ell=1$ term and:

$$V_p(r_p) \underset{r_p\to\infty}{\sim} \frac{-2}{3r_p^4} \sum_{n'\neq 0} \frac{|A_{n'1}|^2}{(E_{n'} - E_0)}$$

$$= -\frac{\alpha}{r_p^4} \qquad 1.48a$$

where $$\alpha = \frac{2}{3}\sum_{n'\neq 0}\frac{|A_{n'1}|^2}{(E_{n'}-E_0)} \qquad 1.48b$$

and α is the polarizability of the atom.

(b) Close Coupling Approximation

If we assume that the effect of any spin-orbit interaction is negligible then the total orbital angular momentum with quantum numbers L and M_L and the total spin with quantum numbers S and M_S are separately conserved during the collision. A convenient representation is one that is diagonal in LM_LSM_S which will be labeled $\Gamma = (k_n n \ell_1\ell_2 L M_L S M_S)$ where ℓ_1 and ℓ_2 are the orbital angular momentum quantum numbers of the atomic electron and the positron respectively and k_n and n are the wave number and principal quantum number of the positron and atom respectively. Thus instead of the expansion given by equation (1.39) we use:

$$\Psi^{\Gamma'}(\underline{r}_1 s_1, \underline{r}_p s_p) = \sum_{\Gamma}\psi_\Gamma(\underline{r}_1 s_1, \hat{r}_p, s_p)\frac{F_{\Gamma\Gamma'}(r_p)}{r_p} \qquad 1.49a$$

where ψ_Γ can be expanded as:

$$\psi_\Gamma = \varphi_\Gamma(\underline{r}_1 s_1 s_p)\,\mathcal{Y}^{M_L}_{\ell_1\ell_2 L}(\hat{r}_1,\hat{r}_p) \qquad 1.49b$$

where $\mathcal{Y}^{M_L}_{\ell_1\ell_2 L}$ is an eigenfunction of the total orbital angular momentum L. s_1 and s_p represent the spins of the electron and positron respectively and the system is initially in the state Γ'. $F_{\Gamma\Gamma'}$ satisfies the following boundary condition:

$$F_{\Gamma\Gamma'}(r_p) \underset{r_p\to\infty}{\sim} k_\Gamma^{-\frac{1}{2}}\left[\sin\left(k_\Gamma r_p - \frac{\ell_2\pi}{2}\right)\delta_{\Gamma\Gamma'} + R_{\Gamma\Gamma'}\cos\left(k_\Gamma r_p - \frac{\ell_2\pi}{2}\right)\right] \qquad 1.50$$

As an illustration we consider the case of a positron incident on a Hydrogen atom without allowance for Positronium formation. Substituting equation (1.49) in the Kohn variational principle (see Section 1.2 and Chapter II) we obtain the following set of coupled second-order differential equations:

$$\left[\frac{d^2}{dr^2} - \frac{\ell_2(\ell_2+1)}{r^2} + k_n^2\right] F_\nu^{LS}(r) = \sum_{\nu'} V^{L}_{\nu\nu'}(r)\, F^{LS}_{\nu'}(r) \qquad 1.51$$

where $\nu = n\ell_1\ell_2$ and the subscript Γ' has been omitted since the above equations are independent of the boundary conditions. We have that:

$$V^{L}_{\nu\nu'}(r) = \frac{2}{r}\delta_{\nu\nu'} - 2\sum_\lambda f_\lambda(\ell_1\ell_2, \ell_1'\ell_2'; L)\, y_\lambda(\rho_{n\ell_1}, \rho_{n'\ell_1'} \mid r) \qquad 1.52a$$

where $$f_\lambda(\ell_1\ell_2, \ell_1'\ell_2'; L) = \int \mathcal{Y}^{M_L}_{\ell_1\ell_2 L}(\hat{r},\hat{r}')\, \mathcal{Y}^{M_L}_{\ell_1'\ell_2' L}(\hat{r},\hat{r}')\, P_\lambda(\hat{r}\cdot\hat{r}')\, d\hat{r}\, d\hat{r}' \qquad 1.52b$$

and $$y_\lambda(P_{n\ell}, P_{n'\ell'}|r) = \int_0^\infty R^*_{n\ell}(r') R_{n'\ell'}(r') \frac{r_<^\lambda}{r_>^{\lambda+1}} dr' \qquad 1.52c$$

where $r_< = r'$, $r_> = r$ if $r' \leq r$

and $r_< = r$, $r_> = r'$ if $r < r'$

$R_{n\ell}$ is defined in equation (1.39b) and P_λ is a Legendre polynomial.

In the Mean Static Field approximation only the ground state of atomic Hydrogen is included in the expansion (1.49). Thus equation (1.51a) reduces to:

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k_1^2\right] F^\ell(r) = V F^\ell(r) \qquad 1.53a$$

where $$V = 2\left(1+\frac{1}{r}\right)e^{-2r} \qquad 1.53b$$

In the Strong Coupling approximation we include any two s-states of the Hydrogen atom - therefore equation (1.51a) reduces to the following pair of equations:

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k_{n_1}^2\right] F^\ell_{n_1 0\ell}(r) = V_{n_1\ell,n_1\ell} F^\ell_{n_1 0\ell} + V_{n_1\ell,n_2\ell} F^\ell_{n_2 0\ell}$$

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k_{n_2}^2\right] F^\ell_{n_2 0\ell}(r) = V_{n_2\ell,n_1\ell} F^\ell_{n_1 0\ell} + V_{n_2\ell,n_2\ell} F^\ell_{n_2 0\ell}$$

In the distorted - wave approximation one of the

coupling terms in the pair of equations is set to zero.

In many problems it is necessary to allow for interactions of intermediate states therefore more terms in the expansion (1.49) would be included.

(c) Positron Hydrogen Collisions

Smith and Burke [19] calculated the L=0 phase shifts in the static and strong coupling approximation. The scattering length in the static case were found to equal +0.582 and the addition of the virtual 2s state of Hydrogen in the strong-coupling approximation only reduced it to +.564. The phase shifts for L=0 calculated in the static, strong coupling and 1s-2s-3s coupling scheme are presented in Table 1-2. Comparing these to the reliable variational results of Schwartz [11] it can be seen that spherically symmetric states in the close-coupling expansion are not adequate allowance for polarization of the atom.

This was confirmed by Castillejo et al. [18] who considered the contributions of different states of the Hydrogen atom to the formula (1.48). Using the matrix elements tabulated by Green, Rush and Chandler [20] they found that the 2p state accounted for 65.8% of the polarizability. Therefore Burke, Schey and Smith [21] (see Burke and Smith [22]) performed a 1s-2s-2p calculation and McEachran and Fraser [23] calculated S, P and D partial wave phase shifts using various combinations of the 1s, 2s, 2p, 3s, 3p and 3d states of Hydrogen. The results for S-wave scattering presented in

TABLE 1-2

Phase shifts for L=0 scattering of positrons by Hydrogen atoms. Row (a) static approximation; row (b) strong coupling approximation; row(c) 1s-2s-2s coupling; row (d) 1s-2s-2p coupling; row (e) 1s-2s-2p-3s coupling; row (f) 1s-2s-2p-3s-3p coupling; row (g) 1s-2s-2p-3s-3p-3d coupling; row (h) ground state of Hydrogen and Positronium only (i) variational.

ka_o	0.0†	0.1	0.2	0.3	0.4	0.5	0.6	Reference
(a)	+.582	-.0580	-.1145	.	-.2181	-.2636	-.3043	19
(b)	+.564	-.0562	-.1109	.	-.2110	-.2547	-.2936	19
(c)	.	.	-.1102	.	-.2095	-.2529	-.2914	19
(d)	-.1337*	-.0054	-.0426	-.0931	-.1472	-.1990	-.2461	21,22
(e)	-.1374	-.0046	-.0418	-.0925	-.1462	-.1979	-.2447	23
(f)	-.2698	+.0055	-.0275	-.0771	-.1313	-.1842	-.2327	23
(g)	-.2898	+.0072	-.0251	-.0748	-.1295	-.1829	-.2317	23
(h)	+.1704	-.0188	-.0465	-.0858	-.1339	-.1861	-.2379	25
(i)	-2.10	+.151	+.188	+.168	+.120	+.062	+.007	11

† The zero entries represent scattering lengths.
* This scattering length is taken from reference (23) whose results differ in the fourth figure from these in row (d).

Table 1-2, demonstrate the extremely slow convergence of the close-coupling expansion with respect to the bound states of atomic Hydrogen.

Since Spruch and Rosenberg[12] demonstrated the importance of allowing for virtual formation of Positronium, Cody and Smith[24] formulated a close-coupling expansion including the 1s and 2s states of Positronium. Results for the 1s state were given by Cody, Lawson, Massey and Smith[25] and are presented in Table 1-2. For $k \gtrsim .3$ the Cody et al.[25] results are as good as those of the 5-term close-coupling expansion of McEachran et al.[23] but for $k < .3$ the phase shifts remain negative. It is necessary to include the 2p state of Hydrogen before the scattering length becomes negative.

An interesting modification to the close coupling expansion was suggested by Perkins [26] who replaced the exponential terms of the orbital radial functions (equation (1.40b) by terms containing a parameter in the exponent. Explicitly, the 2p and 3d functions ($re^{-\frac{r}{2}}$ and $r^2e^{-\frac{r}{3}}$) are replaced by $re^{-\alpha r}$ and $r^2e^{-\beta r}$ respectively where α and β are chosen to maximise the phase shifts. The bound theorems on the phase shift are still valid provided that the exact ground-state wave function is used. The s-wave phase shifts using the 1s and modified 2p and 3d terms were comparable to the 6 term close coupling expansion of McEachran and Fraser. [23]

(c) Positron Helium Collisions

Massey and Moussa [5] performed s-, p- and d-wave calculations in the static approximation and then included a polarization potential $\frac{-\alpha e^2}{(r^2+d^2)^2}$ where d is of the order of atomic dimensions. The addition of the polarization for k=1 resulted in an increase in the phase-shift as is to be expected.

In comparison, Kraidy [27] allowed for Positronium formation in the ground state and found that the phase shifts were up to three times larger than the corresponding static results and were positive for energies less than or equal to .16. The scattering length was negative (-.9193) and since there is no exact Helium ground state function there are no rigorous bounds on the scattering length in this problem. From the results presented in Chapter V it can be seen that this change in sign of the phase shift at low energies is directly

attributable to the choice of the Hylleras uncorrelated hydrogenic function for the Helium ground state:

$$\psi_0(r_1, r_2) = \frac{\mu^3}{\pi} e^{-\mu(r_1+r_2)} \qquad 1.54$$

where $\mu = \frac{27}{16}$

The S-wave phase shifts are presented in Table 1-3.

1.5 The Method of Polarized Orbitals

In the adiabatic theory we assume that the projectile's velocity is so small that allowance for the distortion of the charge distribution of the atomic electron may be calculated assuming that the projectile is at a fixed point. If we consider the case of a positron incident on a Hydrogen atom in its ground state, then the perturbation potential due to the positron fixed at $\underline{r}_p$ is:

$$V(\underline{r}_1, \underline{r}_p) = \frac{2}{r_p} - \frac{2}{|\underline{r}_1 - \underline{r}_p|}$$

where $\underline{r}_1$ is the atomic electron coordinate relative to the proton. According to the first order perturbation theory, the perturbed wave function of the electron will be:

$$\psi(\underline{r}_1, \underline{r}_p) = \varphi_0(r_1) - \sum_{q \neq 0} \frac{(0|V|q)}{E_q - E_0} \varphi_q(\underline{r}_1) \qquad 1.55$$

TABLE 1-3

Phase shifts for L=0 scattering of positrons by Helium atoms. Row (a) static approximation; row (b) static approximation + dipole polarization; row (c) ground state of Helium and Positronium; row (d) ground state of Helium and Positronium + dipole polarization.

ka_o	0.0 †	0.1	0.2	0.3	0.4	0.5	0.6	Reference
(a)	.386	-.0382	-.0759	-.1131	-.1493	-.1843	-.2180	27
(b)	-.3006	-.0193	.0197	.0066	-.0153	-.0426	-.0729	27
(c)	-.9193	.0770	.1019	.0753	.0212	-.0407	-.1023	27
(d)	-2.047	.1662	.2279	.2123	.1626	.1043	.0483	27

† The zero-entries represent scattering lengths.

where $(0|V|_q) = \int \varphi_0(r_1) V(\underline{r}_1, \underline{r}_p) \varphi_q(\underline{r}_1) d\underline{r}_1$ 1.56a

$$\varphi_q(\underline{r}) = \varphi_{nlm} = \frac{R_{nl}(r)}{r} Y_{lm}(\hat{r}) \qquad 1.56b$$

and $\varphi_0(r) \equiv \varphi_{100}(r)$ 1.56c

It is clear that the perturbed wave function depends on $\underline{r}_p$ so in the Polarized Orbitals method we write:

$$\psi(\underline{r}_1, \underline{r}_p) = \varphi_0(r_1) + \varphi^{pol}(\underline{r}_1, \underline{r}_p) \qquad 1.57$$

where $\varphi^{pol}(\underline{r}_1, \underline{r}_p) = 0$ for $r_p < r_1$

We expand $V(\underline{r}_1, \underline{r}_p)$ in a multipole series keeping the dipole term only:

$$V(\underline{r}_1, \underline{r}_p) \doteq -\frac{2r_1}{r_p^2} \cos\theta_{1p} \qquad r_p > r_1 \qquad 1.58$$

where θ_{1p} is the angle between $\underline{r}_1$ and $\underline{r}_p$. The ground state Hydrogen function φ_0 with associated energy E_0 satisfies:

$$[H_r - E_0]\varphi_0(r_1) = 0 \qquad 1.59a$$

where $H_r = -\nabla_1^2 - \frac{2}{r_1}$ and $E_0 = -1$ 1.59b

The Hamiltonian for the positron and the Hydrogen atom is:

$$H = H_r - \nabla_p^2 + V(\underline{r}_1, \underline{r}_p) \qquad 1.59c$$

and since we are assuming that the positron is at rest we neglect the ∇_ρ^2 term. Letting E_1 be the first-order perturbation of the energy E_0 we obtain:

$$\left[H_r + V \right] (\varphi_0 + \varphi^{pol}) = \left[E_0 + E_1 \right] (\varphi_0 + \varphi^{pol}) \tag{30}$$

Using equation (1.59a) and the result given by Sternheimer that $E_1 = (0|V|0) = 0$, the above equation reduces to:

$$\left[H_r - E_0 \right] \varphi^{pol} = -V\varphi_0$$

Substituting $\varphi_0 = \pi^{-\frac{1}{2}} e^{-r}$ and using equation (1.57b) we obtain:

$$\left[-\nabla_1^2 - \frac{2}{r_1} + 1 \right] \varphi^{pol}(\underline{r}_1, \underline{r}_\rho) = -\frac{2 r_1 e^{-r_1}}{\sqrt{\pi}} \cdot \frac{\cos\theta_{1\rho}}{r_\rho^2}$$

The substitution: $\varphi^{pol} = \frac{2}{\sqrt{\pi}} \cdot \frac{R(r_1)}{r_1} \cdot \frac{\cos\theta_{1\rho}}{r_\rho^2}$ gives:

$$\left[-\frac{d^2}{dr_1^2} - \frac{2}{r_1} + \frac{2}{r_1^2} + 1 \right] R(r_1) = r_1^2 e^{-r_1} \tag{1.60}$$

The solution to equation (1.60) has been given by Sternheimer (30) and is:

$$R(r_1) = \frac{e}{2}^{-r_1} \left(r_1^2 + \frac{r_1^3}{2} \right)$$

Therefore the expansion for φ^{pol} is given by:

$$\varphi^{pol}(\underline{r}_1, \underline{r}_\rho) = -\mathcal{E}(r_\rho, r_1) \frac{1}{\sqrt{\pi}} e^{-r_1} \left(r_1 + \frac{r_1^2}{2} \right) \frac{\cos\theta_{1\rho}}{r_\rho^2} \tag{1.61}$$

where $\xi(r_p, r_1) = 1$ if $r_p > r_1$

$= 0$ if $r_p < r_1$

Temkin[28] has shown that in the limit as $r_p \to \infty$ this technique for determining φ^{pol} is equivalent to first order perturbation theory. If we consider the total expansion of $V(\underline{r}_1, \underline{r}_p)$, equation (1.58) will be replaced by:

$$V(\underline{r}_1, \underline{r}_p) = -2 \sum_{\ell=1}^{\infty} \frac{r_1^{\ell}}{r_p^{\ell+1}} P_\ell(\hat{r}_1 \cdot \hat{r}_p) \qquad 1.62$$

and the corresponding expression for $\psi(\underline{r}_1, \underline{r}_p)$ is:

$$\psi(\underline{r}_1, \underline{r}_p) = \varphi_0(r_1) - \frac{e^{-r_1}}{\sqrt{\pi}} \sum_{\ell=1}^{\infty} \left(\frac{r_1^{\ell+1}}{\ell+1} + \frac{r_1^{\ell}}{\ell} \right) \frac{P_\ell(\cos\theta_{1p})}{r_p^{\ell+1}} \qquad r_p > r_1 \quad 1.63$$

Thus φ^{pol} is merely the dominant dipole term ($\ell=1$) of the asymptotic form of the first-order perturbation of the total wave function. The total wave function $\Psi(\underline{r}_1, \underline{r}_p)$ is given by:

$$\Psi(\underline{r}_1, \underline{r}_p) = \psi(\underline{r}_1) F_0(r_p)$$

It can readily be seen that substitution of this wave functioninto the variational methods described in Section 1.2 would produce terms quadratic in φ^{pol} which would invalidate the first-order perturbation theory. Thus Temkin and Lamkin[24] projected the Schroedinger wave equation onto the known part

of the asymptotic wave function as follows:

$$\int \varphi_0(r_1)\left[H-E\right]\Psi(\underline{r}_1,\underline{r}_\rho)\,d\underline{r}_1 = 0 \qquad 1.64$$

Thus the scattering length obtained from this method cannot be taken as an upper bound. Simplifying equation (1.64) we obtain the following equation:

$$\left[\nabla_\rho^2 + k_0^2\right] F_0(r_\rho) = \left[V_{00}(r_\rho) - \frac{\alpha}{r_\rho^4}\right] F_0(r_\rho) \qquad 1.65a$$

where $$\alpha = \frac{9}{2} - \frac{2}{3}e^{-2r_\rho}\left(r_\rho^5 + \frac{9}{2}r_\rho^4 + 9r_\rho^3 + \frac{27}{2}r_\rho^2 + \frac{27}{2}r_\rho + \frac{27}{4}\right) \qquad 1.65b$$

This is identical to equation (1.42a) except for the addition of the attractive potential $\frac{\alpha}{r_\rho^4}$. In the limit as $r_\rho \to \infty$ we see that $\alpha = 4.5$, the atomic polarizability of Hydrogen.

(a) Positron Hydrogen Collisions

Cody et al.[35] gave results for a close coupling expansion with the addition of the polarization potential. Two cases were considered:

(1) Mean Static Field.

(2) Virtual Positronium Formation.

The s-wave phase shift results are displayed in Table 1-4 where it can be seen that the polarization potential is sufficiently attractive to produce a negative scattering length in both cases.

Bransden[31] included virtual Positronium formation in

TABLE 1-4

Phase shifts for L=0 scattering of positrons by Hydrogen atoms. Row (a) static approximation + dipole polarization; row (b) ground state of Hydrogen and Positronium + dipole polarization; row (c) perturbation method: row (d) perturbation method minimizing the atomic energy; row (e) non-adiabatic; row (f) rigorous lower bound.

ka_o	0.0 †	0.1	0.2	0.3	0.4	0.5	0.6	Reference
(a)	-.267	.0803	.0853	.0528	.0048	-.0476	-.0989	25
(b)	-3.06	.2260	.2929	.2754	.2228	.1588	.0950	25
(c)	-	.044	.057	.022	-.051	-.144	-.236	31
(d) *	-1.276	.102	.111	.078	.031	-.027	-.082	32
(e)	-	.0022	.22	-	-	-	-	37
(f)	-	-	.1494	-	.0818	-	-.0272	43

† The zero-entries represent scattering lengths.

* This approximation is equivalent to the inclusion of all p states and the 2s state of Hydrogen.

the ground state by a perturbation procedure and calculated S- and P- wave phase shifts. The $L=0$ results are displayed in Table 1-4, the L=1 in Table 1-5.

An interesting method was formulated by Stone (32) who considered the distorted atomic wave function to be of the form given by perturbation theory. The total wave function is taken as:

$$\Psi(\underline{r}_1,\underline{r}_p) = \left[\varphi_0(r_1) + \beta(r_p)\psi_1(\underline{r}_1) + \alpha(r_p)\varphi_2(r_1)\right] F(\underline{r}_p) \qquad 1.66$$

where $\varphi_0(r_1)$ and $\varphi_2(r_1)$ are the 1s and 2s states of atomic Hydrogen respectively and $\alpha(r)$ and $\beta(r)$ are chosen such that the energy E_A of the atom is a minimum. Three cases were considered:

(1) $\alpha(r_p)=0$ and $\psi_1(\underline{r}_1) = \varphi_1(\underline{r}_1)$ the 2p state of Hydrogen.

(2) $\alpha(r_p)=0$ and $\psi_1(\underline{r}_1)=(r_1+\frac{r_1^2}{2})\cos\theta_{1p}$ the $\underline{r}_1$ part of φ^{pol} defined in equation (1.61). This corresponds to the addition of all p states of Hydrogen.

(3) $\alpha(r_p)\neq 0$ and $\psi_1(\underline{r}_1)=(r_1+\frac{r_1^2}{2})\cos\theta_{1p}$ which therefore includes all p states and the 2s state of Hydrogen.

To illustrate the method we will consider the simplest case, namely case (1). The functions $\varphi_n(\underline{r}_1)$ satisfy equation (1.39). Now consider the distorted Hydrogen atom with energy E_A. We have:

$$\left[-\nabla_1^2 - \frac{2}{r_1} + \frac{2}{r_p} - \frac{2}{|\underline{r}_1-\underline{r}_p|} - E_A\right]\left[\varphi_0(r_1) + \beta(r_p)\varphi_1(r_1)\right] = 0$$

Multiplying on the left by $[\varphi_0(r_1) + \beta(r_p)\varphi_1(r_1)]^*$ and integrating with respect to r_1 we obtain:

$$E_A = \frac{1}{2} \cdot \frac{\beta^2(r_p)\left[E_1 + V_{11}(r_p) + 2\beta(r_p)V_{01}(r_p) + E_0 + V_{00}(r_p)\right]}{\left(\beta^2(r_p) + 1\right)}$$

where $V_{ij}(r_p)$ is defined by equation (1.42b) Thus to minimize E_A we consider $\frac{\partial E_A}{\partial \beta} = 0$ which gives:

$$\frac{\beta}{1-\beta^2} = \frac{V_{01}}{E_0 - E_1 + V_{00} - V_{11}}$$

As $r_p \to \infty$, $\beta \to 0$ and the atom is left in the unperturbed ground state. Hence for large r_p, β^2 is small and V_{00} and V_{01} may be neglected. Therefore:

$$\beta \to \frac{V_{01}}{E_0 - E_1} = -\frac{1}{3} V_{01} \qquad r_p \to \infty \qquad 1.67$$

This is exactly the perturbation result obtained from equation (1.55) when only the 2p state is included. Therefore the Schroedinger wave equation will be:

$$\left[-(\nabla_1^2 + \nabla_p^2) - \frac{2}{r_1} + \frac{2}{r_p} - \frac{2}{|r_1 - r_p|} - E\right]\left[\left\{\varphi_0(r_1) + \beta(r_p)\varphi_1(r_1)\right\}F(r_p)\right] = 0$$

Premultiplying by $\varphi_0^*(r_1)$ and integrating over r_1 we obtain:

$$\left[\nabla_p^2 + E - E_o\right] F(\underline{r}_p) = \left[V_{oo}(r_p) + V_p(r_p) \right] F(\underline{r}_p) \qquad 1.68$$

where the polarization potential V_p is given by:

$$V_p(r_p) = -\beta(r_p)\, V_{o1}(r_p)$$

It can be seen that:

$$V_p(r_p) \underset{r_p \to \infty}{\sim} -\frac{4}{3} \left| V_{o1}(r_p) \right|^2$$

$$\underset{r_p \to \infty}{\sim} -\frac{2.96}{r_p^4}$$

By inspection of equation (1.65b) the total polarization potential for large r_p resulting from the inclusion of all p states is $-\frac{4.5}{r_p^4}$ and $-\frac{2.96}{r_p^4}$ is 65.8% of this in agreement with Castillejo et al.(18)

Equation (1.68) was solved by using the partial wave expansion as in the close coupling method. Exactly the same procedure is followed for cases (2) and (3). The $\ell=0$ phase shift for case (3) are displayed in Table 1-4 from which it may be concluded that this procedure gives equivalent results to the more complicated coupled equations method.

A modification of the close-coupling method that gives the correct dipole polarizability by explicitly including the polarization term of equation (1.61) was suggested by Damburg and Karule(33). If in the 1s-2s-2p approximation the term

R_{21} (see equation (1.56b) is replaced by:

$$C\left(\frac{r_1^3}{2} + r_1^2\right)e^{-r_1}$$

where C is a normalization factor and adjustment made to the corresponding energy, then the dipole polarization is fully accounted for without losing the lower bound on the phase shift. In addition an extra term whose atomic radial part contains:

$$\left(\frac{r_1^4}{3} + \frac{r_1^3}{2}\right)e^{-r_1}$$

will account for the quadrupole polarization.

(b) Positron Helium Collisions

Kraidy [27] added the Temkin-Lamkin polarization to the following cases:

(1) Mean static field.

(2) Virtual Positronium formation in the ground state.

As was to be expected from the positron Hydrogen results, the scattering length for both cases was negative, see Table 1-3. The Hylleraas function given by equation (1.54) gives a polarizability of 1.1 in comparison to the experimental value of 1.376. Calculations (1) and (2) were repeated using this "modified" dipole term and the phase shifts increased accordingly.

Similar calculations to case (1) by Massey, Lawson and Thompson[34] using the numerical Hartree Fock Helium function produced elastic cross-sections slightly larger than those of Kraidy.[27] This was to be expected since the Hartree Fock Helium function gives a polarizability of 1.56 so increasing the attractive polarization term.

A scattering length calculation including the dipole and quadrupole distortion terms of the Helium atom was performed by Hashino[35]. The Helium ground state function of Green et al.[20] defined in equation (1.38a), was used in the Kohn and Hulthen variational methods. The best value of the scattering length was -.546.

1.6 Expansion in Sturmian Functions

The Sturmian functions $S_{n\ell}(r)$ are a complete basis without a continuum and are the solutions of the following equation:

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} - \alpha_{n\ell}\cdot V(r) + E_0\right] S_{n\ell}(r) = 0 \qquad 1.69$$

where E_0 is a fixed negative number and the eigenvalue $\alpha_{n\ell}$ is chosen to ensure that $S_{n\ell}(0)=0$ and $S_{n\ell}(r)$ decays exponentially for aymptotic r. If V(r) is the potential energy of the system and E_0 the ground state binding energy then $\alpha_{10}=1$ and S_{10} equals the ground state radial function. This is the only Sturmian function that equals a physical wave function.

The normalization of the $S_{n\ell}$ is such that:

$$\int S_{n\ell}(r)\,\big|\,V(r)\,\big|\,S_{n'\ell}(r)\,dr = \delta_{nn'} \qquad 1.70$$

Instead of the expansion given by equation (1.38) we use:

$$\Psi(r_1,r_2) = \sum_{n\ell_1\ell_2} \frac{S_{n\ell_1}(r_1)}{r_1}\,\frac{\psi_{\ell_2}^{n\ell_1}(r_2)}{r_2}\,\mathcal{Y}^{M}_{\ell_1\ell_2 L}(\hat{r}_1,\hat{r}_2) \qquad 1.71a$$

where $$\mathcal{Y}^{M}_{\ell_1\ell_2 L}(\hat{r}_1,\hat{r}_2) = \sum_{m_1,m_2} Y_{\ell_1 m_1}(\hat{r}_1)\,Y_{\ell_2 m_2}(\hat{r}_2)\,C(\ell_1\ell_2 L; m_1 m_2 M) \qquad 1.71b$$

where $C(\ell_1\ell_2 L; m_1 m_2 M)$ is a Clebsch Gordan coefficient defined in Section 2.4b and L is the total angular momentum of the

system.

Substituting equation (1.71a) into (1.41) we obtain:

$$\sum_{n\ell_1\ell_2}\left[-\frac{\partial^2}{\partial r_1^2}-\frac{\partial^2}{\partial r_p^2}+\frac{\ell_1(\ell_1+1)}{r_1^2}+\frac{\ell_2(\ell_2+1)}{r_p^2}-\frac{2}{r_1}+\frac{2}{r_p}-\frac{2}{\rho}-E\right]S_{n\ell_1}(r_1)\psi_{\ell_2}^{n\ell_1}(r_p)\mathcal{Y}_{\ell_1\ell_2 L}^{M}=0 \qquad 1.72$$

The Sturmian equation for positron Hydrogen scattering is:

$$\left[\frac{d^2}{dr^2}-\frac{\ell(\ell+1)}{r^2}+\lambda_{n\ell}\cdot\frac{2}{r}+E_0\right]S_{n\ell}(r)=0$$

Substituting this into equation (1.72) we obtain the

$$\sum_{n\ell_1\ell_2}\left[-\frac{\partial^2}{\partial r_p^2}+\frac{\ell_2(\ell_2+1)}{r_p^2}+\frac{2}{r_p}+\frac{2}{r_1}(\lambda_{n\ell_1}-1)-\frac{2}{\rho}-(E-E_0)\right]S_{n\ell_1}\psi_{\ell_2}^{n\ell_1}\mathcal{Y}_{\ell_1\ell_2 L}^{M}=0$$

Multiplying on the left by $S_{n'\ell_1'}(r_1)\frac{2}{r_1}\mathcal{Y}^{M\,*}_{\ell_1'\ell_2' L}$, integrating with respect to r_1, $\hat{r}_1$, $\hat{r}_p$ and using equation (1.70) with $V(r)=\frac{-2}{r}$ we obtain:

$$\left[-\frac{d^2}{dr_p^2}+\frac{\ell_2(\ell_2+1)}{r_p^2}-(E-E_0)\right]\psi_{\ell_2}^{n\ell_1}(r_p)+4\sum_{n'}(\lambda_{n'\ell_1}-1)\int\frac{S_{n\ell_1}S_{n\ell_1}}{r^2}dr\cdot\psi_{\ell_2}^{n'\ell_1}(r_p)$$

$$+\sum_{n'\ell_1'\ell_2'}U_L(n\ell_1\ell_2;n'\ell_1'\ell_2';r_p)\cdot\psi_{\ell_2'}^{n'\ell_1'}=0 \qquad 1.73a$$

where

$$U_L(n,\ell_1,\ell_2;n'\ell_1'\ell_2';r_p)=$$

$$\sum_{n'\ell_1'\ell_2'} \int dr_1\, d\hat{r}_1\, d\hat{r}_\rho\, S_{n\ell_1}(r_1)\, \mathcal{Y}^M_{\ell_1\ell_2 L}\, \frac{4}{r_1}\left[\frac{1}{r_\rho} - \frac{1}{\rho}\right] S_{n'\ell_1'}(r_1)\, \mathcal{Y}^M_{\ell_1'\ell_2' L}. \qquad 1.73b$$

U_L can be simplified by performing the angular integrations as shown in Section 2.4 for the positron Helium problem.

(a) Positron Hydrogen Collisions

Rotenberg's (36) phase shifts obtained from the above Sturmian expansion were in good agreement with the variational results of Schwartz.(11) As in the usual eigenfunction expansion, the ρ Sturmian functions had a large effect on the phase shifts. The Sturmian function expansion gives very good convergence in comparison to close coupling but unfortunately no bound theorems exist for this case.

1.7 Non-Adiabatic Theory

Temkin [37] applied a non-adiabatic method to positron Hydrogen scattering. Considering the Schroedinger wave equation (1.41) the total s-wave function $\Psi(\underline{r}_1, \underline{r}_p)$ can be expanded in terms of the Legendre polynomial P_ℓ as follows:

$$\Psi(\underline{r}_1, \underline{r}_p) = \frac{1}{r_1 r_p} \sum_{\ell=0}^{\infty} (2\ell+1)^{\frac{1}{2}} \Phi_\ell(r_1, r_p) P_\ell(\cos\theta_{1p}) \qquad 1.74$$

where θ_{1p} is the angle between $\underline{r}_1$ and $\underline{r}_p$. Therefore the Schroedinger equation simplifies to:

$$\left[\Delta_{1p} - \ell(\ell+1)\left(\frac{1}{r_1^2} + \frac{1}{r_p^2}\right) - \frac{2}{r_p} + \frac{2}{r_1} + V_{ee}(r_1, r_p) + E\right]\Phi_\ell = -\sum_{m\neq\ell} V_{\ell m}\Phi_m \qquad 1.75$$

where $$\Delta_{1p} = \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_p^2}$$

$$V_{\ell m} = \left[(2\ell+1)(2m+1)\right]^{\frac{1}{2}} \sum_{n=0}^{\ell+m} \gamma_n C_{\ell m n}$$

and $$C_{\ell m n} = \int_0^{\pi} P_\ell(\cos\theta) P_m(\cos\theta) P_n(\cos\theta) \sin\theta \, d\theta$$

where $$\gamma_n = \left(\frac{r_<}{r_>}\right)^n \frac{1}{r_>}$$

$r_< = r_1$, $r_> = r_p$ if $r_1 < r_p$

$r_< = r_p$, $r_> = r_1$ if $r_1 > r_p$

We write $\Phi_\ell = \Phi_\ell^<$ if $r_p < r_1$

$= \Phi_\ell^>$ if $r_p > r_1$

For $\ell = 0$ we have that $C_{omn} = \frac{2}{2m+1}\delta_{mn}$ and equation (1.73) reduces to the following two equations:

$$\left[\Delta_{1p} - \frac{2}{r_p} + \frac{4}{r_1} + E\right]\Phi_0^< = -2\sum_m (2m+1)^{-\frac{1}{2}} \frac{r_p^m}{r_1^{m+1}} \Phi_m^< \qquad 1.76a$$

$$\left[\Delta_{1p} + \frac{2}{r_1} + E\right]\Phi_0^> = -2\sum_m (2m+1)^{-\frac{1}{2}} \frac{r_1^m}{r_p^{m+1}} \Phi_m^> \qquad 1.76b$$

Φ_ℓ satisfies the following boundary conditions:

$$\Phi_\ell(r_1, 0) = \Phi_\ell(0, r_p) = 0 \qquad 1.77a$$

$$\Phi_{\ell\cdot}(r_1, r_p) \underset{r_p\to\infty}{\sim} \sin(kr_p + \delta) R_{10}(r_1).\delta_{\ell 0}$$

$$\underset{r_1\to\infty}{\sim} 0 \qquad 1.77b$$

where $R_{10}(r_1) = \pi^{-\frac{1}{2}} r_1 e^{-r_1}$ is r_1 times the ground state Hydrogen function. Φ_ℓ also satisfies the following continuity conditions:

$$\left[\Phi_\ell^<\right]_{r_1=r_p} = \left[\Phi_\ell^>\right]_{r_1=r_p}$$

$$\left[\frac{\partial}{\partial n}\Phi_\ell^<\right]_{r_1=r_p} = \left[\frac{\partial}{\partial n}\Phi_\ell^>\right]_{r_1=r_p}$$

As a first approximation the coupling terms on the right hand sides of equation (1.76) are neglected to give a zero- order solution $\Phi_0^{(0)}$. Performing the usual pre-multiplication, subtraction and integration of this equation and equation (1.76) and simplifying using Green's Theorem, the following expression for the exact phase shift δ is obtained:

$$\sin(\delta-\delta_0) = \frac{1}{k}\sum_{m=1}^{\infty} 2(2m+1)^{-\frac{1}{2}} \int_0^{\infty}\int_0^{\infty} dr_1 dr_p \Phi_0^{(0)} \gamma_m \Phi_m \qquad 1.78$$

where δ_0 is the zero-order phase shift and $\gamma_m = \frac{r_<^m}{r_>^{m+1}}$.

Since the right hand sides of equations (1.76) will not be negligible for $r_1 \doteq r_p$, the zero-order solution will not give good results in this region. Therefore Temkin (37) considered equations (1.76) for $m=0$ and 1 and substituted the zero-order solution $\Phi_0^{(0)}$ in the coupling term of the equation to produce a $\Phi_1^{(0)}$. The forms of Φ_1 and Φ_0 were chosen as:

$$\Phi_0 = \Phi_0^{(0)} \{1 + C_0 g(r_1, r_p)\} \qquad 1.79a$$

$$\Phi_1 = \Phi_1^{(0)} \{1 + C_1 g(r_1, r_p)\} \qquad 1.79b$$

where $$\Phi_1^{(0)} = \frac{2}{\sqrt{3}} \frac{\sin(kr_p+\delta_0)}{r_p^2+D} R_{10}(r_1) \left\{\frac{r_1^2}{2} + r_1\right\} \qquad 1.79c$$

and $$g(r_1, r_p) = \frac{r_1}{r_p} e^{-\frac{r_1}{r_p}} \qquad 1.79d$$

and D is a parameter. Three types of expansion were considered for $\Phi_0^{(0)}$:

(1) 1s-2s-3s close coupling expansion

(2) the Sturmian functions S_{10}, S_{20} and S_{30} replacing 1s-2s-3s Hydrogen functions

(3) the same Sturmian expansion as in case (2) except that

$$\Phi_1^{(0)} = \frac{2}{\sqrt{3}} \frac{u_1(r_p)}{r_p^2 + D} R_{10}(r_1) \left\{ \frac{r_1^2}{2} + r_1 \right\}$$

where $u_1(r_p)$ is the coefficient of $S_{10}(r_1)$ in the Sturmian expansion. The phase shifts for k=.2 were as follows:

Case (1) .0359

Case (2) .224

Case (3) .219

Since Schwartz's[11] result at this k-value is +.135, the inadequacy of close coupling expansion using s-states only is emphasised.

The non-adiabatic theory can be extended to higher partial waves by defining the Lth partial wave function as:

$$\Psi_L(r_1, r_p) = \frac{1}{r_1 r_p} \sum_{l_1 l_2} \Phi_{l_1 l_2}^{(L)}(r_1, r_p) \mathcal{Y}_{l_1 l_2 L}^{M_L}(\hat{r}_1, \hat{r}_p)$$

Temkin[37] calculated p-wave phase shifts by retaining terms in the Schroedinger equation in Φ_{10} and Φ_{01} only.

There was no agreement between these and Bransden's (31) perturbation results, see Table 1-5.

1.8 Bounds on the Reactance Matrix.

(a) The Optical Potential Model (38)

The essence of this method is to reduce the many-body problem to an equivalent one-body problem with a suitable potential term. We first introduce the concept of projection operators. Two operators P and Q are defined such that P projects on to the ground state of the target and Q on to the excited states. If $\Psi(\underline{r}_1, \underline{r}_p)$ is the total wave function in a positron Hydrogen collision then:

$$P\Psi(\underline{r}_1, \underline{r}_p) \underset{r_p \to \infty}{\sim} \varphi_{10}(r_1) \frac{Y_{LM}(\hat{r}_p)}{r_p} \sin\left(kr_p - \frac{L\pi}{2} + \eta\right) \qquad 1.80$$

where φ_{10} is r_1 times the ground state Hydrogen function defined in equations (1.39). Thus:

$$P\Psi(\underline{r}_1, \underline{r}_p) \underset{r_p \to \infty}{\sim} \Psi(\underline{r}_1, \underline{r}_p)$$

The operator Q is therefore given by:

$$Q = 1 - P \qquad 1.80a$$

and $$P\varphi = 0 \qquad 1.80b$$

Now consider the Schroedinger equation:

$$[H-E][P+Q]\Psi(\underline{r}_1,\underline{r}_p) \quad 0$$

This can be expressed as a pair of coupled equations by operating either with a P or a Q from the left giving:

$$P[H-E][P+Q]\Psi = 0 \qquad 1.81a$$

$$Q[H-E][P+Q]\Psi = 0 \qquad 1.81b$$

Using equation (1.80b) and the fact that $Q^2 = Q$, equation (1.81b) may be solved for $Q\Psi$ as follows:

$$Q\Psi = -G^Q(E)QHP\Psi \qquad 1.81c$$

where $G^Q(E)$ is the Green's function of the operator $[Q(H-E)Q]^{-1}$. Substituting this into equation (1.81a) gives:

$$P[H+V_{opt}-E]P\Psi = 0 \qquad 1.82a$$

where $$V_{opt} = -PHQ\ G^Q(E)\ QHP \qquad 1.82b$$

Equation (1.82a) is a one-body problem with the potential term V_{opt} known as the optical potential. It should be emphasised that the expression for the optical potential

is purely formal because of the term $[Q(H-E)Q]^{-1}$. Q projects on to an infinite dimensionless space, thus in practice this reciprocal operator cannot be determined. Equation (1.81a) can also be solved for $P\Psi$.

$$P\Psi = P\Psi_p + \frac{1}{P(E-H)P} PHP\Psi \qquad 1.83a$$

where $P\Psi_p$ is the wave function satisfying:

$$P[H-E]P\Psi_p = 0 \qquad 1.83b$$

These are precisely the close coupling equations obtained by retaining open channels in the expression since the coupling to states outside of P is neglected by setting $Q=0$. Substituting equation (1.83a) into (1.81b) we obtain:

$$Q\left[H + HP\frac{1}{P(E-H)P}PH - E\right]Q\Psi = -QHP\Psi_p \qquad 1.84$$

The simplest form for the operator P is:

$$P = |\psi_0(r)\rangle\langle\psi_0(r)|$$

where $\psi_0(r)$ is the ground state of the target.

(b) Multi-Channel Reactions

We first consider a partial wave decomposition of the exact total wave function :

$$\Psi(\underline{r},\underline{x}) = \sum_m \psi_m(\underline{r})\, u_m(\underline{x}) \qquad 1.85$$

where $\psi_m(\underline{r})$ is the nth. state wave function of the target with associated energy E_m and the summation includes an integration over the continuum. We define a projection operator P that projects on to the set of M possible final states (both open and closed). Therefore in the ith. open channel we have:

$$P\Psi \underset{x_i\to\infty}{\sim} d_i\,\psi_i(\underline{r})\,\frac{1}{x_i}\left[a_i \sin\left(k_i x_i - \frac{L_i\pi}{2}\right) + b_i \cos\left(k_i x_i - \frac{L_i\pi}{2}\right)\right]$$

where L_i is the total orbital angular momentum quantum number in the ith. channel, d_i contains the spherical harmonic functions in $\hat{x}_i$ and Clebsch Gordan coefficient required to give the correct orbital angular momentum and a_i and b_i satisfy:

$$b_i = \sum_j R_{ij}\, a_j$$

where R is now the multi-channel R-matrix, and j runs over all open channels. Hence:

$$P\Psi \underset{x_i\to\infty}{\sim} d_i \psi_i(\underline{r}) \sum_j a_j \left[\sin(k_j x_j - \frac{L_j\pi}{2}) \cdot \delta_{ij} + R_{ij} \cos(k_j x_j - \frac{L_j\pi}{2}) \right] \frac{1}{x_i}$$

We now consider the approximate function Ψ^P formed by truncating the infinite sum in equation (1.85):

$$\Psi^P(\underline{r},\underline{x}) = \sum_m \psi_m(\underline{r}) u^P_m(\underline{x}) \qquad 1.86$$

where m runs over all the M coupled channels, N of which are open. The asymptotic boundary conditions are now:

$$P\Psi^P \underset{x_i\to\infty}{\sim} d_i \psi_i(\underline{r}) \sum_j a_j \left[\sin(k_i x_i - \frac{L_i\pi}{2}) \delta_{ij} + R^P_{ij} \cos(k_j x_j - \frac{L_j\pi}{2}) \right] \frac{1}{x_i}$$

Hahn, O'Malley and Spruch (39) imposed this boundary condition and the following:

$$\int \psi_m(\underline{r}) \left[H-E\right] \Psi^P(\underline{r},\underline{x})\, d\underline{r} = 0$$

for each value of m in the sum of equation (1.86) and obtained the following set of M equations:

$$P\left[H-E\right] P\Psi^P = 0$$

By writing the Hamiltonian H as:

$$H(\underline{r},\underline{x}) = H_r(\underline{r}) + T(\underline{x}) + V(\underline{r},\underline{x})$$

where H_T is the target Hamiltonian, T the kinetic energy operator of the incident particle and V the interaction of the incident particle with the target, equation (1.82a) reduces to:

$$\left[(T(\underline{x}) - E)I + \mathcal{U}(\underline{x}) + \underline{E}_T \right] \underline{u}(\underline{x}) = 0$$

where I is the MxM matrix, E_T the diagonal matrix with elements E_m, $\underline{u}(\underline{x})$ the column matrix with elements $u_m(\underline{x})$ and $\mathcal{U}(\underline{x})$ the optical matrix potential given by:

$$\mathcal{U}(\underline{x}) = \int d\underline{r}\, \psi_T(\underline{r}) \left[V + VQ \frac{1}{Q(E - H_T - T) - QVQ} QV \right] \underline{\Phi}_T^{\dagger}(\underline{r})$$

where $\psi_T(\underline{r})$ is a column vector with elements $\psi_m(\underline{r})$. By introducing the (MxM) matrix $\mathcal{U}(\underline{x},\lambda)$ where:

$$\mathcal{U}(\underline{x},\lambda) = \int d\underline{r}\, \psi_T(\underline{r}) \left[V + \lambda VQ \frac{1}{Q(E - H_T - T) - \lambda QVQ} QV \right] \psi_T^{\dagger}(\underline{r})$$

Hahn et al.[39] showed that $\frac{d\mathcal{U}(\underline{x},\lambda)}{d\lambda}$ was a negative definite operator and therefore $\frac{dR(\lambda)}{d\lambda}$ was positive definite where it exists. It follows that for a single open channel where $R^p = \tan \eta^p$

$$\eta^p \leq \eta$$

where η is the true phase shift. This expression is valid for all energies less than that at which the next channel would become open. The theory is easily extended to show that the addition of more virtual excited states of the target will give an improved phase shift. If inelastic channels are open then it can be easily shown that:

$$\eta^{j(p)} \leq \eta^{j}$$

where η^{j} is the jth. eigenphase shift. This result has also been obtained by McKinley and Macek[40] who considered the explicit form of the coupled equations (1.83b) and also by Gailitis[41] who considered an energy where both elastic and inelastic scattering was possible. If the projectile kinetic energy is sufficient to excite the first m lowest states of the target then the projection operator P can be defined as:

$$P = \sum_{i=1}^{m} |\psi_i\rangle\langle\psi_i|$$

where ψ_i is the wave function of the ith. atomic state. Thus if the trial function Ψ^t is chosen as:

$$\Psi^t(r_1, r_p) = \sum_{i=1}^{m} F_i(r_p)\psi_i(r_1) + \sum_{j=1}^{n} c_j \Phi_j(r_1, r_p) \qquad 1.87$$

subject to the conditions:

$$\int \psi_i(\underline{r}) \Phi_j(\underline{r}_1, \underline{r}_p) d\underline{r}_1 = 0 \qquad \text{for} \quad i = 1, \ldots, m \qquad 1.88a$$

$$\text{and} \quad \int | \Phi_j(\underline{r}_1, \underline{r}_p) | d\underline{r}_1 d\underline{r}_p < \infty \qquad \text{for} \quad j \quad 1, \ldots, n \qquad 1.88b$$

then the reactance matrix R satisfies a lower bound principle.

(b) Positron Hydrogen Collisions

Hahn, O'Malley and Spruch [42] derived a minimum principle for single channel scattering by considering equation (1.84) and by using the basic inequality:

$$k\cot(\eta_0 - \theta) \leq k\cot(\eta_0(M.P.) - \theta) \qquad 1.89a$$

where $$k\cot(\eta_0(M.P.) - \theta) = k\cot(\eta_0^P - \theta) + 4(Q\Psi_t, Q H P \Psi^P)$$

$$+ 2\left(Q\Psi_t, Q\left[H + HP\frac{1}{P(E-H)}PH - E\right]Q\Psi_t\right) \qquad 1.89b$$

where θ satisfies $0 \leq \theta \leq \pi$ but is otherwise arbitrary, Ψ_t is the trial wave function and Ψ^P the exact solution of equation (1.83b) with phase η_L^P. (a,b) denotes the inner product of a and b. Solutions for L=0 and incident energies less than 6.8eV - the threshold for Positronium formation - are given by Hahn and Spruch [43] who define P as follows: for an arbitrary function $f(r_1, r_p, \theta_{1p})$:

$$P f(r_1, r_p, \theta_{1p}) = \frac{1}{2}\varphi_0(r_1)\int \varphi_0(r_1') f(r_1', r_p, \theta_{1p}') r_1'^2 dr_1' d(\cos\theta_{1p})$$

Therefore the expressions for $P\Psi^P$ and $Q\Psi_t$ are:

$$P\Psi^P = \varphi_0(r_1)\frac{u_0^P(r_p)}{r_p} \qquad 1.90a$$

$$Q\Psi_t = \sum_{\ell,i} C_{\ell i}\chi_{\ell i}(r_1)\omega_{\ell i}(r_p)\frac{P_\ell(\cos\theta_{1p})}{r_1 r_p} \qquad 1.90b$$

where $$\chi_{\ell i}(r_1) = r_1^{\ell+1} e^{-b_{\ell i} r_1} - \frac{8 r_1}{(1+b_{0i})^3} e^{-r_1}\delta_{0\ell} \qquad 1.90c$$

and $$\omega_{\ell i}(r_p) = r_p^{\ell+1} e^{-d_{\ell i} r_p} \qquad 1.90d$$

P and Q are orthogonal since $\chi_{\ell i}$ has been chosen orthogonal to φ_0 for $\ell=0$ and the Legendre polynomial P_ℓ ensures the orthogonality for $\ell\neq 0$. Hahn and Spruch[43] chose $\theta=(\frac{\pi}{2}+\eta_0^P)$ thereby reducing equation (1.89b) to:

$$k\tan(\eta_0-\eta_0^P) \geq -\Delta \geq 0$$

where $$\Delta = 4(Q\Psi_t, QHP\Psi^P) + 2\left(Q\Psi_t, Q\left[H + HP\frac{1}{P(E-H)}PH - E\right]Q\Psi_t\right)$$

The coefficients $C_{\ell i}$ in equation (1.90b) are chosen by

minimizing Δ . If we substitute $b_{\ell i} = n^{-1}$ in equation (1.90c) $\chi_{\ell i}$ will contain some excited states of the Hydrogen atom (those with $\ell = n-1$). Using this substitution and taking:

$$d_{\ell i} = d_{\ell, i-1} + (.1)i \qquad i = 1, 2, \ldots\ldots, 9$$

where $d_{\ell 0} = .2$, Hahn and Spruch[43] obtained phase shifts equal to or slightly lower than the close coupling results of McEachran et al.[23] By varying the parameters $b_{\ell i}$ and $d_{\ell i}$ in equations (1.90) rigorous lower bounds on η_0 were obtained. These are presented in Table 1-4 and show that Bransden's[31] perturbation results for L=0 are extremely poor and those of Stone[32] are too small.

Kleinman, Hahn and Spruch[44] extended the minimum calculation for total orbital angular momentum L=1 and 2 by suitably modifying the expressions for $P\Psi^P$ and $Q\Psi_t$. Again calculations with $b_{\ell i} = n^{-1}$ gave phase shifts in good agreement with close coupling and rigorous lower bounds were obtained by varying $b_{\ell i}$ and $d_{\ell i}$. Results for L=1 are displayed in Table 1-5 together with variational results of Armstead[45] who extended the Schwartz[11] variational formulation to P-wave scattering.

The minimum principle calculations clearly demonstrate the disadvantage of the close coupling method because of the slow convergence in ℓ - the angular momentum of the Hydrogen states - and also the principle quantum number n. Bransden's[31] L=0 perturbation results were much lower

TABLE 1-5

Phase shifts for L=1 scattering of positrons by Hydrogen atoms. Row (a) perturbation method; row (b) non-adiabatic method: row (c) rigorous lower bounds; row (d) extended polarization; row (e) variational; row (f) lower bound adiabatic calculation.

kao	0.1	0.2	0.3	0.4	0.5	0.6	Reference
(a)	.	.016	.	.104	.	.167	31
(b)	.002	.009	.018	.028	.037	.046	37
(c) †	.0082	.0289	.0548	.0801	.0994	.1117	44
(d)	.0072	.0226	.0370	.0458	.0468	.0408	49
(e)	.009	.033	.065	.102	.132	.156	45
(f)	.007	.026	.052	.076	.095	.109	30

† The expansion includes virtually excited Hydrogen states restricted to angular momenta ≤ 3.

than Hahn et al's.[43] and sometimes of the incorrect sign although the L=1 phase shifts are in reasonable agreement with Kleinman et al's.[44] for higher energies. Temkin's[37] non-adiabatic P-wave phase shifts are also lower than Kleinman et al's.[44] and are therefore a less accurate approximation.

It is clear that the minimum principle is extremely useful in deciding which of the many approximation methods produces the best phase shifts. The form of $Q\Psi_t$ chosen by Hahn et al.[43] and Kleinman et al.[44] is restrictive in the sense that the summation over ℓ must obviously be finite and a limited number of values of ℓ are therefore chosen. For L=0, contributions from $0 \leq \ell \leq 5$ were included whereas for L=1 and 2, $0 \leq \ell \leq 3$. But these phase shifts are still rigorous lower bounds on the true phase shifts.

1.9 Further Adiabatic Methods.

(a) Second Order Polarization Potential

In Section 1.5 it was noted that in the limit as $r_p \to \infty$, the method of Polarized Orbitals was equivalent to first order perturbation theory. The second order adiabatic potential V_2 is given by:

$$V_2(r_p) = -\sum_{\substack{m \\ m \neq 0}} \frac{(0|V|m)(m|V|0)}{E_m - E_0} \qquad 1.91$$

where $(0|V|m) = \int \varphi_0^*(r) V(r, r_p) \varphi_m(r) \, dr$

φ_m is the nth. excited state of the target and V is defined in equation (1.52). Dalgarno and Lewis[46] showed that equation (1.91) could be written as:

$$V_2(r_1) = (0|Vf|0) - (0|V|0)(0|f|0) \qquad 1.92a$$

where f satisfies:

$$\varphi_0 \nabla^2 f + 2\nabla f \cdot \nabla \varphi_0 = V\varphi_0 - (0|V|0)\varphi_0 \qquad 1.92b$$

This is easily derived[46] by considering the Schroedinger equations for φ_0 and φ_m:

$$\left[-\nabla^2 + V - E_0 \right] \varphi_0(r) = 0 \qquad 1.93a$$

$$\left[-\nabla^2 + V - E_m \right] \varphi_m(r) = 0 \qquad 1.93b$$

Pre-multiplying equation (1.93a) by φ_m^* and (1.93b) by φ_0 and subtracting the two gives:

$$(E_0 - E_m) \int f(r) \varphi_0 \varphi_m^* \, dr = \int \left[\varphi_0 \nabla^2 \varphi_m^* - \varphi_m^* \nabla^2 \varphi_0 \right] f(r) \, dr \qquad 1.94$$

where f is an arbitrary function. Using the relation:

$$\nabla^2(\varphi_0 f) = \varphi_0 \nabla^2 f + f \nabla^2 \varphi_0 + 2\nabla f \cdot \nabla \varphi_0$$

the right hand side of equation (1.94) can be written:

$$\int \left[f \varphi_0 \nabla^2 \varphi_m^* - \varphi_m^* \nabla^2 (\varphi_0 f) + \varphi_m^* (\varphi_0 \nabla^2 f + 2 \underset{\sim}{\nabla} f \cdot \underset{\sim}{\nabla} \varphi_0) \right] d\underset{\sim}{r}$$

Therefore if we choose f such that:

$$\varphi_0 \nabla^2 f + 2 \underset{\sim}{\nabla} f \cdot \underset{\sim}{\nabla} \varphi_0 = g \varphi_0$$

where $g(r)$ is an arbitrary function, Green's theorem can be applied to the right hand side of equation (1.94) to give:

$$(E_0 - E_m)(m|f|0) = (m|g|0)$$

Multiplying by $(0|g|m)$ and summing over m gives:

$$\sum_{m \neq 0} \frac{(0|g|m)(m|g|0)}{(E_0 - E_m)} = \sum_{m \neq 0} (m|f|0)(0|g|m)$$

We now apply the summation formula:

$$\sum_{q} (m|L|q)(q|M|m) = (m|LM|m)$$

where L and M are any dynamical variables and obtain:

$$\sum_{m \neq 0} \frac{(0|g|m)(m|g|0)}{(E_0 - E_m)} = (0|fg|0) - (0|f|0)(0|g|0)$$

If we choose $g(r) = V(r)$ then we obtain equations (1.92).

Dalgarno and Lynn[47] solved equation (1.92b) and evaluated (1.92a) exactly. For positron Hydrogen scattering the expression for V_2 is:

$$V_2(r) = r^{-2}\Big[\Big\{5-(4r^2+8r+10)e^{-2r}+(4r^3+7r^2+8r+5)e^{-4r}\Big\}$$

$$-2(r+1)^2(e^{-2r}+e^{-4r})\Big\{Ei(2r)-2\gamma-2\log(2r)\Big\}$$

$$-2E_i(-2r)\Big\{(r-1)^2e^{2r}+(r^2+2r-3)+4(r+1)e^{-2r}\Big\}\Big] \qquad 1.95$$

where $\gamma = .557215$ is Euler's constant and:

$$Ei(r) = -\int_{-r}^{\infty} \frac{e^{-x}}{x}\,dx$$

(b) An Adiabatic Approximation[48]

Referring to Section 1.5 the Hamiltonian for the positron Hydrogen system is given by equation (1.59c). Consider the following adiabatic wave function given by Drachman[48]:

$$\psi(\underline{r}_1,\underline{r}_\rho) = \Big[1+G(\underline{r}_1,\underline{r}_\rho)\Big]\varphi_0(r_1)F(\underline{r}_\rho) \qquad 1.96$$

where G is an adiabatic correlation function describing the distortion of the target and $F(\underline{r}_\rho)$ is the positron scattering function. Equation (1.96) is substituted into the Schroedinger equation, the usual premultiplication by φ_0 and integration over $\underline{r}_1$ performed to give:

$$-(1+\langle G\rangle)\left[\nabla_\rho^2+k^2\right]F+(\langle V\rangle+\langle GV\rangle)F=\left[\nabla_\rho^2\langle G\rangle+2\underset{\sim}{\nabla}_\rho\langle G\rangle\cdot\underset{\sim}{\nabla}_\rho\right]F \qquad 1.97$$

where $k^2 = E+1$ and use has been made of the fact that the function φ_0 is a bound state so that:

$$\langle\,[H_r, G]\,\rangle = 0$$

If G is now chosen such that $\langle G\rangle = 0$ then equation (1.97) reduces to:

$$\left[-(\nabla_\rho^2+k^2)+\langle V\rangle+\langle GV\rangle\right]F(\underset{\sim}{r}_\rho)=0 \qquad 1.98$$

Substituting $f=G$ in equation (1.92a) it follows that:

$$V_2 = \langle GV\rangle$$

and $$V_1 = \langle V\rangle$$

where V_1 is the familiar static potential. Therefore equation (1.98) becomes:

$$\left[-(\nabla_\rho^2+k^2)+V_1+V_2\right]F(\underset{\sim}{r}_\rho)=0$$

where V_1 and V_2 are defined in equations (1.53b) and (1.95) respectively.

(c) Positron Hydrogen Collisions

Drachman[48] used the adiabatic method just described to calculate low-energy S-wave phase shifts. These were larger than those of Schwartz[11] and the scattering length obtained was -2.54 showing that the polarization potential is too attractive. Since the adiabatic method is least accurate when the positron is near to the nucleus Drachman[48] modified the potential by considering the monopole term of V_2. $G(r_1, r_p)$ is expanded in terms of the Legendre polynomials:

$$G(r_1, r_p) = \sum_{m=0}^{\infty} G_m(r_1, r_p) P_m(\cos\theta_{1p})$$

and G_0, the monopole term, contains all the short-range effects of V_2 since terms for $m>0$ will contain inverse powers of r_p. G_0 satisfies:

$$\varphi_0 \nabla^2 G_0 + 2 \nabla G_0 \cdot \nabla \varphi_0 = (V_0 - \langle V_0 \rangle)\varphi_0 \qquad 1.99$$

where $V_0 = 2\left(\frac{1}{r_p} - \frac{1}{r_1}\right)$ for $r_p < r_1$

$= 0$ for $r_p > r_1$

Referring back to equation (1.92a) the expression for the potential V_{20} due to the perturbation V_0 is given by:

$$V_{20} = \langle V_0 g \rangle - V_1 \langle g \rangle$$

where $g_<$ and $g_>$ satisfy equation (1.99) for $r_p < r_1$ and $r_p > r_1$ respectively. In this case $\langle g \rangle \neq 0$. Drachman [48] repeated the adiabatic calculation by using the following expression for the full potential in the Schroedinger equation:

$$V_1 + V_2 + (\alpha - 1) V_{20}$$

where α is a parameter. Agreement with Schwartz's scattering length necessitated choosing $\alpha = .1$ and this value gave good agreement over the whole energy range up to the threshold for Positronium formation.

An alternative method of reducing the over attractive polarization potential near the origin was formulated by Callaway, LaBahn, Fu and Duxler [49] who calculated a repulsive correction term to the dipole polarization which falls off asymptotically as r_p^{-6}. For Hydrogenic wave functions, this term exactly cancelled with the monopole part of the polarization term at the origin. The S-wave phase shifts are presented in Table 1-6 and are considerably smaller than Schwartz's [11] showing that the correction term is too repulsive.

In order to apply the lower-bound principle of Gailitis [41], Drachman [48] defines a trial wave function as

TABLE 1-6

Phase shifts for L=0 scattering of positrons by Hydrogen atoms. Row (a) extended polarization; row (b) lower bound adiabatic; row (c) variational.

ka_o	0.0 †	0.1	0.2	0.3	0.4	0.5	0.6	Reference
(a)	-.783	.036	.0137	-.0352	-.0939	.1539	-.2112	49
(b)	-1.85	.127	.157	.134	.089	.034	-.022	50
(c)	-2.10	.151	.188	.168	.120	.062	.007	11

† The zero-entries represent scattering lengths.

follows:

$$\psi(r_1,r_2) = \left[H(r_2) + G(r_1,r_2)F(r_2) \right] \varphi_0(r_1) \qquad 1.100$$

where ψ satisfies equations (1.88). G is the usual correlation function satisfying equation (1.92b) and H contains short-range non-adiabatic terms. Substituting ψ into the Kohn variational expressions yields two coupled equations in F and H whose solution for L=0 gives phase shifts roughly 10% lower than those of Schwartz[11] with a scattering length of -1.85, see Table 1-6. The L=1 phase shifts presented in Table 1-5 are close to the lower bound results of Kleinman et al.[44]

By considering the effect on the S- and P- wave phase shifts of various multipole components of the adiabatic polarization potential, Bransden and Jundi[51] showed that the dipole and quadrupole components were the most important. The addition of these two components to the static interaction produced phase shifts less than Schwartz's but the further addition of the monopole component cancels the phase shifts to exceed those of Schwartz[11] thereby giving weight to Drachman's[48] argument of empirically suppressing this term for S-wave scattering.

The inclusion of Positronium states in a wave function expansion introduces special difficulties because the two different sets of centre of mass coordinates produce integral operators. In operator formalism this would require the

projection operator for separating out the two channels to be determined from an integral equation. An interesting alternative was suggested by Chen and Mittleman[52] who used the positron coordinate to label the Positronium. The ensuring coupled equations contain no integral operators but the centrifugal term $\frac{\ell(\ell+1)}{r_p^2}$ of the equation representing the closed Positronium channel is modified by the addition of an energy dependent term.

Fels and Mittleman[53] used this coordinate change and the projection operator P defined by Chen and Mittleman[52] which results in:

$$P\Psi(\underline{r}_1,\underline{r}_p) = \varphi_0(r_1)\,F(\underline{r}_p) + \omega_0(\rho_1)\,G(\underline{r}_p)\,e^{ik_2\hat{r}_p\cdot\frac{\rho}{2}}$$

where φ_0 and ω_0 are the ground state Hydrogen and Positronium functions respectively and $\frac{1}{2}k_2^2$ is the energy of the outgoing Positronium. This expression is substituted into equation (1.83b) with a partial wave expansion of F and G to produce two coupled ordinary differential equations. Terms such as:

$$\left(f_i \mid V_{opt} \mid f_j\right) \qquad i,j = 1,2$$

where $f_1(r_1) = \varphi_0(r_1)$ and $f_2(\rho_1) = \omega_0(\rho_1)e^{ik_2\hat{r}_p\cdot\frac{\rho_1}{2}}$ in the limit as $r_p \to \infty$ reduce to the polarization potentials of Hydrogen ($i=j=1$) and Positronium ($i=j=2$). The off-diagonal

terms vanish exponentially as $r_p \to \infty$. For above threshold energies Fels et al.[53] considered various types of polarization terms including the $\frac{-\alpha}{(r^2+d^2)^2}$ form[5] and a modification of the Temkin-Lamkin[29] form. The dominant P-wave partial elastic cross section was found to be very sensitive to the form of polarization and the inclusion of any of these terms reduced the total elastic cross section. The S-wave phase shift at threshold was a factor of six smaller than Schwartz's[11] and it may be concluded that the additional centrifugal term effectively makes the interaction less attractive so reducing the phase shift.

Bransden and Jundi[51] performed a two-state approximation calculation above threshold including various combinations of the monopole, dipole and quadrupole polarizations of Hydrogen and the dipole polarization of Positronium. A linear extrapolation of the M-matrix in the no-polarization case predicted values of the S-wave elastic phase shift below threshold in good agreement with Cody et al.[25] The elastic cross sections are smaller than the equivalent results of Fels and Mittleman[53] and near threshold were sensitive to the form of polarization.

A recent calculation of rigorous bounds on eigenphase shifts was performed by Hahn and Dirks[55] who used a generalized variational bounds formulation by Hahn.[56] The elastic cross sections were smaller than both Fels et al's[53] and Brandsen et al's[54] being somewhat closer

to the latter.

(d) Positron Helium Collisions

Drachman (57) applied the same procedure to the case of Helium choosing the function ψ as follows:

$$\psi(r_1, r_2, R_p) = \left[1 + C(G - G_0) + \alpha G_0 \right] \psi_0(r_1, r_2) F(R_p)$$

where ψ_0 is the ground state Helium function, G and G_0 the first and second order adiabatic correlation function and its monopole part respectively and C and α are parameters. The static potential V_1 was calculated using the two term analytic approximation to the best Hartree function which gave (56):

$$V_1(r) = \frac{1}{r}\left[5e^{-2.4915} - e^{-5.4741} \right]$$

whereas V_2 and V_{20}, calculated using the uncorrelated shielded Hydrogenic function defined by equation (1.54), are given by:

$$V_2^{\text{Helium}}(r) = 2V_2^{\text{Hydrogen}}(\mu r)$$

where V_2^{Hydrogen} is defined in equation (1.95) and $\mu = \frac{27}{16}$. With reference to part (a) it can be seen that a Hydrogenic ground state wave function must be chosen for the target atom if the Dalgarno-Lynn (47) method for calculating V_2

is to be used. C and α are chosen to ensure that V_2 has the correct polarizability.

The S-, P- and D- wave phase shifts are smaller than the close-coupling results of Kraidy [27]. The S-wave phase shifts are displayed in Table 1-7.

Kestner, Jortner, Cohen and Rice [59] used an effective potential evaluated in the adiabatic approximation but retained only the monopole, dipole and quadrupole terms. Their phase shifts are comparable to Drachman's [57] adiabatic results, with a best scattering length of -.575. No allowance for virtual Positronium formation was made.

Callaway et al. [49] calculated S-, P- and D- wave phase shifts for the following four cases:

(1) Mean static field

(2) Adiabatic approximation with dipole polarization

(3) Adiabatic approximation with monopole, dipole and quadrupole polarization

(4) Adiabatic approximation with "extended" polarization i.e., case (2) + correction terms.

The S-wave phase shifts for cases (2), (3) and (4) are presented in Table 1-7. Cases (2) and (4) produce smaller phase shifts than Drachman [57] whereas case (3) results are quite close to both Drachman's [57] and Kestner et al's. [59] Referring to the Hydrogen case, the extended polarization is probably too repulsive and this could perhaps be correc-

TABLE 1-7

Phase shifts for L=0 scattering of positrons by Helium atoms. Row (a) adiabatic + dipole polarization; row (b) adiabatic + monopole, dipole and quadrupole polarization; row (c) adiabatic + extended polarization; row (d) non-variational adiabatic with complete monopole suppression; row (e) variational.

ka_o	0.0*	0.1	0.2	0.3	0.4	0.5	0.6	Reference
(a)	-.437	.0293	.0092	.0178	.0268	.0348	.0409	49
(b)	-.697	.0539	.0781	.0802	.0675	.0457	.0185	49
(c)	-.202	.0069	-.0068	-.0304	-.0676	-.1057	-.1454	49
(d)	-.659	-.050	.072	.071	.056	.032	.002	57
(e)	-.511	.036	.047	.039	.020	-.007	-.039	50

* The zero-entries represent scattering lengths.

ted by addition of virtual Positronium terms which are known to be attractive.

Drachman [50] extended the lower bound calculations to Helium by defining a trial wave function as follows:

$$\psi(\underline{r}_1, \underline{r}_2, \underline{r}_\rho) = \left[H(\underline{r}_\rho) + G(\underline{r}_1, \underline{r}_2, \underline{r}_\rho) \right] \psi_0(\underline{r}_1, \underline{r}_2) F(\underline{r}_\rho)$$

where G satisfies:

$$\left[G, H \right] \psi_0(r_1, r_2) = \left(V - \langle V \rangle \right) \psi_0(\underline{r}_1, \underline{r}_2)$$

and H is the appropriate Hamiltonian. The ensuing S-wave phase shifts are displayed in Table 1-7. If the Helium wave function was exact these would be rigorous lower bounds and would show that Callaway et al's. [49] extended polarization results are too small. One immediate source of error is the use of the uncorrelated Hydrogenic function ψ_0 given by equation (1.54).

Fels and Mittleman [60] applied their coordinate change method using Clementi's analytic fit to the Hartree-Fock wave function:

$$\psi_0(r_1, r_2) = u(r_1)\, u(r_2)$$

where $$u(r) = \frac{1}{\sqrt{\pi}} \sum_{i=1}^{5} R_i \beta_i^{\frac{3}{2}} e^{-\beta_i r}$$

and A_i and ρ_i are defined by Fels et al.[60] The ground state Helium energy used was Schwartz's[61] variational value of -5.897448. The total elastic cross-sections above threshold for L=0 are a little higher than Kraidy's[27] virtual Positronium results but the L=1 are an order of magnitude larger. The addition of the Temkin-Lamkin potential reduced the cross-sections by two and the L=1 results are now smaller than those of Kraidy[27] allowing for the dipole polarization.

1.10 Resonances in Positron atom scattering

(a) Resonance Mechanisms

A resonance can be interpreted as a quasi-bound state of the compound system of the target and projectile. At a resonance energy the phase shift increases by π and the cross sections exhibit the familiar Breit-Wigner[86] profile.

With reference to Section 1.8(a) we consider the solution of equation (1.82a):

$$P\left[H-E\right]P\Psi = PH\Phi\, G^{\Phi}(E)\, \Phi HP\Psi \qquad 1.101$$

A set of functions Φ_n which are eigenfunctions of the operator QHQ with eigenvalues ε_n^{Φ} can be introduced:

$$\left[\Phi H\Phi - \varepsilon_n^{\Phi}\right]\Phi_n(r_1, r_2) = 0 \qquad 1.102$$

Since these functions span Q-space we may use:

$$\sum_n |\Phi_n\rangle\langle\Phi_n| = Q$$

where $\sum_n$ denotes a sum over the discrete and an integration over the continuous spectrum. Since for simplicity we are considering only one open channel, below the energy of the Positronium formation threshold (E_{ps}), the only non-zero part of the total wave function is $P\Psi$, thus QHQ will possess a discrete spectrum (bound states) in this energy region with eigenfunctions Φ_n that vanish as $r_p \to \infty$. For energies $\mathcal{E}_n^Q > E_{ps}$ the Φ_n do not vanish asymptotically and the eigenvalues $\mathcal{E}_n^Q$ form a continuous spectrum.

$G^Q(E)$ is now expanded in terms of the Φ_n as follows:

$$G^Q(E) = \sum_n \frac{|\Phi_n\rangle\langle\Phi_n|}{(\mathcal{E}_n^Q - E)} \qquad 1.103$$

Thus equation (1.101) may be written as:

$$P[H-E]P\Psi = \sum_n \frac{H_{PQ}|\Phi_n\rangle\langle\Phi_n|H_{QP}}{(\mathcal{E}_n^Q - E)} \cdot P\Psi$$

where the notation used is H_{PQ} = PHQ and H_{QQ} = QHP etcetera. Consider the case when E is close to an eigenvalue $\mathcal{E}_s^Q$ of H_{QQ} and re-write equation (1.103) as follows:

$$[H'-E]P\Psi = \frac{H_{PQ}|\Phi_s\rangle\langle\Phi_s|H_{QP}|}{(\mathcal{E}_s^Q - E)} \cdot P\Psi \qquad 1.104a$$

where $H' = H_{pp} - \sum_{n \neq s} \frac{|H_{p\varphi}|\Phi_n\rangle\langle\Phi_n|H_{\varphi p}|}{(\mathcal{E}_n^{\varphi} - E)}$ 1.104b

The formal solution to equation (1.104a) is:

$$P\Psi = P\Psi_0 - \frac{1}{(\mathcal{E}_s^{\varphi} - E)} G' |H_{p\varphi}|\Phi_s\rangle\langle\Phi_s|H_{\varphi p}| \cdot P\Psi \qquad 1.105$$

where $[H' - E]\, P\Psi_0 = 0$

and Ψ_0 satisfies equation (1.80) with η_0 replacing η. The Green's function G' of the operator $[H' - E]^{-1}$ can be written in standing wave form in terms of a product of a regular and irregular solution:

$$G'(\xi_1, \xi_p; \xi_1', \xi_p') \underset{r_p \to \infty}{\sim} -\sqrt{\frac{2\pi}{k}} \frac{\varphi_0(r_1) Y_{LM}(\hat{r}_p) \cos(kr_p - \frac{L\pi}{2} + \eta_0)}{r_p} P\Psi_0(\xi_1', \xi_p') \qquad 1.106$$

Multiplying equation (1.105) on the left by $\langle \Phi_s | H_{\varphi p}|$ and rearranging we obtain:

$$\langle \Phi_s | H_{\varphi p} | \psi \rangle = \frac{\langle \Phi_s | H_{\varphi p} | \Psi_0 \rangle}{1 + (\mathcal{E}_s^{\varphi} - E)^{-1} \langle \Phi_s | H_{\varphi p} G H_{p\varphi} | \Phi_s \rangle}$$

and substituting this into equation (1.105) gives:

$$P\Psi = P\Psi_0 + \frac{G' |H_{p\varphi}|\Phi_s\rangle\langle\Phi_s|H_{\varphi p}|\Psi_0\rangle}{E - \mathcal{E}_s^{\varphi} - \Delta_s} \qquad 1.107a$$

where $\Delta_s = \langle \Phi_s | H_{QP} G' H_{PQ} | \Phi_s \rangle$ 1.107b

and Δ_s is the shift in energy from $\mathcal{E}_s^Q$ caused by interaction with the continuum term Φ_o.

Using equations (1.80) and (1.106) the asymptotic form of $P\Psi$ will be:

$$P\Psi \underset{r_p \to \infty}{\sim} \sqrt{\frac{2}{\pi k}} \varphi_{10}(r_1) \frac{Y_{LM}(\hat{r}_p)}{r_p} \frac{\sin\left(kr_p - \frac{L\pi}{2} + \eta_o + \eta_r\right)}{\cos \eta_r} \qquad 1.108a$$

where $$\tan \eta_r = \frac{-\frac{1}{2}\Gamma_s}{E - \mathcal{E}_s^Q - \Delta_s} \qquad 1.108b$$

and $$\tfrac{1}{2}\Gamma_s = \pi \left| \langle \Phi_o | H_{PQ} | \Phi_s \rangle \right|^2$$

The resonance position E_r can be seen to equal $(\mathcal{E}_s^Q + \Delta_s)$. The total phase shift is $(\eta_o + \eta_r)$ and if it is assumed that the level shifts Δ_s are small, the resonance energies can be determined by a calculation of the eigenvalues of H_{QQ}.

Operating on the left of equation (1.102) with $\langle \Phi_s | Q = \langle \Phi_s | Q^2$ gives:

$$\langle \Phi_s | H_{QQ} | \Phi_s \rangle = \mathcal{E}_s^Q \langle \Phi_s | Q^2 | \Phi_s \rangle \qquad 1.109a$$

which by the Hermiticity of Q and QH can be written:

$$\langle Q\Phi_s | H | Q\Phi_s \rangle = \mathcal{E}_s^{\mathcal{P}} \langle Q\Phi_s | Q\Phi_s \rangle \qquad 1.109b$$

A trial wave function $Q\Phi$ can now be chosen for substitutions into a variational calculation.

(b) Resonances in positron Hydrogen scattering

Mittleman (63) employed a projection operator (64) that projected out the ground state of Hydrogen and Positronium to investigate the resonance structure just below the n=2 level of Hydrogen. The trial wave function $Q\Phi_t$ was chosen as:

$$Q\Phi_t = \sum_{\substack{\ell_1 m_1 \\ \ell_2 m_2}} \varphi_{2\ell_1}(r_1)\, C(\ell_1 \ell_2 L; m_1 m_2 M)\, Y_{\ell_2 m_2}(\hat{r}_p)\, \frac{F_{\ell_2}(\hat{r}_p)}{r_p}$$

To investigate the regions below the Positronium formation thresholds the following trial wave function applicable to the energy region below the nth. level of Positronium was used:

$$Q\Phi_t = \sum_{\substack{\ell_1 m_1 \\ \ell_2 m_2}} w_{n\ell_1}(\rho)\, C(\ell_1 \ell_2 L; m_1 m_2 M)\, Y_{\ell_2 m_2}(\hat{\sigma})\, \frac{F_{\ell_2}(\sigma)}{\sigma}$$

In both cases, infinite sequences of resonances were found because of the degeneracy of the eigenfunctions of different angular momenta for $n \geq 2$. Consequently no resonances of this

type are possible below the ground state Positronium formation threshold and the possibility of resonances here was investigated numerically by Bhatia and Temkin[65] where Φ_t was taken as an S-state of the Hylleraas type:

$$\Phi_t(r_1, r_p) = e^{-(\alpha r_p + \beta r_1 + \gamma \rho)} \sum_{lmn} C_{lmn} r_p^l r_1^m \rho^n$$

and $Q = 1 - |\phi_0(r_1)\rangle\langle\phi_0(r_1)|$

It was found that $\varepsilon^q \to .5$ rydbergs from above with $\alpha, \beta \to 0$ and $\gamma \to \frac{1}{2}$. This of course corresponds to a Positronium at infinity with respect to a stationary proton which means that there is no resonance.

Bransden and Jundi[54] found a very steep rise in the L=0 cross-section for Positronium formation when any form of polarization was included. It would seem that this was due to a pole in the R-matrix just below the Positronium threshold giving rise to a resonance in the positron Hydrogen channel at this energy. However Drachman[66] showed that this effect was spurious on account of the omission of the coupling terms in Bransden et al's.[54] formulation.

1.11 Processes involving Positronium

Positronium may exist in two forms: para-Positronium (singlet spin data) with a lifetime of approximately 10^{-10} seconds and ortho-Positronium (triplet spin state) with a lifetime of approximately 10^{-7} seconds. The annihilation of para-Positronium leads to the emission of two photons whereas that of ortho-Positronium gives at least three photons. There are several processes whereby the three-photon annihilation is replaced by the two-photon annihilation thereby effectively resulting in the destruction or "quenching" of the ortho-Positronium. These are discussed in part (c) of this section.

(a) Scattering of Positronium

Fraser [67],[68],[69] and Fraser and Kraidy [70] used a close coupling expansion in the Kohn variational method to calculate low-energy S-wave phase shifts for ortho-Positronium scattering from Hydrogen and Helium. In the former case, allowance for the possibility of conversion to para-Positronium by electron exchange must be made. In the case of Helium this conversion is not possible for ortho-Positronium energies less than 19.8 eV (see part (c)). The cross sections were found to be highly energy dependent, in contrast to the assumptions of Teutsch et al.[3] The Hydrogen results can be compared to those of Massey and Mohr[4] who used the Born-Oppenheimer approximation to calculate elastic cross sections. Fraser's[67] values of $192\pi a_0^2$

and $2.92\pi a_o^2$ for zero energy and 6.8 eV respectively were smaller than those of Massey et al.[4] who obtained $230\pi a_o^2$ and $25\pi a_o^2$ respectively. These Hydrogen calculations were a crude approximation neglecting all angular terms except the zeroth and making no allowance for polarization.

The addition of an attractive effect such as the Van der Waal's interaction term (this is the force of largest range acting between Positronium and an atom and is in fact the dipole-dipole interaction which occurs between two neutral polarizable systems. It varies as where σ is the distance of separation of the two systems) and a better Helium function than the Hylleraas uncorrelated function would probably improve Fraser's Helium results* since the exchange terms are repulsive. The calculation for L=0, 1 and 2 was repeated by Barker and Bransden[71] with the Van der Waal's term included and the phase shifts are presented in Table 1-8. The long-range potential has quite a small effect.

(b) Formation of Positronium

In the case of Hydrogen Massey and Moussa[4] determined the cross sections for the formation of Positronium in the 1s and 2s state using Born's approximation. This has already been described in Section 1.1 so it will just be emphasised here that the maximum cross section of $4\pi a_o^2$ at an energy of 14 eV clearly demonstrates the importance of

*A mistake in Fraser's first Helium paper[68] resulting in excessively large cross sections was corrected by Fraser.[69]

TABLE 1-8

Phase shifts given by Barker and Bransden [71] for L=0, 1 and 2 scattering of ortho-Positronium by Helium atoms.

Rows (a), (b) and (c) static-exchange; rows (d), (e) and (f) static-exchange + Van der Waal's interaction.

ka_o	L	0.0*	0.1	0.2	0.4	0.6	0.8
(a)	0	1.80	-.181	-.359	-.701	-1.011	-1.274
(b)	1	.	-.0021	-.0155	-.0967	-.2359	-.3912
(c)	2	.	.	-.0003	-.0073	-.0393	-.1056
(d)	0	2.05	-.203	-.391	-.716	-.987	-1.218
(e)	1	.	-.0022	-.0166	-.1034	-.2462	-.3967
(f)	2	.	.	-.0003	-.0076	-.0489	-.1085

* The zero-entries represent scattering lengths.

allowing for virtual Positronium formation. The calculations were repeated by Cheshire [72] whose cross sections were 20% higher.

Fels and Mittleman's [53] Hydrogen results differ from Bransden et al's. [54] of course but were in qualitative agreement with a variational calculation by Drachman [73] which showed the Positronium formation cross-sections to be greatly reduced relative to the Born approximation near threshold.

Massey and Moussa [74] used Born's approximation for the case of Helium and obtained a maximum cross section of $\cdot 4\pi a_0^2$ at an energy of 27 eV. A similar calculation by Kraidy [27] produced larger cross-sections for energies 22 eV. The addition of virtual Positronium and the Positronium dipole polarization to the static field of a close coupling expansion tripled the total cross sections without polarization for energies up to 30 eV. Fels and Mittleman's [60] Helium results* bear no resemblance to the close coupling results being a factor of a thousand smaller.

A cross section that is frequently used in experimental work is the diffusion or momentum transfer cross-section defined by:

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

*The Positronium cross sections given in figures 2 and 4 of this paper are to be reduced by a factor of 2.

in units of πa_o^2 where δ_ℓ is the phase shift for the ℓth. partial wave. At low energies, the momentum transfer cross-section is approximately the same as the elastic scattering cross-section.

Leung and Paul[75] studied the diffusion of slow positrons by the method of delayed coincidences and, contrary to the findings of Marder et al.[1], found no enhancement of Positronium formation upon application of an electric field. Near the Positronium threshold, the momentum transfer cross sections were found to be $> .115 \pi a_o^2$. Diffusion cross sections were calculated by taking a linear combination of Drachman's non-variational[57] and variational[50] results as follows:

$$\delta_o = A\delta_o^{(1)} + (1-A)\delta_o^{(2)}$$

where $\delta_o^{(1)}$ are the non-variational[57] S-wave phase shifts and $\delta_o^{(2)}$ the variational[50]. The P- and D-wave non-variational phase shifts were used. The optimum value of A was found to lie between 0 and 2. Leung and Paul[75] eliminated the results of Massey et al.[34] and Kraidy[27] from consideration since their wave functions did not produce adequate values of Z_{eff} (see part (c)).

A similar conclusion was reached by Tao and Kelly[76] who calculated the allowable values of the averaged momentum - transfer cross-sections in an energy range .1 eV to 17.8 eV to be $\cdot 6\pi a_o^2$ to $\cdot 2\pi a_o^2$. However the Massey et al.[34]

results fitted the experimental results quite well but not to such a degree as Drachman's.[50],[57]

(c) Positron Annihilation

The rate of annihilation of positrons in an atomic gas is given by[77]:

$$\lambda_s = \pi r_0^2 c N {}'Z_{eff}$$

where r_0 is the classical electron radius $\frac{e^2}{mc^2}$, c is the speed of light, N the number of electrons in the target gas (N is proportional to the pressure p) and ${}'Z_{eff}$ is the effective number of electrons per atom in a singlet state relative to the positron. The rate of annihilation into three photons of a positron-electron pair in a relative triplet state is smaller by a factor of 1115 therefore the total contribution of three-photon annihilation[78] to the total decay rate is $\frac{3}{1115} \doteq \frac{1}{372}$ of λ_s.

If we consider the wave function $\Psi(\underline{r}_1, \underline{r}_2 \cdots\cdots, \underline{r}_N ; \underline{r}_p)$ having asymptotic form:

$$\Psi(\underline{r}_1, \underline{r}_2, \cdots\cdots, \underline{r}_N ; \underline{r}_p) \underset{r_p \to \infty}{\sim} \varphi(\underline{r}_1, \underline{r}_2, \cdots\cdots, \underline{r}_N) F(\underline{r}_p)$$

where $\underline{r}_1, \cdots\cdots, \underline{r}_N$ are the electron coordinates and $\underline{r}_p$ the

positron coordinates then φ is the normalized atomic wave function and $F(r_p)$ is normalized to correspond to one positron per unit volume asymptotically then $^1Z_{eff}$ is given by:

$$^1Z_{eff} = \sum_{i=1}^{N} \int dr_1 \cdots dr_N dr_p \, |\Psi(r_1, \cdots, r_N; r_p)|^2 \, \delta(r_i - r_p)$$

It can be seen that $^1Z_{eff}$ gives a measure of the probability of finding the positron and an electron at the same point in space.

During a collision, the positron of the orth-Positronium pair may find itself at the position of an atomic electron, form a singlet spin state and promptly annihilate. This process is termed "pick-off" quenching and should not be confused with "exchange" quenching which occurs when the atom and Positronium exchange an electron, so converting ortho-Positronium to para-Positronium. Since the ground state Helium function is in a singlet spin state, exchange quenching cannot occur for orth-Positronium energies below the triplet excitation threshold of 19.8 eV.

Duff and Heyman's [79] measurement of the pick-off quenching rate of ortho-Positronium in Helium gave:

$$^1Z_{eff} = .118 \pm .01$$

Fraser [68][69] calculated $^1Z_{eff}$ with the static exchange trial wave function with no allowance for polarization effects. This value of .033 obtained at a Positronium

energy of .0018 (corresponding to a mean Positronium speed of 6.6×10^6 cm/sec as given by Duff and Heymann[74] clearly demonstrates the inadequacy of the trial wave function for quenching calculations particularly since other experimental values are even higher.[80]

Barker and Bransden[71] repeated Fraser's[69] calculations with the Van der Waal's interaction and found that Z_{eff} was increased to .048 which is still considerably smaller than the experimental values.

Massey, Lawson and Thompson[34] used their static field plus polarized orbital wave function to calculate Z_{eff} for positrons on Helium. Their results are in reasonable agreement with a similar calculation by Kraidy.[27] In these calculations $Z_{eff} < 2$ (the Dirac rate = number of electrons in the Helium atom) but the addition of virtual Positronium terms[27] produced values greater than 2 for low energies, see Table 1-9. This is to be expected since virtual Positronium formation is essentially a short-range correlation effect providing an increase in attraction for the positron.[81] Most experimental results yield values of Z_{eff} lying between 3.0 and 4.0.

A variational calculation by Houston[82] using the trial wave function of Houston and Moiseiwitsch[16] (see Section 1.3b) produced a very high value of 4.61.

Drachman[83] applied his adiabatic non-variational method with complete monopole suppression[57] to the annihilation of positrons in Helium and obtained Z_{eff}

TABLE 1-9

Positron-Helium annihilation rate Z_{eff}.

Row (a) static field; row (b) static field + dipole polarization; row (c) virtual Positronium formation; row (d) virtual Positronium formation + dipole polarization; row (e) non-variational adiabatic; row (f) variational adiabatic.

k^2	0.01	0.04	0.09	0.16	0.25	0.36	Reference
(a)	.7334	.7485	.7728	.8048	.8430	.8859	27
(b)	1.247	1.194	1.152	1.127	1.120	1.127	27
(c)	2.446	2.095	1.851	1.727	1.679	1.650	27
(d)	3.703	2.804	2.266	2.00	1.866	1.792	27
(e)	.	5.58	5.16	4.86	4.70	4.62	83
(f)	.	3.30	3.14	3.02	2.98	2.98	50

The positron kinetic energy is k^2 in units of 13.6 eV.

values a factor of 2 larger than Kraidy's[27] with a zero energy value of 6.32. Application of a variational method[50] reduced the values giving 3.66 at zero energy. The two sets of Z_{eff} are displayed in Table 1-9.

Leung and Paul[75] found that Drachman's[50] variational calculations the best theoretical fit to their experimental results, their optimum value of Z_{eff} in thermal equilibrium at 77°K being $3.677 \pm .025$.

Recent work by Fels and Mittleman (private communication to M. H. Mittleman) suggests that the direct annihilation of positrons by capture dominates the annihilation process except in a very small energy band above threshold.

It clearly is obvious that more work needs to be done on the positron Helium system since this is a case of practical interest. It would be instructive to investigate the disagreement between the above threshold close coupling results and the adiabatic approximation with coordinate change.[60] Several additions to the close coupling expansion that take into account long-range attraction as well as short-range correlation effects are discussed in Chapter VI.

CHAPTER II

CLOSE COUPLING THEORY OF POSITRON HELIUM SCATTERING

2.1 The Schroedinger Wave Equation

The wave equation for the Positron Helium system is given by:

$$\left[-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2+\nabla_p^2\right)+\frac{2e^2}{r_p}-\frac{2e^2}{r_1}-\frac{2e^2}{r_2}+\frac{e^2}{r_{12}}-\frac{e^2}{r_{1p}}-\frac{e^2}{r_{2p}}-E\right]\Psi(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_p)=0 \qquad 2.1$$

where the Helium nucleus is considered to be of infinite mass and therefore taken as the origin of coordinates.

$\underset{\sim}{r}_1$, $\underset{\sim}{r}_2$ and $\underset{\sim}{r}_p$ are the coordinate vectors of the two electrons and the positron respectively, m the common electron and positron mass, $\underset{\sim}{r}_{ij} = \underset{\sim}{r}_i - \underset{\sim}{r}_j$ for $i = 1, 2$ and p and E is the total energy of the system.

To change to atomic units we substitute ra_0 for r in equation (2.1) where $a_0 = \frac{\hbar^2}{me^2} = .53 \times 10$ c.m. is the Bohr radius.

The unit of energy is the Rydberg $= \frac{e^2}{2a_0} = 13.6$ eV therefore in atomic units equation (2.1) becomes:

$$\left[-\left(\nabla_1^2+\nabla_2^2+\nabla_p^2\right)+\frac{2}{r_p}-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{r_{12}}-\frac{1}{r_{1p}}-\frac{1}{r_{2p}}-E\right]\Psi(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_p)=0 \qquad 2.2$$

The Hamiltonian H of the whole system may be expressed in the following forms:

$$H = -\left(\nabla_1^2+\nabla_2^2+\nabla_p^2\right)+\frac{4}{r_p}-\frac{4}{r_1}-\frac{4}{r_2}+\frac{2}{r_{12}}-\frac{2}{r_{1p}}-\frac{2}{r_{2p}} \qquad 2.3a$$

$$= -\left(\frac{1}{2}\nabla_{\sigma_i}^2+2\nabla_{\rho_i}^2+\nabla_j^2\right)+\frac{4}{r_p}-\frac{4}{r_1}-\frac{4}{r_2}+\frac{2}{r_{12}}-\frac{2}{\rho_1}-\frac{2}{\rho_2} \qquad 2.3b$$

for $i = 1$, $j = 2$

and $i = 2$, $j = 1$

where $\underset{\sim}{\rho}_i = \underset{\sim}{r}_{ip}$ and $\underset{\sim}{\sigma}_i = \frac{1}{2}\left(\underset{\sim}{r}_i + \underset{\sim}{r}_p\right)$

2.2 The Variational Method

(a) The Exact Wave Function

Consider an axially symmetric wave function $\Psi(\underset{\sim}{x}, s_x, \underset{\sim}{y}, s_y)$ satisfying equation (2.2) where $\underset{\sim}{x}$ and s_x are the coordinate vector and spin function respectively of the separation of the two clusters and $\underset{\sim}{y}$ and s_y represent the remaining coordinates and spin respectively. For example, if we are considering the configuration of a positron and a Helium atom then:

$$\underset{\sim}{x} = \underset{\sim}{r}_p \quad , \quad \underset{\sim}{y} = (\underset{\sim}{r}_1, \underset{\sim}{r}_2)$$

Neglecting spin-orbit interactions we take advantage of the fact that the total orbital angular momentum with quantum numbers L and M_L, the total spin with quantum numbers S and M_S and overall parity of the system with quan-

tum number Π are all separately conserved and expand the total wave function, initially in the state Γ', as follows:

$$\Psi_{\Gamma'}(\underset{\sim}{x}, s_x, y, s_y) = \sum_{\Gamma} \psi^{\Gamma\Gamma'}(\hat{x}, s_x, y, s_y) \underset{x}{F^{LS}_{\nu\nu'}(x)} \qquad 2.4$$

where $\Gamma = (n k_n \ell_1 \ell_2 L M_L S M_S)$ and the channel index $\nu = (n k_n \ell_1 \ell_2)$. Here n and ℓ_1 are the principle and orbital angular momentum quantum numbers respectively of the target and k_n and ℓ_2 the wave number and orbital angular momentum respectively of the projectile. The function $F^{LS}_{\nu\nu'}$ satisfy the following boundary conditions:

$$F^{LS}_{\nu\nu'}(x) = 0 \qquad 2.5a$$

$$F^{LS}_{\nu\nu'}(x) \underset{x\to\infty}{\sim} k_\nu^{-\frac{1}{2}} \left[\sin\left(k_\nu x - \frac{\ell_2 \pi}{2}\right) \cdot \delta_{\nu\nu'} + R^{LS}_{\nu\nu'} \cos\left(k_\nu x - \frac{\ell_2 \pi}{2}\right) \right] \qquad k_\nu^2 > 0$$

$$\underset{x\to\infty}{\sim} e^{-|k_\nu| x} \qquad k_\nu^2 < 0 \qquad 2.5b$$

where R^{LS} is the real symmetric Reactance or R-matrix. Consider the following expression:

$$I_{\Gamma_1\Gamma_2} = \int \Psi^*_{\Gamma_1} \left[H - E\right] \Psi_{\Gamma_2} \, d\tau \qquad 2.6$$

where H is defined in equations (2.3) and $d\tau$ is the volume element for integration of the independent variables over all space. For arbitrary variations $\delta\Psi$ about the exact wave function Ψ we obtain the following expression for $\delta I_{\Gamma_1\Gamma_2}$:

$$\delta I_{\Gamma_1\Gamma_2} = \int \Psi^*_{\Gamma_1} [H-E] \, \delta\Psi_{\Gamma_2} \, d\tau \qquad 2.7$$

correct to the first order in $\delta\Psi$. We note that $I_{\Gamma_1\Gamma_2} = 0$ since Ψ_{Γ_2} is an exact solution of equation (2.2). We have that:

$$\delta\Psi_{\Gamma'} = \sum_{\Gamma} \psi^{\Gamma\Gamma'} \frac{\delta F^{LS}_{\nu\nu'}(x)}{x}$$

and $\delta F^{LS}_{\nu\nu'}$ satisfies equation (2.5a) and the following:

$$\delta F^{LS}_{\nu\nu'}(x) \underset{x\to\infty}{\sim} k_\nu^{-\frac{1}{2}} \delta R^{LS}_{\nu\nu'} \cos\left(k_\nu x - \frac{\ell_2 \pi}{2}\right) \qquad 2.8$$

Equation (2.7) can be written as follows:

$$\delta I_{\Gamma_1\Gamma_2} = \int \Psi^*_{\Gamma_1} [H-E] \, \delta\Psi_{\Gamma_2} d\tau - \int \delta\Psi^*_{\Gamma_2} [H-E] \, \Psi_{\Gamma_1} d\tau$$

$$= \int \Psi^*_{\Gamma_1} [T] \, \delta\Psi_{\Gamma_2} d\tau - \int \delta\Psi^*_{\Gamma_2} [T] \, \Psi_{\Gamma_1} d\tau$$

where $T = -\nabla_x^2 - \nabla_y^2$ is the sum of the appropriate kinetic energy operators. For example we have:

$T = = \left(\nabla_1^2 + \nabla_2^2 + \nabla_\rho^2\right)$ for a positron and a Helim atom.

$= = \left(\frac{1}{2}\nabla_{\sigma_1}^2 + 2\nabla_{\rho_1}^2 + \nabla_2^2\right)$ for Positronium and a Helium ion.

where $\underset{\sim}{\sigma}_1 = \frac{1}{2}\left(\underset{\sim}{r}_1 + \underset{\sim}{r}_\rho\right)$ and $\underset{\sim}{\rho}_1 = \underset{\sim}{r}_1 - \underset{\sim}{r}_\rho$

Consider the expression $\delta J^{(x)}_{\Gamma_1\Gamma_2}$ given by

$$\delta J^{(x)}_{\Gamma_1\Gamma_2} = \int \Phi^*_{\Gamma_1}\left[\nabla_x^2\right]\delta\Phi_{\Gamma_2}\,d\tau - \int \delta\Phi^*_{\Gamma_2}\left[\nabla_x^2\right]\Phi_{\Gamma_1}\,d\tau \qquad 2.9$$

Applying Green's Theorem we obtain:

$$\delta J^{(x)}_{\Gamma_1\Gamma_2} = -\int d\tau_y \int_{S_x} \Phi^*_{\Gamma_1}\left[\underset{\sim}{\nabla}_x\right]\delta\Phi_{\Gamma_2} - \delta\Phi^*_{\Gamma_2}\left[\underset{\sim}{\nabla}_x\right]\Phi_{\Gamma_1} \cdot d\underset{\sim}{S}_x \qquad 2.10$$

where the surface integration is taken over the surface of a sphere with centre at the origin of coordinates and radius large enough to ensure that Φ_Γ has assumed its asymptotic form. The surface vector element $d\underset{\sim}{S}_x = x\,\underset{\sim}{x}\,d\hat{x}$ and $d\tau_y$ is the volume element of the y coordinates.

We expand $\psi^{\Gamma\Gamma'}$ as follows:

$$\psi^{\Gamma\Gamma'}(\hat{x},s_x,y,s_y) = \varphi_\nu(y)\,\mathcal{Y}^{M_L}_{\ell_1\ell_2 L}(\hat{x},\hat{y})\,\chi^{M_S}_S(s_x,s_y) \qquad 2.11a$$

where $$\mathcal{Y}^{M_L}_{\ell_1\ell_2 L}(\hat{x},\hat{y}) = \sum_{m_1 m_2} C(\ell_1\ell_2 L; m_1 m_2 M)\,Y_{\ell_1 m_1}(\hat{y})\,Y_{\ell_2 m_2}(\hat{x}) \qquad 2.11b$$

and $$\chi^{M_S}_S(s_x,s_y) = \sum_{m_s m_s'} C(\ell_s \ell_s' S; m_s m_s' M_S)\,\chi_{\ell_s m_s}(s_y)\,\chi_{\ell_s' m_s'}(s_x) \qquad 2.11c$$

The C's are Clebsch Gordan coefficients (as defined in Rose "Elementary Theory of Angular Momentum"). We will use the following orthonormalization formula for the spherical harmonics function $Y_{\ell m}$:

$$\int d\hat{x}\; Y_{\ell m}(\hat{x})\,Y_{\ell' m'}(\hat{x}) = \delta_{\ell\ell'}\,\delta_{mm'} \qquad 2.12$$

Substituting equation (2.11) into (2.10) and using equations (2.8) and (2.12) we obtain:

$$\delta J^{(x)}_{\Gamma_1\Gamma_2} = \sum_{LS} \delta J^{(x)\,LS}_{\nu_1\nu_2} = \sum_{LS} \delta R^{LS}_{\nu_1\nu_2}$$

Following the same procedure for the y coordinates we obtain:

$$\delta J^{(y)}_{\Gamma_1\Gamma_2} = -\int d\tau_x \int_{S_y} \left[\Psi^*_{\Gamma_1} \underline{\nabla}_y \delta\Psi_{\Gamma_2} - \delta\Psi^*_{\Gamma_2} \underline{\nabla}_y \Psi_{\Gamma_1} \right] \cdot d\underline{S}_y$$

$$= 0$$

since $\lim_{y\to\infty} \phi_\nu(y) = 0$

Therefore the final expression for $\delta I_{\Gamma_1\Gamma_2}$ is:

$$\delta I_{\Gamma_1\Gamma_2} = \sum_{LS} \delta I^{LS}_{\nu_1\nu_2} = -\sum_{LS} \delta R^{LS}_{\nu_1\nu_2}$$

That is : $$\sum_{LS} \delta \left[I^{LS}_{\nu_1\nu_2} + R^{LS}_{\nu_1\nu_2} \right] = 0$$

Therefore we may consider the variation of the wave function for each L and S. Thus:

$$\delta \left[I^{LS}_{\nu_1\nu_2} + R^{LS}_{\nu_1\nu_2} \right] = 0 \qquad 2.13$$

This provides the basis for a variational principle since $\left[I^{LS}_{\nu_1\nu_2} + R^{LS}_{\nu_1\nu_2} \right]$ is stationary with rexpect to the arbitrary variations considered.

(b) The Approximate Wave Function

Consider an approximate wave function $\Psi^t_{\Gamma'}$ which can be

everywhere expanded in the following form:

$$\Psi^{t}_{\Gamma'}(\underline{x},s_x,\underline{y},s_y) = \sum_{\Gamma} \Psi^{t}_{\Gamma\Gamma'}(\underline{x},s_x,\underline{y},s_y)$$

$$= \sum_{\Gamma} \psi^{\Gamma\Gamma'}(\hat{x},s_x,\underline{y},s_y)\,\frac{F^{t\,LS}_{\nu\nu'}(x)}{x}$$

where Γ runs over the number of coupled channels considered in the asymptotic region. $F^{t\,LS}_{\nu\nu'}$ satisfies equations (2.5) except that the trial R-matrix $R^{t\,LS}_{\nu\nu'}$ will also be approximate. We consider the expression:

$$I^{t\,LS}_{\nu_1\nu_2} = \sum_{\Gamma\Gamma'}\int \Psi^{t\,*}_{\Gamma\Gamma_1}\left[H-E\right]\Psi^{t}_{\Gamma'\Gamma_2}\,d\tau\,.\,\delta_{LL'}\,\delta_{SS'}$$

Following through the steps of part (a) but remembering that we are considering a particular total orbital angular momentum L we obtain:

$$\delta\left[I^{t\,LS}_{\nu_1\nu_2} + R^{t\,LS}_{\nu_1\nu_2}\right] = \sum_{\Gamma\Gamma'}\delta_{LL'}\delta_{SS'}\int \delta\Psi^{t}_{\Gamma'\Gamma_2}\left[H-E\right]\Psi^{t\,*}_{\Gamma\Gamma_1}\,d\tau$$

$$+ \sum_{\Gamma\Gamma'}\delta_{LL'}\delta_{SS'}\int \delta\Psi^{t\,*}_{\Gamma\Gamma_1}\left[H-E\right]\Psi^{t}_{\Gamma'\Gamma_2}\,d\tau \qquad 2.14$$

by using Green's Theorem. We require the approximate wave function to satisfy equation (2.13) therefore:

$$\delta\left[I^{t\,LS}_{\nu_1\nu_2} + R^{t\,LS}_{\nu_1\nu_2}\right] = 0 \qquad 2.15$$

and the righthand side of equation (2.14) must therefore be

zero.

Writing the following:

$$R^{t\,LS}_{\nu_1\nu_2} = R^{LS}_{\nu_1\nu_2} + \Delta R^{LS}_{\nu_1\nu_2}$$

and using the fact that $I^{LS}_{\nu_1\nu_2} = 0$ and equation (2.15) we obtain:

$$I^{t\,LS}_{\nu_1\nu_2} = I^{LS}_{\nu_1\nu_2} + \Delta I^{LS}_{\nu_1\nu_2}$$

$$= -\Delta R^{LS}_{\nu_1\nu_2}$$

Therefore we have the following expression for the exact R-matrix:

$$R^{LS} = R^{t\,LS} + I^{t\,LS} \qquad 2.16$$

Consider the expressions $A_{\Gamma_2\Gamma_1}$ and $B_{\Gamma_1\Gamma_2}$ where:

$$A_{\Gamma_2\Gamma_1} = \sum_{\Gamma\Gamma'} \int \delta\Psi^{t}_{\Gamma'\Gamma_2} \left[H-E\right] \Psi^{t\,*}_{\Gamma\Gamma_1}\, d\tau \cdot \delta_{LL'}\delta_{SS'}$$

$$B_{\Gamma_1\Gamma_2} = \sum_{\Gamma\Gamma'} \int \delta\Psi^{t\,*}_{\Gamma\Gamma_1} \left[H-E\right] \Psi^{t}_{\Gamma'\Gamma_2}\, d\tau \cdot \delta_{LL'}\delta_{SS'}$$

It can be seen that $B_{\Gamma_1\Gamma_2} = A^{*}_{\Gamma_1\Gamma_2}$ and the right hand side of equation (2.14) equals $\left(A_{\Gamma_2\Gamma_1} + B_{\Gamma_1\Gamma_2}\right)$, therefore we consider $A_{\Gamma_2\Gamma_1}$ only:

$$A_{\Gamma_2\Gamma_1} = \sum_{\Gamma\Gamma'} \int \frac{\delta F^{L^S}_{\nu\nu_2}}{\times} \; \psi^{\Gamma'\Gamma_2} \left[H-E\right] \Psi^{L^*}_{\Gamma\Gamma_1} \, d\tau_{\cdot} \, \delta_{LL'} \, \delta_{SS'}$$

Since $A_{\Gamma_2\Gamma_1} + B_{\Gamma_1\Gamma_2} = 0$ for arbitrary variations δF^L then the terms independent of δF^L must each be zero. Therefore we have:

$$\sum_{\Gamma} \delta_{LL'}\delta_{SS'} \int \psi^{\Gamma'\Gamma_2}(\hat{x}, s_x, y, s_y) \left[H-E\right] \psi^{\Gamma\Gamma_1}(\hat{x}, s_x, y, s_y) \frac{F^{L^S}_{\nu\nu_1}(x)}{\times} \, d\hat{x} \, d\tau_y = 0 \qquad 2.17$$

This defines the radial equations for the general system.

2.3 Derivation of the Radial Equations

(a) The Trial Wave Function

Since we are only considering the ground state of the Helium atom and the Helium ion the trial wave function $\Psi^L(r_1, s_1, r_2, s_2, r_p, s_p)$ for a particular total orbital angular momentum L reduces to:

$$\Psi^L(1,2,p) = \psi_0(\bar{12})\chi(p,\bar{12})F^{(L)}_{(p)} + (1-P_{12})\varphi_0(2)\omega(\rho_1)\left[g^{p(L)}(\bar{r})\chi(2,\bar{rp}) + g^{0}(\bar{r}_1)\chi(2,\bar{1p})\right] \qquad 2.18$$

where 1, 2 and p refer to the two electrons and the positron coordinates respectively, $\psi_0(\bar{12})$ is the ground state Helium atom function, $F^{(L)}_{(p)}$ describes the motion of the positron relative to the proton, $\varphi_0(r)$ is the ionized Helium ground state function and $\omega(\rho)$ is the Positronium ground state

function. $g^{(L)}(\underline{r})$ describes the motion of the Positronium relative to the proton and the superscripts p and 0 denote para-positronium (parallel spins) and ortho-positronium (anti-parallel spins) respectively. χ is the normalized overall spin function of the positron and the electrons where $A(\overline{xy})$ denotes symmetry with respect to interchange of x and y and $A(\tilde{xy})$ denotes anti-symmetry with respect to the same interchange. P_{12} is the operator interchanging all coordinates 1 and 2.

To reduce equation (2.18) to a simpler form we express the Positronium spin functions as linear combinations of the electron spin functions as follows:

$$\chi(2,\hat{1}_p) = -\frac{\sqrt{3}}{2}\chi(p,\overline{12}) + \frac{1}{2}\chi(p,\hat{12}) \qquad 2.19a$$

$$\chi(2,\overline{1}_p) = -\frac{1}{2}\chi(p,\overline{12}) - \frac{\sqrt{3}}{2}\chi(p,\hat{12}) \qquad 2.19b$$

$$\chi(1,\hat{2}_p) = -\frac{\sqrt{3}}{2}\chi(p,\overline{12}) - \frac{1}{2}\chi(p,\hat{12}) \qquad 2.19c$$

$$\chi(1,\overline{2}_p) = -\frac{1}{2}\chi(p,\overline{12}) + \frac{\sqrt{3}}{2}\chi(p,\tilde{12}) \qquad 2.19d$$

For example: $\chi(p,\tilde{12}) = \alpha(p)\chi_0(\tilde{12})$

where $\chi_0(\tilde{12}) = \frac{1}{\sqrt{2}}\left\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\right\}$ is the singlet spin state of electrons 1 and 2 and $\alpha(a)$ and $\beta(a)$ are the spinors representing "spin up" and "Spin down" of particle a respectively. Hence:

$$(1-P_{12})\varphi_0(2)\omega(\rho_1)\left[g^{p(L)}(\underline{r}_1)\chi(2,\bar{1}_p)+g^{o(L)}(\underline{r}_1)\chi(2,\bar{1}_p)\right]$$

$$=(1-P_{12})\varphi_0(2)\omega(\rho_1)\left[-\chi(\rho,\bar{1}\bar{2})\tfrac{1}{2}\left\{\sqrt{3}\,g^{p(L)}(\underline{r}_1)+g^{o(L)}(\underline{r}_1)\right\}\right.$$

$$\left.+\chi(\rho,\bar{1}2)\tfrac{1}{2}\left\{g^{p(L)}(\underline{r}_1)-\sqrt{3}\,g^{o(L)}(\underline{r}_1)\right\}\right]$$

To satisfy the Pauli Exclusion principle $\Psi^t_L(1,2,p)$ must be anti-symmetric in the electron coordinates since there are no spin-dependent interactions. Therefore the coefficient of $\chi(\rho,\bar{1}\bar{2})$ in the above equation must be zero. This leads to the following expressions:

$$\sqrt{3}\,g^{p(L)}(\underline{r})+g^{o(L)}(\underline{r})=0 \qquad 2.20a$$

$$g^{p(L)}(\underline{r})-\sqrt{3}\,g^{o(L)}(\underline{r})=4\,g^{p(L)}(\underline{r}) \qquad 2.20b$$

Thus if we write $G^{(L)}(\underline{r})=2g^{p(L)}(\underline{r})$ and use the fact that $\chi(\rho,\bar{2}\bar{1})=-\chi(\rho,\bar{1}2)$, equation (2.18) becomes:

$$\Psi^t=\chi(\rho,\bar{1}2)\left[\psi_0(12)F^{(L)}(\rho)+(1+P_{12})\varphi_0(2)\omega(\rho_1)G^{(L)}(\underline{r}_1)\right] \qquad 2.21$$

Since the spin function $\chi(\rho,\bar{1}2)$ is normalized to unity any summation over the spins will give a factor of one. Hence we may consider the spatial part only of equation (2.21) for substitution into the variational principle outlined in

Section 2.2. Our total spatial wave function is therefore:

$$\Psi^{L}_{L}(1,2,\rho) = \psi_0(\vec{12})\, F^{L}_{(\rho)} + (1+P_{12})\varphi_0(2)\,\omega(\rho_1)\, G^{(L)}_{(\sigma_1)} \qquad 2.22$$

(b) Wave Functions and Energy Values.

The normalized Helium ion ground-state wave function $\varphi_0(r)$ with binding energy $E_{He^+} = 4$ satisfies:

$$\left[-\nabla^2 - \frac{4}{r} + 4 \right] \varphi_0(r) = 0 \qquad 2.23a$$

$$\varphi_0(r) = \sqrt{\frac{8}{\pi}}\, e^{-2r} \qquad 2.23b$$

and the normalized Positronium ground-state wave function $\omega(\rho)$ with binding energy $E_{ps} = \frac{1}{2}$ satisfies:

$$\left[-2\nabla_\rho^2 - \frac{2}{\rho} + \frac{1}{2} \right] \omega(\rho) \quad 0 \qquad 2.24a$$

$$\omega(\rho) = \frac{1}{\sqrt{8\pi}}\, e^{-\frac{\rho}{2}} \qquad 2.24b$$

The exact eigenfunction of the unperturbed Helium ground state Hamiltonium is not known so in this work we will use the 3-parameter Hartree-Fock wave function $\psi_0(r_1, r_2)$ given by:

$$\psi_0(r_1, r_2) = u(r_1)\,u(r_2) \qquad 2.25$$

where $$u(r) = \frac{N}{\sqrt{4\pi}}\left(e^{-ar} + Ce^{-br}\right) \qquad 2.25b$$

and $a = 1.455799$, $b = 2a$, $c = 0.6$ 2.25c

$$N^{-2} = \frac{1}{4a^3} + \frac{C^2}{4b^3} + \frac{4C}{(a+b)^3} \qquad 2.25d$$

$\psi_0(r_1, r_2)$ satisfies:

$$\left[-(\nabla_1^2 + \nabla_2^2) + \frac{2}{r_{12}} - \frac{4}{r_1} - \frac{4}{r_2} + E_{He}\right]\psi_0(r_1, r_2) = 0 \qquad 2.26$$

where the variational Helium binding energy $E_{He} = 5.72334$ rydbergs is 1.4% away from the experimental binding energy value of 5.808 rydbergs.

If we denote the kinetic energy of the positron by k_1^2 and that of the positronium by $\frac{1}{2}k_2^2$ then the total energy E of the system can be written as follows:

$$E = k_1^2 - E_{He} = \frac{1}{2}k_2^2 - E_{He^+} - E_{Ps}$$

Therefore:

$$k_2^2 = 2\left(k_1^2 + \frac{q}{2} - E_{He}\right) \qquad 2.27$$

(c) The Radial Equations for Positron Helium Scattering

In the notation of Section 2.2 we have three sets of coordinates:

(1) $\underset{\sim}{x} = \underset{\sim}{r}_p$ and $\underset{\sim}{y} = (\underset{\sim}{r}_1, \underset{\sim}{r}_2)$ Positron plus Helium atom

(2) $\underset{\sim}{x} = \underset{\sim}{\sigma}_1$ and $\underset{\sim}{y} = (\underset{\sim}{\rho}_1, \underset{\sim}{r}_2)$ Positronium plus Helium ion

(3) $\underset{\sim}{x} = \underset{\sim}{\sigma}_2$ and $\underset{\sim}{y} = (\underset{\sim}{\rho}_2, \underset{\sim}{r}_1)$ " " " "

Hence substituting equation (2.22) into (2.17) we obtain the following two expressions denoted by $A_L^{(1)}(r_p)$ and $A_L^{(2)}(\sigma_1)$ respectively:

$$A_L^{(1)}(r_p) = \int \psi_0(\bar{12}) Y_{LM}(\hat{r}_p)\left[H-E\right]\psi_0(\bar{12}) F^{(L)}(\rho) + (1+P_{12})\varphi_0(2) w(\rho_1) G^{(L)}(\underset{\sim}{\sigma}_1)\, d\hat{r}_p\, d\underset{\sim}{r}_1\, d\underset{\sim}{r}_2$$
$$= 0 \qquad 2.28a$$

$$A_L^{(2)}(\sigma_1) = \int \varphi_0(2) w(\rho_1) Y_{LM}(\sigma_1)\left[H-E\right]\psi_0(\bar{12}) F^{(L)}(\rho) + (1+P_{12})\varphi_0(2) w(\rho_1) G^{(L)}(\underset{\sim}{\sigma}_1)\, d\hat{\sigma}_1\, d\underset{\sim}{\rho}_1\, d\underset{\sim}{r}_2$$
$$= 0 \qquad 2.28b$$

The simplification of $A_L^{(1)}$ and $A_L^{(2)}$ is outlined in detail in Appendix A. The final result is:

$$A_L^{(1)}(r_p) = -\int Y_{LM}(\hat{r}_p)\left[\nabla_p^2 + U(\underset{\sim}{r}_p) + k_1^2\right] F^{(L)}(\rho)\, d\hat{r}_p$$
$$-\int Y_{LM}(\hat{r}_p)\, G^{(L)}(\underset{\sim}{\sigma}_1) K_1(\underset{\sim}{r}_p, \underset{\sim}{\sigma}_1)\, d\hat{r}_p\, d\underset{\sim}{\sigma}_1 \qquad 2.29a$$

$$A^{(2)}_L(\sigma_1) = -\frac{1}{2}\int Y_{LM}(\hat{\sigma}_1)\left[\nabla^2_{\sigma_1}+k_2^2\right] G^{(L)}(\underline{\sigma}_1)\, d\hat{\sigma}_1$$

$$-\frac{1}{2}\int Y_{LM}(\hat{\sigma}_1) F^{(L)}_{(\rho)} K_1(\underline{r}_\rho,\underline{\sigma}_1)\, d\hat{\sigma}_1\, d\underline{r}_\rho - \int Y_{LM}(\hat{\sigma}_1) G^{(L)}(\underline{\sigma}_2) K_2(\underline{\sigma}_1,\underline{\sigma}_2)\, d\hat{\sigma}_1 d\underline{\sigma}_2 \qquad 2.29b$$

where $$K_1(\underline{r}_\rho,\underline{\sigma}_1) = 8\left[S\left(\nabla^2_{\sigma_1} - \frac{8}{r_\rho} + \frac{8}{r_1} + k_2^2\right) + 4P(r_\rho) - 4P(r_1)\right] u(1)\omega(\rho_1) \qquad 2.30a$$

$$K_2(\underline{\sigma}_1,\underline{\sigma}_2) = 4^2(1+P_{12})\int d\underline{r}_\rho\left[\nabla^2_2 - \frac{8}{r_\rho} + \frac{8}{r_1} + \frac{4}{\rho_2} - \frac{4}{r_{12}} + k_2^2\right]\varphi_0(1)\varphi_0(2)\omega(\rho_1)\omega(\rho_2) \qquad 2.30b$$

and $$S = \int d\underline{r}\, \varphi_0(r) u(r) \qquad 2.31a$$

$$P(r) = \int d\underline{r}' \frac{\varphi_0(r') u(r')}{|\underline{r}-\underline{r}'|} \qquad 2.31b$$

$$U(\underline{r}_\rho) = \iint d\underline{r}_1 d\underline{r}_2 \left\{\psi_0(\overline{12})\right\}^2\left[\frac{2}{\rho_1} + \frac{2}{\rho_2} - \frac{4}{r_\rho}\right] \qquad 2.31c$$

We now expand $F^{(L)}(r)$ and $G^{(L)}(r)$ in terms of the spherical harmonic functions $Y_{\ell m}$. Since we only consider the Helium atom and Helium ion in their ground state, the total orbital angular momentum L is equal to the orbital angular momentum ℓ of the projectile. Thus:

$$F^{(L)}(r) = \frac{f^{(\ell)}(r)}{r} Y_{\ell m}(\hat{r})\, \delta_{\ell L}\, \delta_{mM} \qquad 2.32a$$

$$G^{(L)}(\sigma) = \frac{g^{(\ell)}(\sigma)}{\sigma} Y_{\ell m}(\hat{\sigma})\, \delta_{\ell L}\, \delta_{mM} \qquad 2.32b$$

Using the formula:

$$\nabla_r^2 \frac{f(r)}{r} Y_{\ell m}(\hat{r}) = \frac{1}{r} Y_{\ell m}(\hat{r}) \frac{d^2}{dr^2} f(r) - \frac{\ell(\ell+1)}{r^2} Y_{\ell m}(\hat{r}) \frac{f(r)}{r} \qquad 2.33$$

the orthonormalization formula (2.12) and equations (2.32), equations (2.29) reduce to:

$$\left[\frac{d^2}{dr_p^2} - \frac{\ell(\ell+1)}{r_p^2} + V_1(r_p) + k_1^2\right] f^{(\ell)}(r_p) = -\int_0^\infty d\sigma_1 \, g^{(\ell)}(\sigma_1) K_{12}^{(\ell)}(r_p, \sigma_1) \qquad 2.34a$$

$$\left[\frac{d^2}{d\sigma_1^2} - \frac{\ell(\ell+1)}{\sigma_1^2} + k_2^2\right] g^{(\ell)}(r_p) = -\int_0^\infty dr_p f^{(\ell)}(r_p) K_{12}^{(\ell)}(r_p, \sigma_1) - \int_0^\infty d\sigma_2 \, g^{(\ell)}(\sigma_2) K_{22}^{(\ell)}(\sigma_1, \sigma_2) \qquad 2.34b$$

The Kernels $K_{12}^{(\ell)}$ and $K_{22}^{(\ell)}$ are given by:

$$K_{12}^{(\ell)}(r_p, \sigma_1) = \int Y_{\ell m}(\hat{r}_p) Y_{\ell m}(\hat{\sigma}_1) r_p \sigma_1 K_1(\underline{r}_p, \underline{\sigma}_1) d\hat{r}_p \, d\hat{\sigma}_1 \qquad 2.35a$$

$$K_{22}^{(\ell)}(\sigma_1, \sigma_2) = 2\int Y_{\ell m}(\hat{\sigma}_1) Y_{\ell m}(\hat{\sigma}_2) \sigma_1 \sigma_2 K_2(\underline{\sigma}_1, \underline{\sigma}_2) d\hat{\sigma}_1 \, d\hat{\sigma}_2 \qquad 2.35b$$

and the local potential $V_1(r_p)$ by:

$$V_1(r_p) = \int Y_{\ell m}(\hat{r}_p) Y_{\ell m}(\hat{r}_p) U(\underline{r}_p) d\hat{r}_p$$

$$= -4N^2 \left[\frac{e^{-2ar_p}}{4a^2}\left(1+\frac{1}{ar_p}\right) + \frac{C^2 e^{-2br_p}}{4b^2}\left(1+\frac{1}{br_p}\right) + \frac{2Ce^{-(a+b)r_p}}{(a+b)^2}\left(1+\frac{2}{(a+b)r_p}\right)\right] \qquad 2.36$$

2.4 Simplification of the Kernels

(a) The Functions S and P

From equation (2.23), (2.24) and (2.31a) we obtain:

$$S = 8N\sqrt{2}\left[\frac{1}{(a+2)^3} + \frac{C}{(b+2)^3}\right] \qquad 2.37$$

$$P(r) = \frac{S}{r} + P^N(r) \qquad 2.38a$$

$$P^N(r) = -4N\sqrt{2}\left[\frac{e^{-(a+2)r}}{(a+2)^3}\left\{a+2+\frac{2}{r}\right\} + \frac{Ce^{-(b+2)r}}{(b+2)^3}\left\{b+2+\frac{2}{r}\right\}\right] \qquad 2.38b$$

(b) Kernel $K_{12}^{(e)}$

Using equations (2.24) and substituting $\underset{\sim}{r}_1 = 2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p$, $\underset{\sim}{\rho}_1 = 2(\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p)$ we obtain the following expression:

$$\nabla^2_{\sigma_1}\left[u(r_1)w(\rho_1)\right] = w(\rho_1)\left[u(r_1)\left\{1-\frac{4}{\rho_1}\right\} + 4u'(r_1)\left\{\frac{2}{r_1} - \frac{\underset{\sim}{r}_1\cdot\underset{\sim}{\rho}_1}{r_1\rho_1}\right\} + 4u''(r_1)\right] \qquad 2.39$$

where primes denote differentiation. Thus equation (2.30a) reduces to:

$$K_1(\underset{\sim}{r}_p, \underset{\sim}{\sigma}_1) = 8\left[Su(r_1)\left\{1 - \frac{4}{\rho_1} + \frac{4}{r_1} - \frac{4}{r_p} + k_2^2\right\} + 4Su'(r_1)\left\{\frac{2}{r_1} - \frac{\underset{\sim}{r}_1\cdot\underset{\sim}{\rho}_1}{r_1\rho_1}\right\}\right.$$

$$\left. + 4Su''(r_1) + 4u(r_1)\left\{P^N(r_p) - P^N(r_1)\right\}\right] w(\rho_1) \qquad 2.40$$

The following substitutions, originally suggested by Fraser , are now used:

$$u^{(A)}(|\underline{\xi}-\underline{r}|)\omega(2|\underline{\sigma}-\underline{r}|) = \frac{1}{4\pi\sigma} \sum_{\lambda} H_{\lambda}^{o}(A,r,\sigma)P_{\lambda}(\eta) \qquad 2.41a$$

$$\frac{u(|\underline{\xi}-\underline{r}|)\omega(2|\underline{\sigma}-\underline{r}|)}{|\underline{\sigma}-\underline{r}|} = \frac{1}{4\pi\sigma} \sum_{\lambda} H_{\lambda}^{1}(r,\sigma)P_{\lambda}(\eta) \qquad 2.41b$$

$$\frac{u^{(A)}(|\underline{\xi}-\underline{r}|)\omega(2|\underline{\sigma}-\underline{r}|)}{|\underline{\xi}-\underline{r}|} = \frac{1}{4\pi\sigma} \sum_{\lambda} H_{\lambda}^{2}(A,r,\sigma)P_{\lambda}(\eta) \qquad 2.41c$$

$$\frac{u'(|\underline{\xi}-\underline{r}|)\omega(2|\underline{\sigma}-\underline{r}|)(\underline{\xi}-\underline{r})\cdot(\underline{\sigma}-\underline{r})}{|\underline{\xi}-\underline{r}|\,|\underline{\sigma}-\underline{r}|} = \frac{1}{4\pi\sigma} \sum_{\lambda} g_{\lambda}^{*}(r,\sigma)P_{\lambda}(\eta) \qquad 2.41d$$

$$u(|\underline{\xi}-\underline{r}|)\omega(2|\underline{\sigma}-\underline{r}|)P^{N}(|\underline{\xi}-\underline{r}|) = \frac{1}{4\pi\sigma} \sum_{\lambda} g_{\lambda}^{2}(r,\sigma)P_{\lambda}(\eta) \qquad 2.41e$$

where $\eta = \hat{r}\cdot\hat{\sigma}$ and $P_{\lambda}(\eta)$ is the λth. Legendre Polynomial.

The superscript A and u is defined as follows:

If A=1 then $u^{(A)}$ is replaced by u.

If A=-a then $u^{(A)}$ is replaced by the 1st derivative u'.

If $A=a^2$ then $u^{(A)}$ is replaced by the 2nd derivative u''.

Alternatively we may express equation (2.41) in the following form:

$$H_{\lambda}^{\bullet}(A,r,\sigma) = M_{\lambda}(1+CP_{ab}) \int_{-1}^{+1} P_{\lambda}(\eta).Ae^{-|\xi-r|-a|2\xi-r|}\,d\eta \qquad 2.42a$$

$$H_{\lambda}^{1}(r,\sigma) = M_{\lambda}(1+CP_{ab}) \int_{-1}^{+1} P_{\lambda}(\eta)\frac{e^{-|\xi-r|-a|2\xi-r|}}{|\xi-r|}\,d\eta \qquad 2.42b$$

$$\mathcal{H}_\lambda^2(A,r,\sigma) = M_\lambda(1+CP_{ab})\int_{-1}^{+1} P_\lambda(\eta).\frac{Ae^{-|\underline{s}-\underline{r}|-a|2\underline{s}-\underline{r}|}}{|2\underline{s}-\underline{r}|}.\,d\eta \qquad 2.42c$$

$$g_\lambda^1(r,\sigma) = M_\lambda(1+CP_{ab})\int_{-1}^{+1} P_\lambda(\eta)\frac{ae^{-|\underline{s}-\underline{r}|-a|2\underline{s}-\underline{r}|}}{|2\underline{s}-\underline{r}||\underline{s}-\underline{r}|}(2\underline{s}-\underline{r})\cdot(\underline{s}-\underline{r}).\,d\eta \qquad 2.42d$$

$$g_\lambda^2(r,\sigma) = M_\lambda\int_{-1}^{+1} P_\lambda(\eta).P^N(|2\underline{s}-\underline{r}|)\{1+CP_{ab}\}e^{-|\underline{s}-\underline{r}|-a|2\underline{s}-\underline{r}|}\,d\eta \qquad 2.42e$$

where P_{ab} is the interchange operator interchanging a and b and $M_\lambda = \frac{N\sigma r(2\lambda+1)}{8\sqrt{2}\pi}$.

Using equation (2.40) and (2.41), equation (2.35a) may be written as follows:

$$K_{12}^{(e)}(r,\sigma) = \int Y_{\ell m}(\hat{r}_\rho)Y_{\ell m}(\hat{\sigma}_1)\,8\sum_\lambda\Big[2S\Big\{5-E_{He}-\frac{2}{r}+\frac{2P^N(r)}{S}+k_1^2\Big\}\mathcal{H}_\lambda^\circ(r,\sigma)$$

$$+2S\{-\mathcal{H}_\lambda^1(r,\sigma)+2\mathcal{H}_\lambda^2(r,\sigma)+4\mathcal{H}_\lambda^2(-a,r,\sigma)-2g_\lambda^1(r,\sigma)+2\mathcal{H}_\lambda^\circ(a^2,r,\sigma)\}-4g_\lambda^2(r,\sigma)\Big]P_\lambda(\eta)\,d\hat{r}_\rho\,d\hat{\sigma}_1$$

where we have used the notation $\mathcal{H}(1,r,\sigma) = \mathcal{H}(r,\sigma)$.

This expression for $K_{12}^{(e)}$ can be further simplified by use of the addition formula:

$$P_\lambda(\eta) = \frac{4\pi}{2\lambda+1}\sum_{m=-\lambda}^{+\lambda} Y_{\lambda m}^*(\hat{r}_\rho)Y_{\lambda m}(\hat{\sigma}_1) \qquad 2.43$$

and the orthnormalization formula given by equation (2.12). Therefore the kernel $K_{12}^{(e)}$ can be written as follows:

$$K_{12}^{(\ell)}(r,\sigma) = \frac{64\pi}{2\ell+1}\Big[S\Big\{ k_1^2 + 5 - E_{He} - \frac{2}{r} + \frac{2P^N(r)}{S}\Big\} \mathcal{H}_\ell^0(1)$$

$$+ S\Big\{ -\mathcal{H}_\ell^{1}(1) + 2\mathcal{H}_\ell^{2}(1) + 4\mathcal{H}_\ell^{2}(-a) - 2g_\ell^{1}(1) + 2\mathcal{H}_\ell^{0}(a^2)\Big\} - 2g_\ell^{2}(1)\Big] \qquad 2.44$$

with the notation that $\mathcal{H}(z) \equiv \mathcal{H}(z,r,\sigma)$.

Since in this work we are considering $\ell = 0$ scattering the final form of equation (2.34a) will be (dropping the superscript $\ell = 0$):

$$\left[\frac{d^2}{dr_p^2} + V_1(r_p) + k_1^2\right] f(r_p) = -\int_0^\infty d\sigma_1\, g(\sigma_1) K_{12}(r_p,\sigma_1) \qquad 2.45a$$

where $$K_{12}(r,\sigma) = 64\pi\Big[S\Big\{ k_1^2 + 5 - E_{He} - \frac{2}{r} + \frac{2P^N(r)}{S}\Big\} \mathcal{H}_0^0(1)$$

$$+ S\Big\{ -\mathcal{H}_0^{1}(1) + 2\mathcal{H}_0^{2}(1) + 4\mathcal{H}_0^{2}(-a) - 2g_0^{1}(1) + 2\mathcal{H}_0^{0}(a^2)\Big\} - 2g_0^{2}(1)\Big] \qquad 2.45b$$

(c) Kernel $K_{22}^{(\ell)}$

Using equations (2.23) and (2.24) and substituting $\underline{r}_2 = 2\underline{\sigma}_2 - \underline{r}_p$ and $\underline{\rho}_2 = 2(\underline{\sigma}_2 - \underline{r}_p)$ we obtain the following expression:

$$\nabla_{\sigma_2}^2 \Big\{ \varphi_0(r_2)\omega(\rho_2)\Big\} = \varphi_0(r_2)\omega(\rho_2)\Big[17 - \frac{16}{r_2} - \frac{4}{\rho_2} + 8\frac{\underline{r}_2\cdot\underline{\rho}_2}{r_2\rho_2}\Big] \qquad 2.46$$

Therefore substituting equation (2.46) into equation (2.30b) we obtain the following:

$$K_2(\underline{\sigma}_1,\underline{\sigma}_2) = 16(1+P_{12})\int d\underline{\tau}_\rho \left[k_2^2 + 17 - \frac{16}{r_2} - \frac{8}{r_\rho} + \frac{8}{r_1} - \frac{4}{r_{12}} + \frac{8\underline{r}_2\cdot\underline{\rho}_2}{r_2\rho_2}\right] \varphi_0(1)\varphi_0(2)\omega(\rho_1)\omega(\rho_2) \quad 2.47$$

We now make the following substitutions:

$$\varphi_0(|2\underline{\sigma}-\underline{\tau}|)\omega(2|\underline{\sigma}-\underline{\tau}|) = \frac{1}{4\sigma}\sum_\lambda g_\lambda^1(\tau,\sigma)P_\lambda(\eta) \quad 2.48a$$

$$\frac{\varphi_0(|2\underline{\sigma}-\underline{\tau}|)\omega(2|\underline{\sigma}-\underline{\tau}|)(2\underline{\sigma}-\underline{\tau})\cdot(\underline{\sigma}-\underline{\tau})}{|2\underline{\sigma}-\underline{\tau}|\,|\underline{\sigma}-\underline{\tau}|} = \frac{1}{4\sigma}\sum_\lambda g_\lambda^2(\tau,\sigma)P_\lambda(\eta) \quad 2.48b$$

$$\frac{\varphi_0(|2\underline{\sigma}-\underline{\tau}|)\omega(2|\underline{\sigma}-\underline{\tau}|)}{|2\underline{\sigma}-\underline{\tau}|} = \frac{1}{4\sigma}\sum_\lambda g_\lambda^3(\tau,\sigma)P_\lambda(\eta) \quad 2.48c$$

where η and P_λ are defined in part (b). Alternatively we may express equations (2.48) in the following form:

$$g_\lambda^1(\tau,\sigma) = M_\lambda'\int_{-1}^{+1} P_\lambda(\eta)e^{-|\underline{\sigma}-\underline{\tau}|-2|2\underline{\sigma}-\underline{\tau}|}\,d\eta \quad 2.49a$$

$$g_\lambda^2(\tau,\sigma) = M_\lambda'\int_{-1}^{+1} \frac{P_\lambda(\eta)e^{-|\underline{\sigma}-\underline{\tau}|-2|2\underline{\sigma}-\underline{\tau}|}(2\underline{\sigma}-\underline{\tau})\cdot(\underline{\sigma}-\underline{\tau})}{|2\underline{\sigma}-\underline{\tau}|\,|\underline{\sigma}-\underline{\tau}|}\,d\eta \quad 2.49b$$

$$g_\lambda^3(\tau,\sigma) = M_\lambda'\int_{-1}^{+1} \frac{P_\lambda(\eta)e^{-|\underline{\sigma}-\underline{\tau}|-2|2\underline{\sigma}-\underline{\tau}|}}{|2\underline{\sigma}-\underline{\tau}|}\,d\eta \quad 2.49c$$

where $M_\lambda' = \frac{4\sigma(2\lambda+1)}{2\pi}$ 2.49d

Using equations (2.27), (2.46) and (2.48) the kernel $K_{22}^{(e)}$ given by equation (2.35b) may be written as follows:

$$K_{22}^{(e)}(\sigma_1,\sigma_2) = 64 \int Y_{em}(\hat{\sigma}_1)\, Y_{em}(\hat{\sigma}_2)\,(1+P_{12}) \sum_{\lambda\lambda'} \frac{1}{r_p^2} \Big[\Big\{ 13 - \frac{4}{r_p} + k_1^2 - E_{He} \Big\} g_\lambda^1(1) g_{\lambda'}^1(2)$$

$$- 8\, g_\lambda^3(1)\, g_{\lambda'}^1(2) + 4 \Big\{ g_\lambda^1(1)\, g_{\lambda'}^3(2) + g_\lambda^2(1)\, g_{\lambda'}^1(2) \Big\}$$

$$- g_\lambda^1(1)\, g_{\lambda'}^1(2) \sum_q \frac{\sigma_<^q}{\sigma_>^{q+1}} P_q(\hat{\sigma}_1\cdot\hat{\sigma}_2) \Big] P_\lambda(\hat{\sigma}_1\cdot\hat{r}_p) P_{\lambda'}(\hat{\sigma}_2\cdot\hat{r}_p)\, d\hat{\sigma}_1 d\hat{\sigma}_2 d\underline{r}_p \qquad 2.50$$

where $\sigma_< = \sigma_1$, $\sigma_> = \sigma_2$ if $\sigma_1 < \sigma_2$

and $\sigma_< = \sigma_2$, $\sigma_> = \sigma_1$ if $\sigma_2 < \sigma_1$

and we are using the notation $g(1) = g(r,\sigma_1)$ and $g(2) = g(r,\sigma_2)$

Using equation (2.43) and the relation:

$$\int d\hat{r}\, Y_{\lambda m}(\hat{r}) Y_{\lambda' m'}(\hat{r}) Y^*_{\lambda'' m''}(\hat{r}) = \left[\frac{(2\lambda+1)(2\lambda'+1)}{4\pi(2\lambda''+1)} \right]^{\frac{1}{2}} C(\lambda\lambda'\lambda'';000) C(\lambda\lambda'\lambda'';mm'm'') \qquad 2.51$$

where the C's are Clebsch Gordan coefficients defined in Section (2.1). The angular part of the last term of can be written as follows:

$$\int Y_{em}(\hat{\sigma}_1)\, Y_{em}(\hat{\sigma}_2) P_q(\hat{\sigma}_1\cdot\hat{\sigma}_2) P_\lambda(\hat{\sigma}_1\cdot\hat{r}_p) P_{\lambda'}(\hat{\sigma}_2\cdot\hat{r}_p)\, d\hat{\sigma}_1 d\hat{\sigma}_2 d\hat{r}_p$$

$$= (4\pi)^2 \frac{(2q+1)}{(2\lambda+1)^3} \delta_{\lambda\lambda'}\, C^2(q\,q\,\lambda;000)$$

The angular part of the remaining terms of $K_{22}^{(e)}$ is:

$$\int Y_{\ell m}(\hat{\sigma}_1)\, Y_{\ell m}(\hat{\sigma}_2)\, P_\lambda(\hat{\sigma}_1\cdot\hat{r}_p) P_{\lambda'}(\hat{\sigma}_2\cdot\hat{r}_p)\, d\hat{\sigma}_1\, d\hat{\sigma}_2\, d\hat{r}_p = \frac{(4\pi)^2}{(2\lambda+1)^2}\,\delta_{\lambda\lambda'}\,\delta_{\ell\lambda}$$

Therefore $K_{22}^{(\ell)}$ can be written as follows:

$$K_{22}^{(\ell)}(\sigma_1,\sigma_2) = 64(4\pi)^2(1+P_{12})\int_0^\infty dr_p \frac{1}{(2\ell+1)^2}\Bigg[\left\{13-\frac{4}{r_p}+k_1^2-E_{Hc}\right\} g_\ell^1(1)\, g_\ell^1(2)$$

$$+4\left\{g_\ell^2(1)-g_\ell^3(1)\right\} g_\ell^1(2) - (2\ell+1)^3 \sum_{\lambda,q} \frac{\sigma_<^q}{\sigma_>^{q+1}} \frac{C^2(q\,\ell\lambda;000)}{(2\lambda+1)^2} g_\lambda^1(1)\, g_\lambda^1(2)\Bigg] \qquad 2.52$$

For $\ell=0$ we use the relation $C(q\,0\lambda\,;000) = \delta_{q\lambda}$ and obtain the following forms of the second radial equation (2.34b):

$$\left[\frac{d^2}{d\sigma_1^2} + k_2^2\right] g(\sigma_1) = -\int_0^\infty dr_p\, f(r_p) K_{12}(r_p,\sigma_1) - \int_0^\infty d\sigma_2\, g(\sigma_2) K_{22}(\sigma_1,\sigma_2) \qquad 2.53a$$

where $$K_{22}(\sigma_1,\sigma_2) = 1024\pi^2(1+P_{12})\int_0^\infty dr_p\Bigg[\left\{13-\frac{4}{r_p}+k_1^2-E_{Hc}\right\} g_0^1(1)\, g_0^1(2)$$

$$+4\left\{g_0^2(1)-g_0^3(1)\right\} g_0^1(2) - \sum_\lambda \frac{\sigma_<^\lambda}{\sigma_>^{\lambda+1}} \frac{g_\lambda^1(1)\, g_\lambda^1(2)}{(2\lambda+1)^2}\Bigg] \qquad 2.53b$$

2.5 Cross-Section Formulation

(a) The Scattering Amplitude

The total wave function Ψ must satisfy the following

boundary condition:

$$\Psi(\underset{\sim}{x}, s_x, y, s_y) \underset{x\to\infty}{\sim} \sum_{\gamma} \left[e^{i\underset{\sim}{k}_n \cdot \underset{\sim}{x}} \delta_{\gamma\gamma'} + f_{\gamma'\gamma}(\theta_\gamma, \varphi_\gamma) \frac{e^{ik_n x}}{x} \right]$$

$$\times \phi_\gamma(y) Y_{\ell_1 m_1}(\hat{y}) \chi_{\ell_{s_1} m_{s_1}}(s_y) \chi_{\ell_{s_2} m_{s_2}}(s_x) \qquad 2.54$$

which represents an incident scattered wave and superimposed outgoing spherical waves. The system is in an initial state $\gamma' = (n' k_n' \ell_1' m_1' \ell_2' m_2' \ell_{s_1}' \ell_{s_2}' m_{s_1}' m_{s_2}')$. $f_{\gamma'\gamma}$ is the scattering amplitude for the reaction $\gamma' \to \gamma$ and the notation follows that of Section 2.2.

(b) <u>The differential Cross-Section</u>

The flux of particles passing through an area <u>dS</u> is given by

$$\frac{\hbar}{2im} \left[\phi^* \underset{\sim}{\nabla} \phi - (\underset{\sim}{\nabla}\phi)^* \phi \right]$$

where ϕ is the wave function of the particle and m its mass. The differential cross-section Q is defined as follows:

$$Q(\theta, \varphi) = \frac{\text{Scattered flux per unit solid angle}}{\text{Incident flux per unit area}}$$

Referring to equation (2.54) we obtain:

$$Q_{\gamma'\gamma}(\theta_\gamma,\phi_\gamma)d\Omega = \frac{k_n}{k_{n'}} \left| f_{\gamma'\gamma}(\theta_\gamma,\phi_\gamma) \right|^2 \frac{\left| \chi_{\ell_{s_1} m_{s_2}} \right|^2}{\left| \chi_{\ell_{s_2}' m_{s_2}'} \right|^2} d\Omega \qquad 2.55$$

$Q_{\gamma'\gamma}(\theta_\gamma,\phi_\gamma)$ is the differential cross-section for a collision in which the emerging particle has changed its spin from m_{s_2}' to m_{s_2} after exciting the target atom from the state $(n'\ell_1'\ell_{s_1}')$ to $(n\ell_1\ell_{s_1})$.

(c) Total Cross-Sections

The total cross-section Q of an atom for particles of a given velocity scattered by the target per unit time is obtained by integrating the corresponding differential cross-section over all scattering angles, averaging over initial spins and summing over final spins. Therefore:

$$Q(n'\ell_1'\ell_{s_1}' \to n\ell_1\ell_{s_1}) = 2\pi \frac{k_n}{k_{n'}} \sum_{\substack{m_1 m_{s_1} m_{s_2} \\ m_1' m_{s_1}' m_{s_2}'}} \frac{1}{(2\ell_{s_2}+1)(2\ell_{s_1}+1)(2\ell_1+1)} \int_0^{2\pi} \left| f_{\gamma'\gamma} \right|^2 \sin\theta \, d\theta \qquad 2.56$$

(d) The Scattering Matrix

Since the various formulae have been given by Blatt and Biedenharn[84] and Percival and Seaton[85], only a brief description will be given here. With reference to Section 2.1, asymptotically the total wave function consists of the target atom and a superposition of ingoing and outgoing spherical waves.

$$\Psi^{total}_{\Gamma'}(\underline{x}, s_x, \underline{y}, s_y) = \sum_{\Gamma} \phi_\nu(y)\, \mathcal{Y}^{M_L}_{\ell_1\ell_2 L}(\hat{x},\hat{y})\, \chi^{M_S}_{S}(s_x, s_y)\, \underline{F^{LS}_{\nu\nu'}(x)} \qquad 2.57$$

where $$F^{LS}_{\nu\nu'}(x) \underset{x\to\infty}{\sim} \frac{1}{k_n^{\frac{1}{2}}} \left[A^{L M_L S M_S}_{\nu} \cdot e^{-i\Theta_\nu} - B^{L M_L S M_S}_{\nu} \cdot e^{+i\Theta_\nu} \right] \qquad 2.58$$

$$\Theta_\nu = k_n x - \frac{\ell_2 \pi}{2} \quad , \quad \Gamma = (n k_n \ell_1 \ell_2 L M_L S M_S) \quad , \quad \nu = (n \ell_1 \ell_2 \ell_{s_1})$$

The scattering matrix S is defined by:

$$B^{L M_L S M_S}_{\nu} = \sum_{\nu''} S^{LS}_{\nu\nu''} A^{L M_L S M_S}_{\nu''}$$

where the sum is taken over all incident channels - S is related to the R-matrix in the following manner:

$$S = \frac{1 + iR}{1 - iR} \qquad 2.59$$

Equation (2.58) is written as:

$$F^{LS}_{\nu\nu'}(x) \underset{x\to\infty}{\sim} \frac{1}{k_n^{\frac{1}{2}}} \sum_{\nu''} A^{L M_L S M_S}_{\nu''} \left[e^{-i\Theta_\nu} \cdot \delta_{\nu\nu''} - S^{LS}_{\nu\nu''} e^{+i\Theta_\nu} \right] \qquad 2.60$$

The incident total wave function $\Psi^{inc}_{\gamma'}$ is composed of an incoming plane wave with the target in the state γ'.

$$\Psi^{inc}_{\gamma'} = \phi_{\gamma'}(y)\, Y_{\ell_1' m_1'}(\hat{y})\, \chi_{\ell_{s_1}' m_{s_1}'}(s_y)\, e^{i\underline{k}_n' \cdot \underline{x}}\, \chi_{\ell_{s_2}' m_{s_2}'}(s_x) \qquad 2.61$$

Using the expansion:

$$e^{ik\cdot x} \underset{x\to\infty}{\sim} i\sqrt{\pi} \sum_{\ell} i^{\ell} \frac{(2\ell+1)}{kx}^{\frac{1}{2}} \left[e^{-i\theta} - e^{+i\theta} \right] Y_{\ell 0}(\hat{x})$$

and combining the angular and spin functions using Clebsch-Gordan coefficients, equation (2.61) can be written as:

$$\Psi_{p'}^{inc} \underset{x\to\infty}{\sim} \frac{i\sqrt{\pi}}{k_n' x} \sum_{\substack{L\,M_L \\ S\,M_S \\ \ell_2}} \varphi_\nu(y)\, i^{\ell_2}(2\ell_2+1)^{\frac{1}{2}}\, \mathcal{Y}_{\ell_1'\ell_2 L}^{M_L}\, \chi_S^{M_S} \left[e^{-i\theta_\nu} - e^{+i\theta_\nu} \right]$$

$$\times C(\ell_1'\ell_2 L; m_1' 0 M_L)\, C(\ell_{s_1}'\ell_{s_2} S; m_{s_1}' m_{s_2} M_S)\, \delta_{n\ell_1\ell_{s_1}, n'\ell_1'\ell_{s_1}'}$$

The outgoing part $\Psi_{p'}^{out}$ of the total wave function is defined by:

$$\Psi_{p'}^{out} = \Psi_{p'}^{total} - \Psi_{p'}^{inc}$$

$$\underset{x\to\infty}{\sim} \sum_{p,\nu''} \varphi_\nu(y)\, \mathcal{Y}_{\ell_1\ell_2 L}^{M_L}\, \chi_S^{M_S}\, \frac{1}{k_n^{\frac{1}{2}} x}\, A_{\nu''}^{LM_L SM_S} \left[e^{-i\theta_\nu} \cdot \delta_{\nu\nu''} - S_{\nu\nu''}^{LS} e^{+i\theta_\nu} \right]$$

$$- \frac{i\sqrt{\pi}}{k_n' x} \sum_{n'\ell_1'\ell_{s_1}'} \delta_{n\ell_1\ell_{s_1}, n'\ell_1'\ell_{s_1}'} \sum_{\substack{L\,M_L \\ S\,M_S \\ \ell_2}} \varphi_\nu(y)\, \mathcal{Y}_{\ell_1'\ell_2 L}^{M_L}\, \chi_S^{M_S}\, i^{\ell_2}(2\ell_2+1)^{\frac{1}{2}}$$

$$\times C(\ell_1'\ell_2 L; m_1' 0 M_L)\, C(\ell_{s_1}'\ell_{s_2} S; m_{s_1}' m_{s_2} M_S) \left[e^{-i\theta_\nu} - e^{+i\theta_\nu} \right]$$

Since $\Psi_{p'}^{out}$ must contain outgoing spherical waves only the coefficient of the ingoing waves must vanish:

$$A_{\nu}^{LM_L SM_S} = \frac{i\sqrt{\pi}}{k_n^{\frac{1}{2}}} i^{\ell_2} (2\ell_2+1)^{\frac{1}{2}} C(\ell_1' \ell_2 L; m_1' 0 M_L) C(\ell_{s_1}' \ell_{s_2} S; m_{s_1}' m_s M_S)$$

$$\times \delta_{n\ell_1\ell_{s_1} n'\ell_1'\ell_{s_1}'}$$

Therefore $\Psi_{\Gamma'}^{out}$ reduces to:

$$\Psi_{\Gamma'}^{out} \underset{x\to\infty}{\sim} \frac{i\sqrt{\pi}}{x} \sum_{\Gamma,\ell_2'} \varphi_\nu(y) \mathcal{Y}_{\ell_1\ell_2 L}^{M_L} \chi_S^{M_S} \frac{i^{\ell_2'}(2\ell_2'+1)^{\frac{1}{2}}}{(k_n k_n')^{\frac{1}{2}}} \cdot e^{i\theta_\nu}$$

$$\times C(\ell_1'\ell_2' L; m_1' 0 M_L) C(\ell_{s_1}'\ell_{s_2}' S; m_{s_1}' m_{s_2}' M_S) \left[\delta_{\nu\nu'} - S_{\nu\nu'}^{LS}\right]$$

Expanding the functions $\mathcal{Y}_{\ell_1\ell_2 L}^{M_L}$ and $\chi_S^{M_S}$ we obtain:

$$\Psi_{\gamma'}^{out} \underset{x\to\infty}{\sim} \frac{i\sqrt{\pi}}{x} \sum_{\substack{\gamma\ell_2' \\ LM_L \\ SM_S}} \varphi_\gamma(y) Y_{\ell_1 m_1}(\hat{y}) \chi_{\ell_{s_1} m_{s_1}}(s_y) Y_{\ell_2 m_2}(\hat{x}) \chi_{\ell_2 m_{s_2}}(s_x)$$

$$\times \frac{i^{\ell_2'}(2\ell_2'+1)^{\frac{1}{2}}}{(k_n k_n')^{\frac{1}{2}}} C(\ell_1\ell_2 L; m_1 m_2 M_L) C(\ell_{s_1}\ell_{s_2} S; m_{s_1} m_{s_2} M_S) C(\ell_1'\ell_2' L; m_1' 0 M_L)$$

$$\times C(\ell_{s_1}'\ell_{s_2}' S; m_{s_1}' m_{s_2}' M_S) e^{i(k_n x - \frac{\ell_2\pi}{2})} \left[\delta_{\nu\nu'} - S_{\nu\nu'}^{LS}\right]$$

Comparing this to equation (2.54) results in the following expression for the scattering amplitude:

$$f_{\gamma\gamma'}(\theta_\gamma, \varphi_\gamma) = \frac{i\sqrt{\pi}}{(k_n k_n')^{\frac{1}{2}}} \sum_{\substack{\ell_2\ell_2' \\ LM_L \\ SM_S}} i^{\ell_2'-\ell_2} (2\ell_2'+1)^{\frac{1}{2}} Y_{\ell_2 m_2}(\hat{x}) C(\ell_1\ell_2 L; m_1 m_2 M) \times$$

$$C(\ell_{s_1}\ell_{s_2}S;m_{s_1}m_{s_2}M_S)C(\ell_1'\ell_2'L;m_1'0M_L)C(\ell_{s_1}'\ell_{s_2}'S;m_{s_1}'m_{s_2}'M_S)\left[\delta_{\nu\nu'}-S^{LS}_{\nu\nu'}\right] \qquad 2.62$$

Therefore the total cross-section formula reduces to:

$$Q(n'\ell_1'\ell_{s_1}'\to n\ell_1\ell_{s_1}) = \frac{1}{k_{n'}^2}\sum_{\substack{\ell_2\ell_2'\\ LS}}\frac{(2L+1)(2S+1)}{(2\ell_{s_2}+1)(2\ell_1+1)(2\ell_{s_1}+1)}\left|T_{\nu\nu'}\right|^2 \qquad 2.63$$

where the transition matrix T is defined as:

$$T_{\nu\nu'} = S_{\nu\nu'} - 1 \qquad 2.64$$

CHAPTER III

KERNEL COMPUTATION

3.1 Integration Procedures.

(a) Kernel K_{1a}.

The functions $\mathcal{H}_o^o$, $\mathcal{H}_o^1$, $\mathcal{H}_o^2$, $\mathcal{J}_o^1$ and $\mathcal{J}_o^2$ are defined by equations (2.42) and can be written as follows:

$$\mathcal{H}_o^o(A,r,\sigma) = M_o(1+CP_{ab})\int_{-1}^{+1} d\eta.\, A e^{-(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}} - a(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}} \qquad 3.1a$$

$$\mathcal{H}_o^1(r,\sigma) = M_o(1+CP_{ab})\int_{-1}^{+1} d\eta.\, \frac{e^{-(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}} - a(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}}}{(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}}} \qquad 3.1b$$

$$\mathcal{H}_o^2(A,r,\sigma) = M_o(1+CP_{ab})\int_{-1}^{+1} d\eta.\, \frac{Ae^{-(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}} - a(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}}}{(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}} \qquad 3.1c$$

$$\mathcal{J}_o^1(r,\sigma) = M_o(1+CP_{ab})\int_{-1}^{+1} d\eta.\, \frac{ae^{-(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}} - a(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}}(2\sigma^2+r^2-3\sigma r\eta)}{(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}}} \qquad 3.1d$$

$$\mathcal{J}_o^2(r,\sigma) = M_o\int_{-1}^{+1} d\eta.\, P^N(|2\underset{\sim}{\sigma}-\underset{\sim}{r}|)(1+CP_{ab})e^{-(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}} - a(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}} \qquad 3.1e$$

By inspection of equations (3.1) it is clear that the presence of the radicals $(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}}$ and $(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}$ in the

denominator of the integrands will lead to numerical difficulties, since for $\eta = 1$ the first radical vanishes for $\tau = \sigma$ and the second for $\tau = 2\sigma$. This difficulty can be avoided by the following change of variable suggested by Fraser: (68)

$$\rho = \frac{\tau}{\sigma} \qquad q = \frac{2\sigma}{\tau} \tag{3.2a}$$

$$-1 \le \xi \le +1$$

$$0 < \rho \le 1 : \quad \eta = \frac{\rho}{2} - \xi - \frac{\rho \xi^2}{2} \tag{3.2b}$$

$$1 \le \rho < \sqrt{2} : \quad \eta = \frac{1}{2\rho} - \xi - \frac{1}{2\rho}\xi^2 \tag{3.2c}$$

$$0 \le q \le 1 : \quad \eta = \frac{q}{2} - \xi - \frac{q}{2}\xi^2 \tag{3.2d}$$

$$1 \le q < \sqrt{2} : \quad \eta = \frac{1}{2q} - \xi - \frac{1}{2q}\xi^2 \tag{3.2e}$$

For example, if we consider g_0', its four different forms will be:

$$g_0'(\rho,\sigma) = M_0 (1+CP_{ab}) \frac{a}{2} \int_{-1}^{+1} d\xi \cdot X_1^{-1} e^{-\sigma(1+\rho\xi)-a\sigma X_1} (\rho^2 - 6\rho\xi - 3\rho^2\xi^2 - 4) \qquad 0 < \rho \le 1$$

$$g_0'(\rho,\sigma) = -M_0 (1+CP_{ab}) \frac{a}{2\rho} \int_{-1}^{+1} d\xi \cdot X_2^{-1} e^{-\sigma(\rho+\xi)-a\sigma X_2} (2\rho^2 + 6\rho\xi + 3\xi^2 + 1) \qquad 1 \le \rho < \sqrt{2}$$

$$g_0^1(q,\sigma) = M_0(1+CP_{ab})\frac{a}{2q}\int_{-1}^{+1} d\xi \cdot X_3^{-1}\left(q^2 - 6q\xi - 3q^2\xi^2 - 4\right)e^{-\sigma X_3 - 2a\sigma\left(\xi+\frac{1}{q}\right)} \qquad 0 < q \leq 1$$

$$g_0^2(q,\sigma) = -M_0(1+CP_{ab})\frac{a}{2q}\int_{-1}^{+1} d\xi \cdot X_4^{-1}\left(1+2q^2+6q\xi+3\xi^2\right)e^{-\sigma X_4 - 2a\sigma\left(1+\frac{\xi}{q}\right)} \qquad 1 \leq q < \sqrt{2}$$

where $X_1 = \left(4 - \rho^2 + 4\rho\xi + 2\rho^2\xi^2\right)^{\frac{1}{2}}$, $X_2 = \left(\rho^2 + 2 + 4\rho\xi + 2\xi^2\right)^{\frac{1}{2}}$,

$X_3 = \left(\frac{4}{q^2} - 1 + \frac{4\xi}{q} + 2\xi^2\right)^{\frac{1}{2}}$, $X_4 = \left(\frac{2}{q^2} + 1 + \frac{4\xi}{q} + \frac{2\xi^2}{q^2}\right)^{\frac{1}{2}}$

It should be noted that the new radicals are non-vanishing in the ranges of ρ and q specified. The integration over ξ was performed using a 16-point Gaussian quadrature.

K_{12} can be divided into two parts: one depending on k_1^2 and one independent of k_1^2. Therefore, using the notation of Section 2.4 we can write the following:

$$K_{12}(r,\sigma) = K_{12}^{(1)}(r,\sigma).k_1^2 + K_{12}^{(2)}(r,\sigma) \qquad 3.3$$

where $$K_{12}^{(1)}(r,\sigma) = 64\pi S H_0^0(1) \qquad 3.4a$$

and $$K_{12}^{(2)}(r,\sigma) = 64\pi\left[S\left\{5 - E_{He} - \frac{2}{r} + \frac{2P^N(r)}{S}\right\}H_0^0(1)\right.$$

$$\left. + S\left\{-H_0^1(1) + 2H_0^2(1) - 4H_0^2(-a) - 2g_0^1(1) + 2H_0^0(a^2)\right\} - 2g_0^2(1)\right] \qquad 3.4b$$

$K_{12}^{(1)}$ and $K_{12}^{(2)}$ were tabulated separately for $r = 0(\cdot05)5(\cdot1)32$ and $\sigma = \cdot05(\cdot05)5(\cdot1)17\cdot5$. The expression for $K_{12}(0,\sigma)$

is derived as follows:

By inspection of equation (3.12) it can be seen that: $\mathcal{H}_0^0(1,0,\sigma) = 0$

but Limit $\frac{1}{r}\mathcal{H}_0^0(1,r,\sigma) = \frac{N\sigma}{4\sqrt{2}\,\pi}\left[e^{-\sigma(2a+1)} + e^{-\sigma(2b+1)} \right]$

Therefore $K_{12}^{(1)}(0,\sigma) = 0$ but $K_{12}^{(2)}(0,\sigma) \neq 0$

since $K_{12}^{(2)}$ contains factors of $\frac{1}{r}$. The only terms contributing to $K_{12}^{(2)}(r,\sigma)$ at $r=0$ are the following:

$$64\pi\left[-\frac{2S}{r} + 2P^N(r) \right]\mathcal{H}_0^0(r,\sigma)$$

$$= -128\pi\left[\frac{S}{r} + 4N\sqrt{2}\left\{ \frac{e^{-(a+2)r}}{(a+2)^3}\left(a+2+\frac{2}{r}\right) + \frac{Ce^{-(b+2)r}}{(b+2)^3}\left(b+2+\frac{2}{r}\right)\right\}\right]\mathcal{H}_0^0(r,\sigma)$$

Therefore using the above results we obtain:

$$K_{12}^{(2)}(0,\sigma) = -128\pi\left[S + 4N\sqrt{2}\left\{ \frac{2}{(a+2)^3} + \frac{2C}{(b+2)^3}\right\}\right]\frac{N\sigma}{4\sqrt{2}\,\pi}\left[e^{-\sigma(2a+1)} + Ce^{-\sigma(2b+1)}\right]$$

$$= -32\sqrt{2}\,SN\sigma\left[e^{-\sigma(2a+1)} + Ce^{-\sigma(2b+1)}\right] \qquad 3.5$$

(b) Kernel K_{22}.

The functions $\mathcal{G}_\lambda^1$, $\mathcal{G}_0^2$ and $\mathcal{G}_0^3$ defined by equations (2.49) can be written as follows:

$$G_\lambda^1(r,\sigma) = M_\lambda' \int_{-1}^{+1} d\eta \cdot P_\lambda(\eta)\, e^{-(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}} - 2(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}} \qquad 3.6a$$

$$G_0^2(r,\sigma) = M_0' \int_{-1}^{+1} d\eta \cdot \frac{e^{-(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}} - 2(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}}}{(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}}(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}}(2\sigma^2+r^2-3\sigma r\eta) \qquad 3.6b$$

$$G_0^3(r,\sigma) = M_0' \int_{-1}^{+1} d\eta \cdot \frac{e^{-(\sigma^2+r^2-2\sigma r\eta)^{\frac{1}{2}} - 2(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}}}{(4\sigma^2+r^2-4\sigma r\eta)^{\frac{1}{2}}} \qquad 3.6c$$

where M_λ' is defined by equation (2.49d).

We make the substitutions defined by equations (3.2). Therefore G_λ^1, for example, will be given by:

$$G_\lambda^1(\rho,\sigma) = M_\lambda' \int_{-1}^{+1} d\xi \cdot P_\lambda\left(\frac{\rho}{2} - \xi - \frac{\rho\xi^2}{2}\right)\cdot(1+\rho\xi)\, e^{-\sigma(1+\rho\xi)-2\sigma X_1} \qquad 0<\rho\le 1$$

$$G_\lambda^1(\rho,\sigma) = M_\lambda' \frac{1}{\rho}\int_{-1}^{+1} d\xi \cdot P_\lambda\left(\frac{1}{2\rho} - \frac{\xi}{\rho} - \frac{\xi^2}{2\rho}\right)\cdot(\rho+\xi)\, e^{-\sigma(\rho+\xi)-2\sigma X_2} \qquad 1\le\rho<\sqrt{2}$$

$$G_\lambda^1(q,\sigma) = M_\lambda' q \int_{-1}^{+1} d\xi \cdot P_\lambda\left(\frac{q}{2} - \xi - \frac{q\xi^2}{2}\right)\cdot\left(\xi+\frac{1}{q}\right) e^{-\sigma X_3 - 4\sigma(\xi+\frac{1}{q})} \qquad q<q\le 1$$

$$G_\lambda^1(q,\sigma) = M_\lambda' \int_{-1}^{+1} d\xi \cdot P_\lambda\left(\frac{1}{2q} - \frac{\xi}{q} - \frac{\xi^2}{2q}\right)\cdot\left(1+\frac{\xi}{q}\right) e^{-\sigma X_4 - 4\sigma(1+\frac{\xi}{q})} \qquad 1\le q<\sqrt{2}$$

where X_1, X_2, X_3 and X_4 are defined in part (a). These angular integrations were performed using a 16-point Gaussian quadrature. The Legendre function P_λ was generated using the following recursion formula:

$$P_{\lambda+1}(\omega) = \frac{1}{\lambda+1}\left[(2\lambda+1)\omega P_\lambda(\omega) - \lambda P_{\lambda-1}(\omega)\right] \qquad 3.7a$$

$$P_0(\omega)=1 \quad \text{and} \quad P_1(\omega)=\omega \qquad 3.7b$$

K_{22} can also be divided into two parts as follows:

$$K_{22}(\sigma_1,\sigma_2) = K_{22}^{(1)}(\sigma_1,\sigma_2).k_1^2 + K_{22}^{(2)}(\sigma_1,\sigma_2) \qquad 3.8$$

where $$K_{22}^{(1)}(\sigma_1,\sigma_2) = 128(4\pi)^2\int_0^\infty dr_p\, \zeta_0^1(1)\,\zeta_0^1(2) \qquad 3.9a$$

and $$K_{22}^{(2)}(\sigma_1,\sigma_2) = 128(4\pi)^2\int_0^\infty dr_p\left[\left\{13-E_{He}-\frac{4}{r_p}\right\}\zeta_0^1(1)\zeta_0^1(2)\right.$$

$$\left. + 2(1+P_{12})\left\{\zeta_0^2(1)-\zeta_0^3(1)\right\}\zeta_0^1(2) - \sum_\lambda \frac{\sigma_<^\lambda}{\sigma_>^{\lambda+1}}\,\frac{\zeta_\lambda^1(1)\zeta_\lambda^1(2)}{(2\lambda+1)^2}\right] \qquad 3.9b$$

Here, equation (2.52) has been simplified to give equation (3.9b). The summation over λ was taken from $\lambda=0$ to $\lambda=10$. The integration over r_p will now be described, the interval of integration being .1 and the upper integration limit being taken as 16.

Since K_{22} is symmetric in σ_1 and σ_2 it is only necessary to compute $K_{22}(\sigma_1,\sigma_2)$ for $\sigma_1 \geq \sigma_2$. A brief inspection of equations (3.6) would lead one to assume that the integrand of equation (3.9b) is discontinuous at four points: $r_p = \sigma_1, 2\sigma_1, \sigma_2$ and $2\sigma_2$. But closer examination of the form of ζ_0^2 defined by equation (3.6b) reveals that there is no singularity in the integrand for $-1 \leq \eta \leq +1$

and therefore the function ζ_0^3 defined by equation (3.6c) is the only function with a singular integrand, in this case at $r_\rho = 2\sigma$. Therefore the integrand of $K_{22}^{(2)}(\sigma_1, \sigma_2)$ is discontinuous at the two points $r_\rho = 2\sigma_1$ and $2\sigma_2$ and allowance for this must be made in the integration over r_ρ.

It follows therefore that $K_{22}^{(2)}(\sigma_1, \sigma_2)$ will be discontinuous at the point $\sigma_1 = \sigma_2$. This is clearly shown in the graphical displays, see Section 3.3(c).

$K_{22}^{(1)}$ and $K_{22}^{(2)}$ were tabulated separately for σ_1 and σ_2 $= .1(.1)16.0$. The proof that $K_{22}(0, \sigma_2) = 0$ is as follows:

From equation (3.6a) and (2.45d) it can be seen that:

$$\zeta_\lambda^1(r, 0) = 0$$

but $$\lim_{\sigma \to 0} \frac{1}{\sigma} \zeta_\lambda^1(r, \sigma) = \frac{re^{-3r}}{\pi} \cdot \delta_{\lambda 0}$$

Since we are considering the case $\sigma_1 \geq \sigma_2$ and K_{22} is symmetric we examine $K_{22}(\sigma_2, 0)$. From the above results it is clear that $K_{22}^{(1)}(0, \sigma_2) = 0$. By inspection of equation (3.9b) it can be seen that $K_{22}^{(2)}(\sigma_2, 0)$ has no factors of inverse powers of σ_1 since in this case $\sigma_> = \sigma_2$. Therefore the summation over λ will vanish at $\sigma_1 = 0$ and $K_{22}^{(2)}(\sigma_2, 0) = K_{22}^{(2)}(0, \sigma_2) = 0$.

3.2 Numerical Checking Procedures.

(a) Kernel K_{12}.

At the points $\rho = \sqrt{2}$ the functions given by equations (3.1) can be solved in closed form. Substituting $r = n\sqrt{2}$ and $\sigma = n$, where n is any positive, non-zero integer, equations (3.1) reduce to the following:

$$\mathcal{H}_o^o(A, n\sqrt{2}, n) = M_o(1+CP_{ab})\int_{-1}^{+1} d\eta \cdot Ae^{-n(3-2\sqrt{2})^{\frac{1}{2}}(1+a\sqrt{2})}$$

$$= M_o(1+CP_{ab})\frac{A}{n\sqrt{2}(1+a\sqrt{2})}\left[e^{-nX_1}\left\{(3-2\sqrt{2})^{\frac{1}{2}} + \frac{1}{n(1+a\sqrt{2})}\right\} - e^{-nX_2}\left\{(3+2\sqrt{2}) + \frac{1}{n(1+a\sqrt{2})}\right\}\right] \quad 3.10a$$

$$\mathcal{H}_o^2(A, n\sqrt{2}, n) = M_o(1+CP_{ab})\int_{-1}^{+1} d\eta \cdot \frac{Ae^{-n(3-2\sqrt{2})^{\frac{1}{2}}(1+a\sqrt{2})}}{n\sqrt{2}(3-2\sqrt{2})^{\frac{1}{2}}}$$

$$= M_o(1+CP_{ab})\frac{A}{n^2\sqrt{2}(1+a\sqrt{2})}\left[e^{-nX_1} - e^{-nX_2}\right] \quad 3.10b$$

$$\mathcal{H}_o^1(n\sqrt{2}, n) = \sqrt{2}\,\mathcal{H}_o^2(1, n\sqrt{2}, n) \quad 3.10c$$

$$\mathcal{G}_o^1(n\sqrt{2}, n) = M_o(1+CP_{ab})\int_{-1}^{+1} d\eta \cdot \frac{ae^{-n(3-2\sqrt{2})^{\frac{1}{2}}(1+a\sqrt{2})}}{\sqrt{2}(3-2\sqrt{2}\eta)} \cdot (4-3\sqrt{2}\eta)$$

$$= \frac{3}{2\sqrt{2}}\mathcal{H}_o^o(a, n\sqrt{2}, n) - \frac{M_o}{2\sqrt{2}}(1+CP_{ab})a\int_{-1}^{+1} d\eta \cdot \frac{e^{-n(3-2\sqrt{2})^{\frac{1}{2}}(1+a\sqrt{2})}}{(3-2\sqrt{2}\eta)} \quad 3.10d$$

$$\mathcal{G}_o^2(n\sqrt{2}, n) = M_o\int_{-1}^{+1} d\eta \cdot P^N\left(n\sqrt{2}\left\{3-2\sqrt{2}\right\}^{\frac{1}{2}}\right)(1+CP_{ab})e^{-n(3-2\sqrt{2}\eta)^{\frac{1}{2}}(1+a\sqrt{2})}$$

$$= M_o \frac{4N}{n^2}\left(1+C^2 P_{ab}\right) \frac{e^{-n(3-2\sqrt{2})^{\frac{1}{2}} Y_1}}{(a+2)^3 Y_1} \left\{ \frac{(a+2)}{Y_1} - \left[\sqrt{2} + n(a+2)(3-2\sqrt{2})^{\frac{1}{2}}\right]\right\}$$

$$- \frac{e^{-n(3+2\sqrt{2})^{\frac{1}{2}} Y_1}}{(a+2)^3 Y_1} \left\{ \frac{(a+2)}{Y_1} - \left[\sqrt{2} + n(a+2)(3+2\sqrt{2})^{\frac{1}{2}}\right]\right\} \Bigg]$$

$$+ M_o \frac{4NC}{n^2}\left(1+P_{ab}\right) \Bigg[\frac{e^{-n(3-2\sqrt{2})^{\frac{1}{2}} Y_2}}{(a+2)^3 Y_2} \left\{ \frac{(a+2)}{Y_2} - \left[\sqrt{2} + n(a+2)(3-2\sqrt{2})^{\frac{1}{2}}\right]\right\}$$

$$- \frac{e^{-n(3+2\sqrt{2})^{\frac{1}{2}} Y_2}}{(a+2)^3 Y_2} \left\{ \frac{(a+2)}{Y_2} - \left[\sqrt{2} + n(a+2)(3+2\sqrt{2})^{\frac{1}{2}}\right]\right\} \Bigg] \qquad 3.10e$$

where $X_1 \quad (3-2\sqrt{2})^{\frac{1}{2}}(1+a\sqrt{2})$ and $X_2 \quad (3+2\sqrt{2})^{\frac{1}{2}}(1+a\sqrt{2})$

$Y_1 \quad \{1+2\sqrt{2}(a+1)\}$ and $Y_2 \quad \{1+(a+b+2)\sqrt{2}\}$

A separate computer code was written to calculate H_o^0, H_o^2 and g_o^2 given by equations (3.10). Because of the symmetry in a and b all cases were checked for $C=0$. g_o^1 as defined by equation (3.10d) introduced special difficulties since the integral term:

$$\int_{-1}^{+1} d\eta \cdot \frac{e^{-n(3-2\sqrt{2}\eta)^{\frac{1}{2}}(1+a\sqrt{2})}}{(3-2\sqrt{2}\eta)}$$

gives a logarithmic term plus an oscillating series. The series did not produce satisfactory results on account of round-off errors. Therefore the substitution $n(3-2\sqrt{2}\eta)^{\frac{1}{2}}(1+a\sqrt{2}) = t$ was performed transforming the above integral to:

$$\frac{1}{\sqrt{2}} \int_{n(3-2\sqrt{2})^{\frac{1}{2}}(1+a\sqrt{2})}^{n(3+2\sqrt{2})^{\frac{1}{2}}(1+a\sqrt{2})} \frac{e^{-t}}{t}\, dt$$

which was then computed using tables and a desk calculator. H_0^0, H_0^2 and g_0^2 were each checked for $n=1$ and 2 giving seven figure agreement. g_0^1 was checked for $n=1$ giving five figure agreement.

A further test is to write a separate routine calculating the H^1s and g^1s using a 16-point Gaussian Quadrature, before the substitution of equations (3.2) is applied. This was done for $\tau = 1{\cdot}6$ and $\sigma = 2{\cdot}4$ and gave a minimum of five figure agreement. It is interesting to note that the same test applied to $\tau = 1{\cdot}6$ and $\sigma = {\cdot}8$ and 1.6 gave disagreement at the third significant figure demonstrating the effect of the singular integrands at the upper limit of integration. The following alternative method was used in the case of $\tau = \sigma = 1{\cdot}6$:

Substituting $(1-\eta) = x$ in equations (3.1a) we obtain for $\tau = \sigma$:

$$H_0^0(A,\sigma,\sigma) = M_0(1+CP_{ab}) \int_0^2 A e^{-\sigma\sqrt{2x} - a\sigma\sqrt{4x+1}}$$

Using Taylor's theorem we expand the well-behaved function about x=0 as follows:

$$e^{-a\sigma\sqrt{4x+1}} = e^{-a\sigma} - 2a\sigma x e^{-a\sigma} + O(x^2)$$

Therefore we may rewrite the expression for H_0^0 :

$$H_0^0(A,\sigma,\sigma) = M_0(1+CP_{ab})\int_0^2 e^{-\sigma\sqrt{2x}} A\left[e^{-a\sigma\sqrt{4x+1}} - e^{-a\sigma}(1-2a\sigma x)\right]dx + I(\sigma,a)$$

where $$I(\sigma,a) = M_0(1+CP_{ab})e^{-a\sigma}\int_0^2 Ae^{-\sigma\sqrt{2x}}(1-2a\sigma x)\,dx$$

$$= M_0(1+CP_{ab})\frac{2e^{-a\sigma}}{\sigma^3}A\left[\frac{\sigma}{2} - 3a - e^{-2\sigma}\left\{\sigma^2+\frac{\sigma}{2} - a(4\sigma^3+6\sigma^2+6\sigma+3)\right\}\right]$$

and the integrand of the integral term is now continuous in the range considered.

An identical process was carried out for the remaining functions and a program computing this form of the integrals gave a minimum of five figure agreement.

(b) Kernel K_{23}.

Substituting $r = n\sqrt{2}$ and $\sigma = n$ in equations (3.6) we obtain:

$$G_\lambda^1(n\sqrt{2},n) = M_\lambda^1\int_{-1}^{+1} d\eta.\,P_\lambda(\eta)\,e^{-n(3-2\sqrt{2}\eta)^{\frac{1}{2}}(2\sqrt{2}+1)}$$

$$G_\lambda^2(n\sqrt{2},n) = M_0^1\int_{-1}^{+1} d\eta.\,\frac{e^{-n(3-2\sqrt{2}\eta)^{\frac{1}{2}}(2\sqrt{2}+1)}}{(3-2\sqrt{2}\eta)}(4-3\sqrt{2}\eta)$$

$$G_\lambda^3(n\sqrt{2},n) = M_0^1\int_{-1}^{+1} d\eta.\,\frac{e^{-n(3-2\sqrt{2}\eta)^{\frac{1}{2}}(2\sqrt{2}+1)}}{(3-2\sqrt{2}\eta)^{\frac{1}{2}}}$$

$$= \frac{M_0'}{M_0} \frac{n}{\sqrt{2}} H_0^2(2, n\sqrt{2}, n, c\ 0)$$

Since $\zeta_0^1(n\sqrt{2}, n) = (2M_0)^{-1} M_0' H_0^0(2, n\sqrt{2}, n, C = 0)$ both ζ_0^1 and ζ_0^3 were checked using the code for K_{1a}. ζ_0^2 was checked in a similar manner to ζ_0^1. The tests were run for $n = 1$ and gave a minimum of five figure agreement. For $r = \sigma$ equations (3.6) reduce to:

$$\zeta_\lambda^1(\sigma,\sigma) = M_\lambda' \int_{-1}^{+1} d\eta \cdot P_\lambda(\eta) e^{-\sigma\sqrt{2}(1-\eta)^{\frac{1}{2}} - 2\sigma(5-4\eta)^{\frac{1}{2}}}$$

$$\zeta_0^2(\sigma,\sigma) = M_0' \frac{3}{\sqrt{2}} \int_{-1}^{+1} d\eta \cdot e^{-\sigma\sqrt{2}(1-\eta)^{\frac{1}{2}} - 2\sigma(5-4\eta)^{\frac{1}{2}}} \cdot \frac{(1-\eta)^{\frac{1}{2}}}{(5-4\eta)^{\frac{1}{2}}}$$

$$\zeta_0^3(\sigma,\sigma) = M_0' \frac{1}{\sigma} \int_{-1}^{+1} d\eta \cdot \frac{e^{-\sigma\sqrt{2}(1-\eta)^{\frac{1}{2}} - 2\sigma(5-4\eta)^{\frac{1}{2}}}}{(5-4\eta)^{\frac{1}{2}}}$$

Using the substitution $y = \sigma\sqrt{2}(1-\eta)^{\frac{1}{2}}$ these become:

$$\zeta_\lambda^1(\sigma,\sigma) = M_\lambda' \frac{1}{\sigma^2} \int_0^{2\sigma} dy \cdot P_\lambda\left(1 - \frac{y^2}{2\sigma^2}\right) y e^{-y - 2(2y^2+\sigma^2)^{\frac{1}{2}}}$$

$$\zeta_0^2(\sigma,\sigma) = M_0' \frac{3}{2\sigma^2} \int_0^{2\sigma} dy \cdot \frac{y^2}{(2y^2+\sigma^2)^{\frac{1}{2}}} e^{-y - 2(2y^2+\sigma^2)^{\frac{1}{2}}}$$

$$\zeta_0^3(\sigma,\sigma) = M_0' \frac{1}{\sigma^2} \int_0^{2\sigma} dy \cdot \frac{y}{(2y^2+\sigma^2)^{\frac{1}{2}}} e^{-y - 2(2y^2+\sigma^2)^{\frac{1}{2}}}$$

and the integrands now have first order derivatives in the range considered. Using the same substitution for $r = 2\sigma$ we obtain the following:

$$g'_\lambda(2\sigma,\sigma) = M'_\lambda \frac{1}{\sigma^2} \int_0^{2\sigma} dy\, P_\lambda\left(1-\frac{y^2}{2\sigma^2}\right) y e^{-4y-(2y^2+\sigma^2)^{\frac{1}{2}}}$$

$$g^2_0(2\sigma,\sigma) = M'_0 \frac{3}{2\sigma^2} \int_0^{2\sigma} dy \frac{y^2}{(2y^2+\sigma^2)} e^{-4y-(2y^2+\sigma^2)^{\frac{1}{2}}}$$

$$g^3_0(2\sigma,\sigma) = M'_0 \frac{1}{2\sigma^2} \int_0^{2\sigma} dy\, e^{-4y-(2y^2+\sigma^2)^{\frac{1}{2}}}$$

Therefore a separate code was written calculating the g's given by equations (3.6). For $r=\sigma$ or 2σ the new forms of the g's described above were used with the transformation:

$$\int_0^{2\sigma} f(y)\,dy = \sigma \int_{-1}^{+1} f\left(\sigma\{y+1\}\right) dy$$

so enabling the same 16-point Gaussian Quadrature to be used. At least five figure agreement was obtained.

3.3 An Alternative Helium Function.

The simple Hylleraas Helium function:

$$\psi_0(r_1,r_2) = \frac{\mu^3}{\pi} e^{-\mu(r_1+r_2)} \qquad \mu = \frac{27}{16}$$

with a corresponding energy $E_{He}^{Hylle} = 2\mu^2 = 5.6953125$ can easily be obtained from the Hartree-Fock function defined in equations (2.25) by substituting $C = 0$ and $\alpha = \mu$. Therefore the code was written to allow the use of both functions. This necessitated generating the Hylleraas Kernels. K_{12} (Hylleraas) was tabulated by re-running the kernel code but K_{22} (Hylleraas) is a linear combination of the energy dependent and energy independent parts of K_{22} (Hartree-Fock) as follows:

$$K_{22}^{(1)} \text{ (Hylleraas)} = K_{22}^{(1)} \text{ (Hartree-Fock)}$$
$$K_{22}^{(2)} \text{ (Hylleraas)} = K_{22}^{(2)}\text{(Hartree-Fock)} + 0.0280275\ K_{22}^{(1)} \text{(Hartree-Fock)}$$

This can be seen by inspection of equation (2.53b) which shows $K_{22}^{(2)}$ to be dependent on the Helium energy. Tables 3-1 and 3-2 present a sample set of values of K_{12} and K_{22}, using each Helium function, for small and large arguments respectively. Although the kernels are similar for small arguments, the Hartree-Fock kernels are a factor of five larger numerically than the Hylleraas at large distances.

For small arguments, the Hylleraas kernels generated by Kraidy[27] (private communication to P. Fraser) agreed to a minimum of 3 figures for K_{22} and 4 for K_{12} (data received from Fraser only gave four figures). It should be mentioned that the angular integrations of Kraidy's[27] calculation used a 10-point Gaussian quadrature.

TABLE 3-1

A comparison of the kernels $K_{12}(x,\sigma)$ and $K_{22}(x,\sigma)$ using the Hartree-Fock (H.F.) and Hylleraas (H.) ground state Helium function.

x σ	$K_{12}^{(1)}$ (H.F.)	$K_{12}^{(1)}$ (H.)	$K_{12}^{(2)}$ (H.F.)	$K_{12}^{(2)}$ (H.)	$K_{22}^{(1)}$ (same)	$K_{22}^{(2)}$ (H.F.)	$K_{22}^{(2)}$ (H.)
.1,.1	.3071	.3009	-18.204	-17.233	.1734	-3.598	-3.594
.2,.1	.5233	.5159	-19.219	-17.258	.3075	-4.234	-4.225
.2,.2	.7452	.7536	-18.696	-19.071	.5550	-7.136	-7.120
.3,.1	.6214	.6206	-11.993	-11.627	.3848	-3.887	-3.876
.3,.2	.9956	1.0055	-18.043	-17.902	.7080	-6.749	-6.729
.3,.3	1.0559	1.0841	-14.938	-15.925	.9270	-8.292	-8.266
.4,.1	.6396	.6473	-7.275	-7.588	.4083	-3.125	-3.114
.4,.2	1.1275	1.1403	-17.689	-16.572	.7650	-5.536	-5.515
.4,.3	1.2884	1.3177	-14.225	-14.897	1.0286	-7.039	-7.010
.4,.4	1.2205	1.2586	-10.948	-11.921	1.1772	-7.627	-7.594

TABLE 3-2

A comparison of the kernels $K_{12}(x,\sigma)$ using the Hartree-Fock(H.F.) and the Hylleraas (H.) ground state Helium function.

x , σ	$K_{12}^{(1)}$ (H.F.)	$K_{12}^{(1)}$ (H.)	$K_{12}^{(2)}$ (H.F.)	$K_{12}^{(2)}$ (H.)
10. ,4.8	.03632	.03350	.01888	.01838
10. ,4.9	.01187	.08864	.02336	.02283
10. ,5.0	-.06005	-.04903	.02710	.02646
10. ,10.0	.1010 (-04)	.2317 (-05)	.4748 (-05)	.6591 (-06)
10. ,10.1	.9331 (-05)	.1926 (-05)	.3549 (-05)	.4705 (-06)
10. ,10.2	.7946 (-05)	.1512 (-05)	.2624 (-05)	.3321 (-06)
10. ,10.3	.6447 (-05)	.1144 (-05)	.1922 (-05)	.2323 (-06)
10. ,10.4	.5065 (-05)	.8433 (-05)	.1398 (-05)	.1613 (-06)

The numbers in parentheses denote the power of 10 by which the equivalent entries should be multiplied.

3.4 Use of the Visual Display Device.

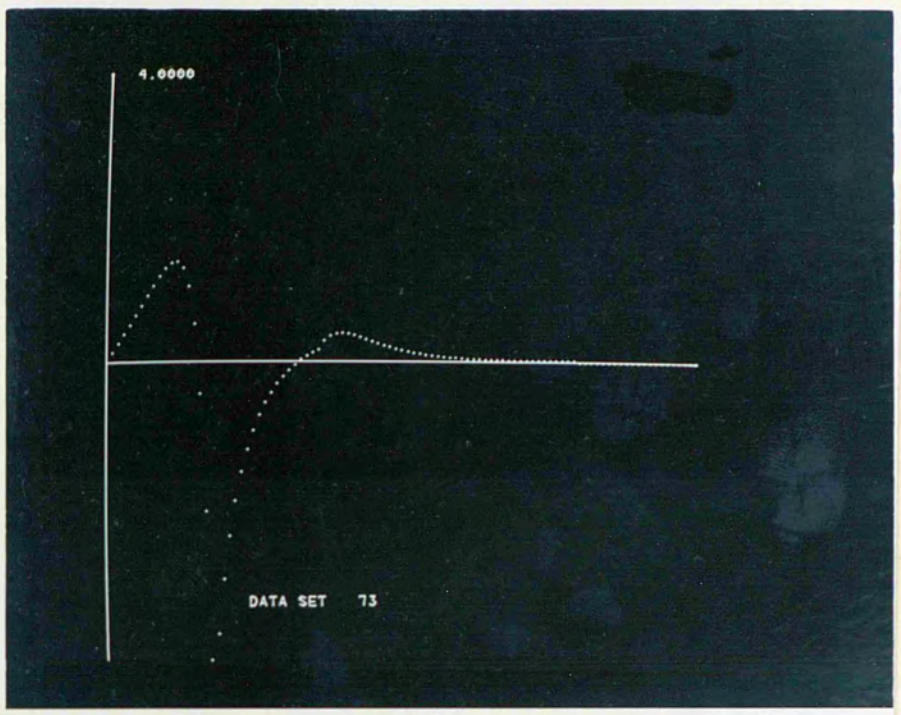
The geometric characteristics of the kernels can easily be verified by the visual display device. K_{12}, $\tilde{K}_{12}$ and K_{22} are continuous and exponentially decaying asymptotically. Figure 3-1 presents photographs of $K_{12}^{(1)}(1.8,\sigma)$ and $K_{12}^{(2)}(1.8,\sigma)$ for $\sigma = 0(.05)5$ which clearly show the discontinuities of $K_{12}^{(2)}$ at $\sigma = .9$ and 1.8. $K_{12}^{(1)}$ is seen to be continuous and both functions exhibit the correct exponential decay.

Figure 3-2 presents photographs of $K_{22}^{(1)}(3.5,\sigma)$ and $K_{22}^{(2)}(3.5,\sigma)$ for $\sigma = 0(.1)10$ which again show the single discontinuity of $K_{22}^{(2)}$ at $\sigma = 3.5$ and the smaller magnitude of the kernel for one of the arguments large.

A simple code was written to transpose K_{12} and Figure 3-3 presents photographs of $\tilde{K}_{12}^{(1)}(1.8,\sigma)$ and $\tilde{K}_{12}^{(2)}(1.8,\sigma)$ for $\sigma = 0(.05)5$. In this case the discontinuities are at $\sigma = 1.8$ and 3.6.

Figure 3-4 presents photographs of $K_{12}^{(2)}(1.8,\sigma)$ and $\tilde{K}_{12}^{(2)}(1.8,\sigma)$ for $\sigma = 0(.05)5$ produced from the Hylleraas Helium function which can be compared to Figures 3-1 and 3-3. The K_{12} curves are very similar but the $\tilde{K}_{12}$ curves are a different shape near the second discontinuity point.

By inspection of Figures 3-1 to 3-4 it is clear that, after a certain value of σ, a larger step size would have been adequate for all three kernels. This value of σ can easily be determined by using the graphical display.



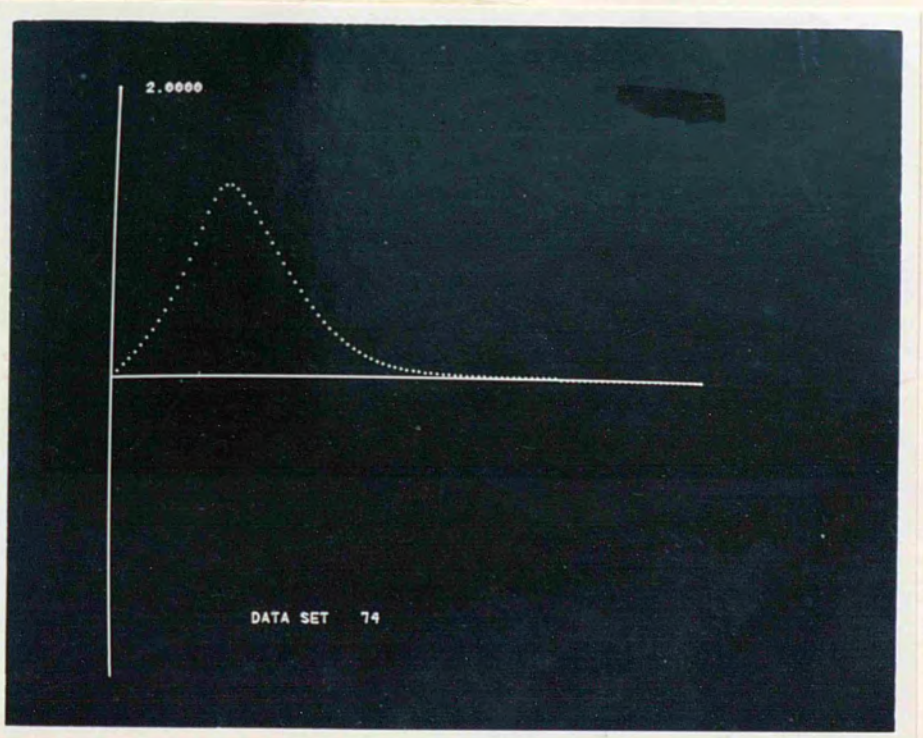
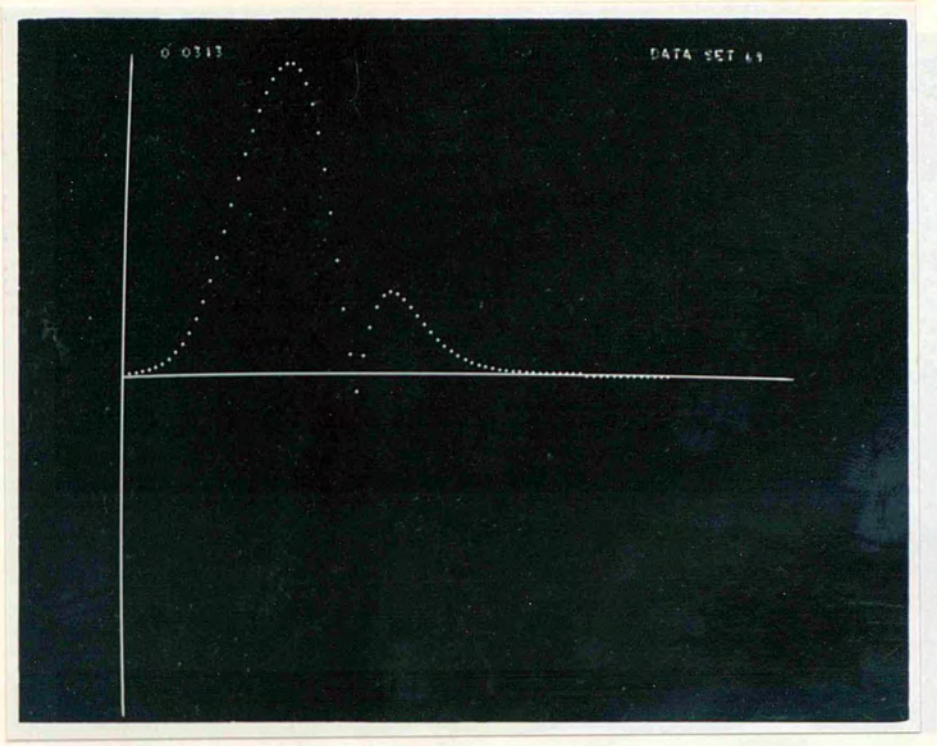


Figure 3-1 The upper photograph shows $K_{12}^{(2)}(1.8,\sigma)$ for $\sigma=0(.05)5$. The lower photograph shows $K_{12}^{(1)}(1.8,\sigma)$ for $\sigma=0(.05)5$.



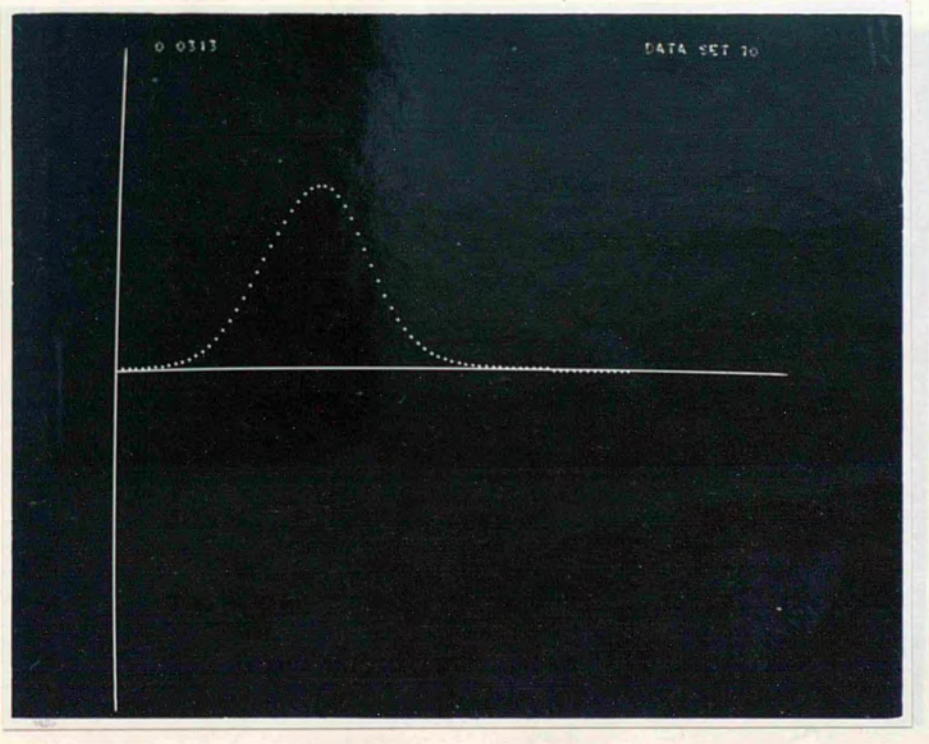
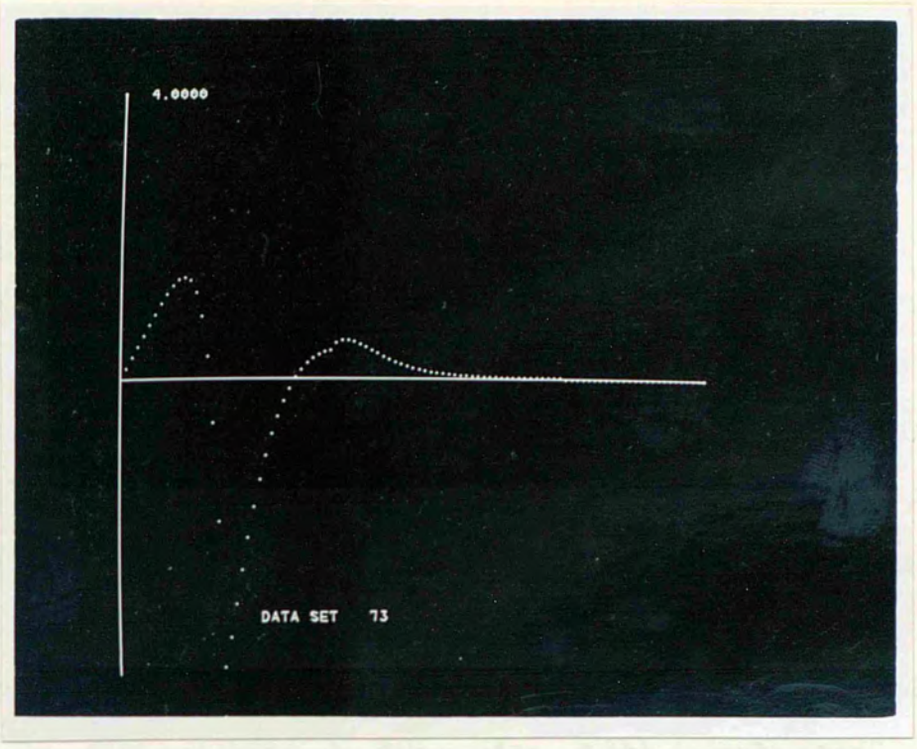


Figure 3-2 The upper photograph shows $K_{22}^{(2)}(3.5,\sigma)$ for $\sigma=0(.1)10.$

The lower photograph shows $K_{22}^{(1)}(3.5,\sigma)$ for $\sigma=0(.1)10.$



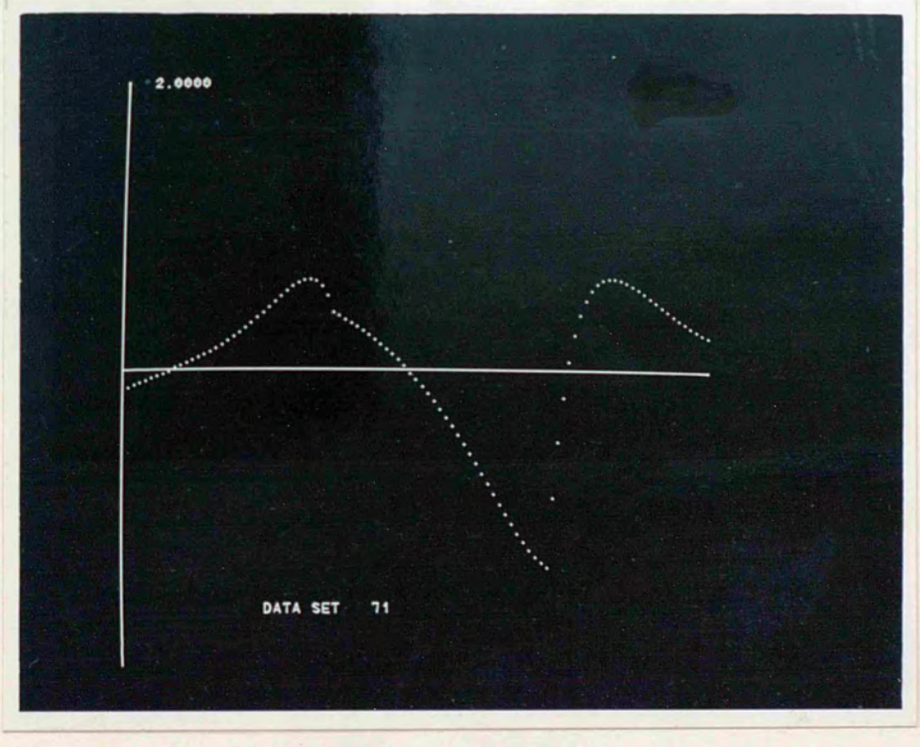


Figure 3-4 The upper photograph shows $K_{12}^{(a)}(1.8,\sigma)$ for $\sigma=0(.05)5.$

The lower photograph shows $\tilde{K}_{12}^{(a)}(1.8,\sigma)$ for $\sigma=0(.05)5.$

Initially K_{12} and K_{22} were generated at a constant step length of .1 but the visual display device demonstrated this to be inadequate near the points lacking a first derivative. After examination of successive graphs it was decided to generate K_{12} (and therefore $\tilde{K}_{12}$) at intervals of .05 for r and $\sigma \leq 5$. Because of the complexity of K_{22} and the large amount of computer time required to generate it, K_{22} was tabulated for the constant step length of .1 and was interpolated for the half-values later in the iteration code.

A further interesting fact brought to light by the graphical displays was the comparatively large size of the kernels when both arguments are large, even though the kernels are almost zero for one argument large but the other small. K_{12} was therefore tabulated out to $x = 32$ and $\sigma = 17.5$ and K_{22} out to $x = \sigma = 11.6$. At these distances both kernels were of the order of 10^{-9}.

CHAPTER IV

ALGORITHM FOR COUPLED INTEGRO-DIFFERENTIAL EQUATIONS

4.1 Matching Procedure and Iteration Strategy.

The algorithm described in this section is the matching algorithm of Smith and Burke.[19] The system under consideration is a set of M second order ordinary integro-differential equations:

$$\frac{d^2}{dx^2} F_i(x) = \sum_{j=1}^{M} U_{ij}(x) F_j(x) \qquad 4.1$$

where $$U_{ij}(x) = -k_i^2 \delta_{ij} - V_{ij}(x) \qquad 4.2$$

and $V_{ij}(x)$ may be either short range exponentially decaying potentials or integral operators. Let there be NA positive k_μ^2 (open channels) and therefore (M-NA) negative k_τ^2 (closed channels). In this section it will be assumed that μ will take the values 1, 2, ------, NA and will be associated with open channels, τ will take the values 1, 2, ----, (M-NA) and will be associated with closed channels and i will take the values 1, 2, -----, M and will label the elements of the total solution vector.

The asymptotic form of the solutions are defined by physical considerations such that $F_\mu(x)$ will be oscillatory and $F_\tau(x)$ will decay exponentially. Each equation has two integration constants so 2M constants must be specified for any value of the independent variable x before the numerical solution can begin. If the closed channel functions are integrated out from the origin, they will asymptotically contain

the components $e^{+|k_\tau|x}$ and $e^{-|k_\tau|x}$. In a numerical calculation the contribution from $e^{+|k_\tau|x}$ will soon swamp that of $e^{-|k_\tau|x}$. In order to obtain a physically meaningful solution, $F_\tau(x)$ must decay exponentially at large x. To avoid the numerical difficulty encountered in outward integration into the asymptotic domain, we show below, in section (a), how linearly independent outward solutions are generated starting at the origin and integrating out to some point r_M where the term $e^{+|k_\tau|x}$ is not too dominant, while other linearly independent inward solutions are generated starting at the asymptotic distance r_A and integrating inwards to r_M. The required solution over the whole range of x is some linear combination of the outward solutions and a different linear combination of the inward solutions. The linear coefficients are determined by matching the solutions and their derivatives at $r = r_M$ and imposing an overall normalization condition.

It is known that we require solutions of equation (4.1) which have the form:

$$F_\mu^\nu(x) \underset{x\to\infty}{\sim} k_\mu^{-\frac{1}{2}} \left[\delta_{\mu\nu} \sin k_\mu x + R_{\mu\nu} \cos k_\mu x \right] \qquad 4.3$$

for $k_\mu^2 > 0$ and $\mu, \nu = 1, 2, \text{------}, NA$

and $\dfrac{dF_\tau^\nu(x)}{dx} = |k_\tau| F_\tau^\nu(x)$ for $k_\tau^2 < 0$ 4.4

where $R_{\mu\nu}$ is the real symmetric Reactance or R-matrix from which we obtain the cross-sections. These asymptotic forms are a linear

superposition of the functions $\sin k_\mu x$, $\cos k_\mu x$ and $e^{-|k_\tau| x}$. Consequently, the problem at hand is to construct the correct linear combination of these basis functions. It can be seen that there is not a single set of the solution vector $\{ F_i(x) \}$ where:

$$\{ F_i(x) \} = \begin{bmatrix} F_\mu(x) \\ F_\tau(x) \end{bmatrix} = \begin{bmatrix} F_1(x) \\ F_2(x) \\ \vdots \\ F_M(x) \end{bmatrix} \qquad 4.5$$

but NA such sets denoted by the superscript ν in equations (4.3) and (4.4). Alternatively, we can examine this problem from the standpoint of needing to find 2M integration constants for the system of equations.

(a) Solution of the System of Homogeneous Equations.

The system of homogeneous equations is obtained from equations (4.1) and (4.2) by setting all integral operators of $V_{ij}(x)$ to zero. A known boundary condition is:

$$F_i(x) = 0 \text{ at } x = 0 \qquad \text{for } i = 1, 2, \text{-----}, M \qquad 4.6$$

where by $F_i(x)$ we mean the total solution vector $\{ F_i(x) \}$, see equation (4.5). Therefore M of the 2M constants for the system of equations are known. The remaining M may be determined by specifying the derivatives of $F_i(x)$ at the origin. There are M linearly independent

ways of choosing these derivatives, designated by α. They are chosen to be:

$$\left[\frac{dF_i^{(\alpha)}(x)}{dx}\right]_{x=0} = \delta_{\alpha i} \qquad \text{for } x=1, 2, \text{------}, M \qquad 4.7$$

Using these boundary conditions we integrate out from the origin to compute the α families of solution vectors which we shall label $F_i^{(\alpha)}$. As already pointed out, these solutions must be terminated at some point r_M and another set of solutions generated starting from the asymptotic distance r_A and integrating inwards. Asymptotic solutions of equation (4.1) will be:

$$F_\mu(x) \underset{x\to\infty}{\sim} A_\mu \sin k_\mu x + B_\mu \cos k_\mu x \qquad \text{for } k_\mu^2 > 0 \qquad 4.8a$$

$$F_\tau(x) \underset{x\to\infty}{\sim} C_\tau e^{-|k_\tau| x} \qquad \text{for } k_\tau^2 < 0 \qquad 4.8b$$

Thus (M-NA) constants have already been eliminated by specifying that the coefficients of $e^{+|k_\tau| x}$ must be zero. There remain (M+NA) coefficients A_μ, B_μ and C_τ to determine. Setting A_μ, B_μ and C_τ equal to unity one at a time with the others zero will generate (M+NA) linearly independent solutions in the region $r_M \le x \le r_A$ denoted by $G_i^{(\beta)}(x)$ for $\beta = 1, 2, \text{----}, (M\ NA)$.

Therefore :

$$\begin{bmatrix} A_\mu \\ B_\mu \\ C_\tau \end{bmatrix}^{(\beta)} = \delta_{j\beta} \qquad \text{for } j = 1, 2, \cdots\cdots, M+NA \qquad 4.9a$$

That is: $\begin{bmatrix} A_M \\ B_M \\ C_\tau \end{bmatrix}^{(1)} = \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \\ 0 \end{bmatrix}, \cdots\cdots, \begin{bmatrix} A_M \\ B_M \\ C_\tau \end{bmatrix}^{(M+NA)} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix} \begin{matrix} 1 \\ 2 \\ \vdots \\ \vdots \\ M+NA \end{matrix}$ 4.9b

We can now construct any solution of the homogeneous portion of equation (4.1) by taking appropriate linear combinations of $F_i^{(\alpha)}$ and $G_i^{(\beta)}$ as follows:

$$\text{General outward homogeneous solution} = \sum_{\alpha=1}^{M} \bar{u}_\alpha^{(\nu)} F_i^{(\alpha)}(x) \quad \text{for } 0 \le x \le r_M \qquad 4.10a$$

$$\text{General inward homogeneous solution} = \sum_{\beta=1}^{M+NA} \bar{w}_\beta^{(\nu)} G_i^{(\beta)}(x) \quad \text{for } r_M \le x \le r_A \qquad 4.10b$$

where the superscript ν denotes that solution vector for the particular ν value.

Determination of the NA sets of (2M+NA) coefficients $\bar{u}_\alpha^{(\nu)}$ and $\bar{w}_\beta^{(\nu)}$.

The two solution vectors and their derivatives must match at r_M giving the following system of equations:

$$\sum_{\alpha=1}^{M} \bar{u}_\alpha^{(\nu)} \begin{bmatrix} F_i(x) \\ F_i'(x) \end{bmatrix}^{(\alpha)}_{x=r_M} = \sum_{\beta=1}^{M+NA} \bar{w}_\beta^{(\nu)} \begin{bmatrix} G_i(x) \\ G_i'(x) \end{bmatrix}^{(\beta)}_{x=r_M} \qquad \text{for } \nu = 1, 2, \cdots, NA \qquad 4.11$$

where a prime denotes differentiation.

A further NA equations depending on ν are required. The value of the inward solution for open channels, see equation (4.10b), at $x = r_A$ is:

$$\sum_{\beta=1}^{M+NA} \bar{w}_\beta^{(\nu)} G_\mu^{(\beta)}(r_A) = \bar{w}_\mu^{(\nu)} \sin k_\mu r_A + \bar{w}_{\mu+NA}^{(\nu)} \cos k_\mu r_A$$

because of the construction of $G_\mu^{(\beta)}$, see equation (4.9). But from equation (4.3) we require that:

$$F_\mu^\nu(x) \underset{x\to\infty}{\sim} k_\mu^{-\frac{1}{2}} \left[\delta_{\mu\nu} \sin k_\mu x + R_{\mu\nu} \cos k_\mu x \right] \qquad \text{for } \nu = 1, 2, \text{---}, NA$$

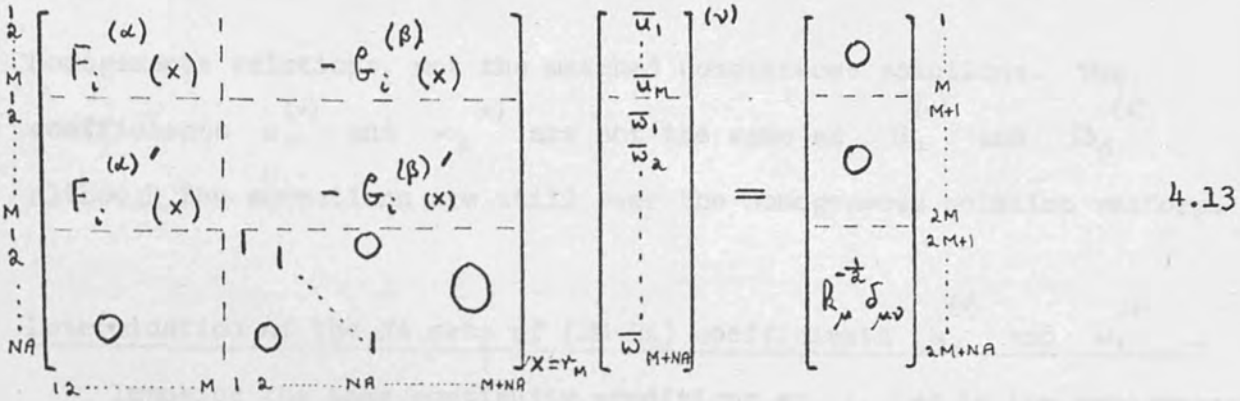
Therefore by comparing coefficients of $\sin k_\mu r_A$ and $\cos k_\mu r_A$ we obtain the following:

$$\bar{w}_\mu^{(\nu)} = k_\mu^{-\frac{1}{2}} \delta_{\mu\nu} \qquad 4.12a$$

$$\bar{w}_{\mu+NA}^{(\nu)} = k_\mu^{-\frac{1}{2}} \bar{R}_{\mu\nu} \qquad 4.12b$$

where $\bar{R}_{\mu\nu}$ is the R-matrix for the system of homogeneous equations.

Thus equation (4.12a) provides the necessary NA equations for each value of ν. The NA sets of (2M+NA) equations determining $\bar{u}_\alpha^{(\nu)}$ and $\bar{w}_\beta^{(\nu)}$ may be conveniently expressed in the following matrix form:



4.13

For example, to calculate the $\nu = 2$ solution vector, this system of equations is solved with $k_2^{-\frac{1}{2}}$ in the $(2M+2)$th. position of the right hand side column matrix and with zeros everywhere else. The R-matrix can then be determined using equation (4.12b).

(b) Solution of the System of Inhomogeneous Equations.

The matched homogeneous solutions are now substituted into the integral terms on the right hand side of equations (4.1). One outward solution vector $f_i^{(\nu)}(x)$ and one inward solution vector $g_i^{(\nu)}(x)$ is generated for each value of ν. In other words, a particular integral is obtained so that we have:

$$\text{General outward solution} = f_i^{(\nu)}(x) + \sum_{\alpha=1}^{M} u_\alpha^{(\nu)} F_i^{(\alpha)}(x) \quad \text{for} \quad 0 \le x \le r_M \qquad 4.14a$$

$$\text{General inward solution} = g_i^{(\nu)}(x) + \sum_{\beta=1}^{M+NA} w_\beta^{(\nu)} G_i^{(\beta)}(x) \quad \text{for} \quad r_M \le x \le r_A \qquad 4.14b$$

where we emphasise that $F_i^{(\alpha)}$ and $G_i^{(\beta)}$ are the linearly independent

homogeneous solutions, not the matched homogeneous solutions. The coefficients $u_\alpha^{(\nu)}$ and $w_\beta^{(\nu)}$ are not the same as $\bar{u}_\alpha^{(\nu)}$ and $\bar{w}_\beta^{(\nu)}$ although the summations are still over the homogeneous solution vectors.

Determination of the NA sets of (2M+NA) coefficients $u_\alpha^{(\nu)}$ and $w_\beta^{(\nu)}$.

Imposing the same continuity conditions at r_M as in the homogeneous case we have:

$$\begin{bmatrix} \gamma_i^{(\nu)}(x) \\ \gamma_i^{(\nu)\prime}(x) \end{bmatrix}_{x=r_M} + \sum_{\alpha=1}^{M} u_\alpha^{(\nu)} \begin{bmatrix} F_i(x) \\ F_i'(x) \end{bmatrix}_{x=r_M}^{(\alpha)} = \begin{bmatrix} \rho_i^{(\nu)}(x) \\ \rho_i^{(\nu)\prime}(x) \end{bmatrix}_{x=r_M} + \sum_{\beta=1}^{M+NA} w_\beta^{(\nu)} \begin{bmatrix} G_i(x) \\ G_i'(x) \end{bmatrix}_{x=r_M}^{(\beta)}$$

and $$\rho_\mu^{(\nu)}(r_A) + \sum_{\beta=1}^{M+NA} w_\beta^{(\nu)} G_\mu^{(\beta)}(r_A) = \rho_\mu^{(\nu)}(r_A) + w_\mu^{(\nu)} \sin k_\mu r_A + w_{\mu+NA}^{(\nu)} \cos k_\mu r_A$$

$$= k_\mu^{-\frac{1}{2}} \left\{ \delta_{\mu\nu} \sin k_\mu r_A + R_{\mu\nu} \cos k_\mu r_A \right\}$$

We have as yet to specify the boundary conditions that will be imposed on the particular integral. We will refer specifically to the nth. iterate ${}^n\gamma_i^{(\nu)}(x)$ for $0 \le x \le r_M$ and ${}^n\rho_i^{(\nu)}(x)$ for $r_M \le x \le r_A$. We choose the value of the (n-1)th. total outward solution and its derivative at x=0 as the initial conditions for generating ${}^n\gamma_i^{(\nu)}(x)$ and the value of the (n-1)th. total outward solution and its derivative at $x = r_A$ as the initial conditions for generating ${}^n\rho_i^{(\nu)}(x)$. That is:

$${}^n\gamma_i^{(\nu)}(x) = 0$$

$$\begin{bmatrix} {}^n\gamma_i^{(\nu)\prime}(x) \end{bmatrix}_{x=0} = \begin{bmatrix} {}^{n-1}\gamma_i^{(\nu)\prime}(x) \end{bmatrix}_{x=0} + \sum_{\alpha=1}^{M} {}^{n-1}u_\alpha^{(\nu)} \begin{bmatrix} F_i'(x) \end{bmatrix}_{x=0}^{(\alpha)} \qquad \text{for } n > 1$$

$$= \sum_{\alpha=1}^{M} \bar{u}_\alpha^{(\nu)} \left[F_i'(x) \right]_{x=0}^{(\alpha)} \qquad \text{for } n=1$$

whereby ${}^{n-1}u_\alpha^{(\nu)}$ we mean the (n-1)th iterated $u_\alpha^{(\nu)}$. But from equation (4.7) we see that $\left[\bar{F}_i'(x) \right]_{x=0}^{(\alpha)} = \delta_{\alpha i}$ therefore the above equations can be rewritten as follows:

$$ {}^{n}J_i^{(\nu)}(x) = 0 \qquad \text{at } x=0 \qquad \text{4.15a}$$

$$\left[{}^{n}J_i^{(\nu)\prime}(x) \right]_{x=0} = \left[{}^{n-1}J_i^{(\nu)\prime}(x) \right]_{x=0} + \sum_{\alpha=1}^{M} {}^{n-1}u_\alpha^{(\nu)} \delta_{\alpha i} \qquad \text{for } n>1$$

$$= \sum_{\alpha=1}^{M} \bar{u}_\alpha^{(\nu)} \delta_{\alpha i} \qquad \text{for } n=1 \qquad \text{4.15b}$$

The coefficients $\bar{u}_\alpha^{(\nu)}$ are defined in part (a) of this section. The asymptotic boundary conditions are:

$$\left[{}^{n}\rho_i^{(\nu)}(x) \right]_{x=r_A} = \begin{bmatrix} k_\mu^{-\frac{1}{2}} \left(\delta_{\mu\nu} \sin k_\mu r_A + R_{\mu\nu}^{(n-1)} \cos k_\mu r_A \right) \\ {}^{n-1}\rho_\tau^{(\nu)}(r_A) + \sum_\beta {}^{n-1}w_\beta^{(\nu)} G_\tau^{(\beta)}(r_A) \end{bmatrix} \qquad \text{for } n>1$$

$$= \begin{bmatrix} k_\mu^{-\frac{1}{2}} \left(\delta_{\mu\nu} \sin k_\mu r_A + \bar{R}_{\mu\nu} \cos k_\mu r_A \right) \\ \sum_\beta w_\beta^{(\nu)} G_\tau^{(\beta)}(r_A) \end{bmatrix} \qquad \text{for } n=1 \qquad \text{4.15c}$$

$R^{(n-1)}$ is the (n-1)th. iterated R-matrix obtained from the (n-1)th. total solution and $\bar{R}$ is the R-matrix obtained from the homogeneous equations.

Using equations (4.9) we can write $G_{\tau}^{(\beta)}(r_A) = \delta_{j\beta}\, e^{-|k_\tau| r_A}$ for $j = \partial NA + 1, \ldots, M + NA$ and therefore $G_{\tau}^{(\beta)\prime}(r_A) = -|k_\tau|\, G_{\tau}^{(\beta)}(r_A)$.

We write the asymptotic boundary condition for the derivative as follows:

$$ {}^{n}\rho_i^{(\nu)\prime}(x) = \begin{cases} k_\mu^{\frac{1}{2}} \left(\delta_{\mu\nu} \cos k_\mu r_A - R_{\mu\nu}^{(n-1)} \sin k_\mu r_A \right) \\ {}^{n-1}\rho_\tau^{(\nu)\prime}(r_A) - |k_\tau| \sum_{\beta}^{n-1} w_\beta^{(\nu)}\, G_\tau^{(\beta)}(r_A) \end{cases} \quad \text{for } n > 1 $$

$$ = \begin{cases} k_\mu^{\frac{1}{2}} \left(\delta_{\mu\nu} \cos k_\mu r_A - \bar{R}_{\mu\nu} \sin k_\mu r_A \right) \\ - |k_\tau| \sum_{\beta}^{n-1} \bar{w}_\beta^{(\nu)}\, G_\tau^{(\beta)}(r_A) \end{cases} \quad \text{for } n = 1 \qquad 4.15d $$

Consequently, the remaining NA matching equations are:

$$ w_\mu^{(\nu)} = 0 \qquad \text{for } \mu = 1, 2, \text{-----}, NA \qquad 4.16a $$

while the elements of the R-matrix are given by:

$$ R_{\mu\nu}^{(n)} = R_{\mu\nu}^{(n-1)} + k_\mu^{\frac{1}{2}}\, w_{\mu+NA}^{(\nu)} \qquad 4.16b $$

Here we have omitted the superscript n from the coefficients $w^{(\nu)}$. We will continue doing so unless we are referring to an iterate other than the nth.

In an analagous way to the homogeneous case, the NA sets of (2M + NA) equations determining $u_\alpha^{(\nu)}$ and $w_\beta^{(\nu)}$ may be written in the following matrix form:

$$\begin{bmatrix} F_i^{(\alpha)}(x) & -G_i^{(\beta)}(x) \\ F_i^{(\alpha)\prime}(x) & -G_i^{(\beta)\prime}(x) \\ 0 & \begin{matrix} 1 & & \\ & \ddots & \\ & & 1 \end{matrix} \end{bmatrix}_{x=r_M} \begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_M \\ w_1 \\ w_2 \\ \vdots \\ w_{M+NA} \end{bmatrix}^{(\nu)} = \begin{bmatrix} g_i^{(\nu)}(x) - f_i^{(\nu)}(x) \\ g_i^{(\nu)\prime}(x) - f_i^{(\nu)\prime}(x) \\ 0 \end{bmatrix}_{x=r_M} \begin{matrix} 1 \\ 2 \\ \vdots \\ M \\ M+1 \\ \vdots \\ 2M \\ 2M+1 \\ \vdots \\ 2M+NA \end{matrix} \qquad 4.17$$

$1\,2 \cdots M \;\; 1 \cdots NA, NA+1 \cdots M+NA$

It should be noted that the $(2M+NA) \times (2M+NA)$ matching matrix is identical to the equivalent matrix in the homogeneous case, only the right hand side column matrix is different.

These matched solutions are now substituted into the integral terms of the right hand side of equation (4.1) and the process repeated until the R-matrix has converged. In other words, the nth. iterated solution ${}^{n}G_i^{(\nu)}(x)$ is forced to have the asymptotic form given by equation (4.15) and the nth. iterated values at r_M are substituted into equation (4.17) yielding ${}^{n}u_\alpha^{(\nu)}$ and ${}^{n}w_\beta^{(\nu)}$. The total contribution of the homogeneous solutions, that is $\sum_\alpha u_\alpha^{(\nu)} \left[F_i(x)\right]^{(\alpha)}$ and $\sum_\beta w_\beta^{(\nu)} \left[G_i(x)\right]^{(\beta)}$ in equations (4.14), must tend toward zero as the particular integral approaches the required solution.

To make the iteration procedure transparent, we write the inhomogeneous system of equations in the form:

$$\frac{d^2}{dx^2}\,{}^{n}F_i^{(\nu)}(x) + \sum_{j=1}^{M} V_{ij}(x)\,{}^{n}F_j^{(\nu)}(x) = {}^{n}U_i^{(\nu)}(x)$$

where $${}^{n}U_i^{(\nu)}(x) = \sum_j \int_0^\infty K_{ij}(x,x')\, {}^{n-1}F_j^{(\nu)}(x')\,dx'$$

and n denotes the number of iterations performed.

In the inner region, $0 \le x \le r_M$ we have:

$$\frac{d^2}{dx^2}\,{}^{n}y_i^{(\nu)}(x) + \sum_{j=1}^{M} V_{ij}(x)\,{}^{n}y_j^{(\nu)}(x) = {}^{n}U_i^{(\nu)}(x)$$

and $$\frac{d^2}{dx^2}\left[\sum_{\alpha=1}^{M} {}^{n}u_\alpha^{(\nu)} F_i^{(\alpha)}(x)\right] + \sum_{j=1}^{M} V_{ij}(x)\left[\sum_{\alpha=1}^{M} {}^{n}u_\alpha^{(\nu)} F_i^{(\alpha)}(x)\right] = 0$$

which can be added together to give:

$$\frac{d^2}{dx^2}\left[{}^{n}y_i^{(\nu)}(x) + \sum_{\alpha=1}^{M} {}^{n}u_\alpha^{(\nu)} F_i^{(\alpha)}(x)\right] + \sum_{j=1}^{M} V_{ij}(x)\left[{}^{n}y_i^{(\nu)}(x) + \sum_{\alpha=1}^{M} {}^{n}u_\alpha^{(\nu)} F_i^{(\alpha)}(x)\right] = {}^{n}U_i^{(\nu)}(x)$$

For convergence we have that:

$${}^{n}y_i^{(\nu)}(x) \xrightarrow[n>N]{} {}^{n-1}y_i^{(\nu)}(x)$$

and $$\sum_{\alpha=1}^{M} {}^{n}u_\alpha^{(\nu)} F_i^{(\alpha)}(x) \xrightarrow[n>N]{} 0$$

where for stability and accuracy we expect $N < 20$.

(c) The Case of 1 Open and 1 Closed Channel.

This is the case when $k_1^2 > 0$ and $k_2^2 < 0$. The homogeneous equations are:

$$\left[\frac{d^2}{dx^2} + V(x) + k_1^2\right] F_1(x) = 0 \qquad 4.18a$$

and $$\left[\frac{d^2}{dx^2} + k_2^2\right] F_2(x) = 0 \qquad 4.18b$$

To determine the outward solution in the range $0 \le x \le r_M$ we follow the process outlined in (a). Two solution vectors $F_i^{(\alpha)} = \begin{bmatrix} F_1 \\ F_2 \end{bmatrix}^{(\alpha)}$ for $\alpha = 1$ and 2 are generated. By inspection of equation (4.18b) we see that:

$$F_2^{(\alpha)}(x) = A^{(\alpha)} e^{|k_2|x} + B^{(\alpha)} e^{-|k_2|x}$$

where $A^{(\alpha)}$ and $B^{(\alpha)}$ are four constants. But we choose the following boundary conditions:

$$F_2^{(\alpha)}(x) = 0 \qquad \text{at } x = 0 \qquad 4.19a$$

and $$\left[\frac{dF_2^{(\alpha)}}{dx}(x)\right]_{x=0} = \delta_{\alpha 2} \qquad 4.19b$$

which leads to $A^{(1)} = B^{(1)} = 0$ and $A^{(2)} = -B^{(2)} = \dfrac{1}{2|k_2|}$

It is known that $F_1^{(\alpha)''}(x)$ will be required for the numerical procedure and this is determined by equation (4.18a). That is,

$F_1^{(\alpha)''}(x) = -\left(k_1^2 + V(x)\right) F_1^{(\alpha)}(x)$ and thus the limiting value of $F_1^{(\alpha)''}(x)$ at $x = 0$ can be calculated, see section 4.2. We choose the linearly independent solutions by imposing the following boundary conditions:

$$F_1^{(\alpha)}(x) = 0 \qquad \text{at } x = 0 \tag{4.20a}$$

$$\text{and} \quad \left[\frac{dF_1^{(\alpha)}(x)}{dx}\right]_{x=0} = \delta_{\alpha 1} \tag{4.20b}$$

Since $F_1^{(2)}(x) = F_1^{(2)'}(x) = 0$ at $x = 0$ it follows by the existence and uniqueness theorems that $F_1^{(2)}(x) \equiv 0$. Therefore, we have the following:

$$F_i^{(1)}(x) = \begin{bmatrix} F_1^{(1)}(x) \\ 0 \end{bmatrix} \tag{4.21a}$$

$$F_i^{(2)}(x) = \begin{bmatrix} 0 \\ \frac{1}{2|k_2|}\left\{e^{|k_2|x} - e^{-|k_2|x}\right\} \end{bmatrix} \tag{4.21b}$$

and $F_1^{(1)}(x)$ is generated using the boundary conditions given by equations (4.20).

To obtain the inward solution in the range $r_M \le x \le r_A$ we generate three solution vectors $G_i^{(\beta)} = \begin{bmatrix} G_1 \\ G_2 \end{bmatrix}^{(\beta)}$ for

$\beta = 1$, 2 and 3. The following boundary conditions are known:

$$G_1^{(\beta)}(x) \underset{x\to\infty}{\sim} A_1^{(\beta)} \sin k_1 x + B_1^{(\beta)} \cos k_1 x$$

and $$G_2^{(\beta)}(x) \underset{x\to\infty}{\sim} C_2^{(\beta)} e^{-|k_2|x}$$

where $A_1^{(\beta)}$, $B_1^{(\beta)}$ and $C_2^{(\beta)}$ are nine constants. Setting:

$$\begin{bmatrix} A_1 \\ B_1 \\ C_2 \end{bmatrix}^{(\beta)} = \delta_{j\beta} \quad \text{for } j = 1, 2 \text{ and } 3,$$

that is: $$\begin{bmatrix} A_1 \\ B_1 \\ C_2 \end{bmatrix}^{(1)} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad \begin{bmatrix} A_1 \\ B_1 \\ C_2 \end{bmatrix}^{(2)} = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \begin{bmatrix} A_1 \\ B_1 \\ C_2 \end{bmatrix}^{(3)} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

we obtain the following:

$$G_i^{(1)}(r_A) = \begin{bmatrix} \sin k_1 r_A \\ 0 \end{bmatrix} \qquad 4.22a$$

$$G_i^{(2)}(r_A) = \begin{bmatrix} \cos k_1 r_A \\ 0 \end{bmatrix} \qquad 4.22b$$

$$G_i^{(3)}(r_A) = \begin{bmatrix} 0 \\ e^{-|k_2| r_A} \end{bmatrix} \qquad 4.22c$$

Starting with these values at $x = r_A$ we can generate the three solution vectors inward to $x = r_M$. The matching matrix equation (4.13) becomes:

$$\begin{bmatrix} F_1^{(1)}(x) & 0 & -G_1^{(1)}(x) & -G_1^{(2)}(x) & 0 \\ 0 & F_2^{(2)}(x) & 0 & 0 & -G_2^{(3)}(x) \\ F_1^{(1)\prime}(x) & 0 & -G_1^{(1)\prime}(x) & -G_1^{(2)\prime}(x) & 0 \\ 0 & F_2^{(2)\prime}(x) & 0 & 0 & -G_2^{(3)\prime}(x) \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \bar{u}_1 \\ \bar{u}_2 \\ \bar{w}_1 \\ \bar{w}_2 \\ \bar{w}_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ k_1^{-\frac{1}{2}} \end{bmatrix} \qquad 4.23$$

and $R_{11} = k_1^{\frac{1}{2}} \bar{w}_2$. In this particular case the R-matrix consists of one element only so the subscripts will be omitted from now on.

Therefore, the matched and normalized solution $F_i(x)$ to be used in the integral terms of equation (4.1) will be:

$$F_i(x) = \begin{bmatrix} \bar{u}_1 F_1^{(1)}(x) \\ 0 \end{bmatrix} \qquad 0 \le x \le r_M \qquad 4.24a$$

$$= \begin{bmatrix} \bar{w}_1 G_1^{(1)}(x) + \bar{w}_2 G_1^{(2)}(x) \\ 0 \end{bmatrix} \qquad r_M \le x \le r_A \qquad 4.24b$$

Since we know that the only solution of $F_2(x)$ that is consistent with both sets of boundary conditions is $F_2(x) \equiv 0$ then the coefficients $\bar{u}_2$ and $\bar{w}_3$ must be zero also - a self consistency numerical feature that the computer code exhibits correctly.

To obtain the particular integral for the inhomogeneous equations, the solution vector $F_i(x)$ given by equations (4.24) is substituted into the integral terms of equation (4.1) and one outward solution vector $\mathcal{J}_i(x)$ and one inward solution vector $\mathcal{G}_i(x)$ is generated. The boundary conditions given by equations (4.15) become:

$$ {}^{n}\mathcal{J}_i(x) = 0 \qquad \text{at } x=0 $$

$$ \left[{}^{n}\mathcal{J}_i'(x) \right]_{x=0} = \left[{}^{n-1}\mathcal{J}_i'(x) \right]_{x=0} + \sum_{\alpha=1}^{2} {}^{n-1}u_\alpha \delta_{\alpha i} \qquad \text{for } n>1 $$

$$ = \sum_{\alpha=1}^{2} \bar{u}_\alpha \delta_{\alpha i} \qquad \text{for } n=1 $$

$$ \left[{}^{n}\mathcal{G}_i(x) \right]_{x=r_A} = \begin{bmatrix} k_1^{-\frac{1}{2}}\left(\sin k_1 r_A + R^{n-1}\cos k_1 r_A\right) \\ {}^{n-1}\mathcal{G}_2(r_A) + {}^{n-1}w_3 e^{-|k_2| r_A} \end{bmatrix} \qquad \text{for } n>1 $$

$$ = \begin{bmatrix} k^{-\frac{1}{2}}\left(\sin k_1 r_A + R\cos k_1 r_A\right) \\ \bar{w}_3 e^{-|k_2| r_A} \end{bmatrix} \qquad \text{for } n=1 $$

$$ {}^{n}\mathcal{G}_i'(x) = \begin{bmatrix} k_1^{\frac{1}{2}}\left(\cos k_1 r_A - R^{n-1}\sin k_1 r_A\right) \\ {}^{n-1}\mathcal{G}_2'(r_A) - |k_2|\,{}^{n-1}w_3 e^{-|k_2| r_A} \end{bmatrix} \qquad \text{for } n>1 $$

$$ = \begin{bmatrix} k^{\frac{1}{2}}\left(\cos k_1 r_A - \bar{R}\sin k_1 r_A\right) \\ -|k_2|\,\bar{w}_3 e^{-|k_2| r_A} \end{bmatrix} \qquad \text{for } n=1 $$

Following the method outlined in (b) the column matrix on the right hand side of equation (4.17) will be:

$$\begin{bmatrix} G_1(x) - \gamma f_1(x) \\ G_2(x) - \gamma f_2(x) \\ G_1'(x) - \gamma f_1'(x) \\ G_2'(x) - \gamma f_2'(x) \\ 0 \end{bmatrix}_{x=r_A}$$

and the matching matrix is defined by equations (4.23). The coefficients u_1, u_2, w_2 and w_3 determine the matched solution vector given by:

$$^n F_i(x) = \begin{bmatrix} {}^n\gamma f_1(x) + u_1 F_1^{(1)}(x) \\ {}^n\gamma f_2(x) + u_2 F_2^{(2)}(x) \end{bmatrix} \quad \text{for } 0 \le x \le r_M \qquad 4.25a$$

$$= \begin{bmatrix} {}^n G_1(x) + w_2 G_1^{(2)}(x) \\ {}^n G_2(x) + w_3 G_2^{(2)}(x) \end{bmatrix} \quad \text{for } r_M \le x \le r_A \qquad 4.25b$$

This process is repeated until the R-matrix converges.

(d) The Case of 2 Open Channels.

Here both k_1^2 and k_2^2 are positive and the homogeneous equations are given by equations (4.18). By inspection of equation (4.18b) we see that:

$$F_2^{(\alpha)}(x) = A_2^{(\alpha)} \sin k_2 x + B_2^{(\alpha)} \cos k_2 x$$

where $A_2^{(\alpha)}$ and $B_2^{(\alpha)}$ are 4 constants. But we choose the boundary conditions:

$$F_i^{(\alpha)}(x) = 0 \qquad \text{at } x=0 \qquad 4.26a$$

$$\text{and} \quad \left[\frac{d}{dx} F_i^{(\alpha)}(x)\right]_{x=0} = \delta_{\alpha i} \qquad 4.26b$$

therefore $F_2^{(1)}(x) = 0$ and $F_2^{(2)}(x) = k_2^{-1} \sin k_2 x$.

Because of equation (4.26) $F_1^{(2)}(x) = 0$ also so we have the following:

$$F_i^{(1)}(x) = \begin{bmatrix} F_1^{(1)}(x) \\ 0 \end{bmatrix} \qquad 4.27a$$

$$F_i^{(2)}(x) = \begin{bmatrix} 0 \\ k_2^{-1} \sin k_2 x \end{bmatrix} \qquad 4.27b$$

To obtain the inward solution in the range $r_M \leq x \leq r_A$ we generate four solution vectors $G_i^{(\beta)}(x) = \begin{bmatrix} G_1(x) \\ G_2(x) \end{bmatrix}^{(\beta)}$ for $\beta = 1, 2, 3$ and 4. The following boundary conditions are known:

$$G_i^{(\beta)}(x) \underset{x\to\infty}{\sim} A_i^{(\beta)} \sin k_i x + B_i^{(\beta)} \cos k_i x$$

where $A_i^{(\beta)}$ and $B_i^{(\beta)}$ are sixteen constants. Setting

$$\begin{bmatrix} A_i \\ B_i \end{bmatrix}^{(\beta)} = \begin{bmatrix} A_1 \\ A_2 \\ B_1 \\ B_2 \end{bmatrix}^{(\beta)} = \delta_{j\beta} \qquad \text{for } j = 1, 2, 3 \text{ and } 4$$

we obtain the following:

$$G_i^{(1)}(r_A) = \begin{bmatrix} \sin k_1 r_A \\ 0 \end{bmatrix}, \quad G_i^{(2)}(r_A) = \begin{bmatrix} \cos k_1 r_A \\ 0 \end{bmatrix}, \quad G_i^{(3)}(r_A) = \begin{bmatrix} 0 \\ \sin k_2 r_A \end{bmatrix}, \quad G_i^{(4)}(r_A) = \begin{bmatrix} 0 \\ \cos k_2 r_A \end{bmatrix}$$

By inspection of (4.18b) it can be seen that $G_2^{(3)}(x) = \sin k_2 x$ and $G_2^{(4)}(x) = \cos k_2 x$ are solutions for all x and since there is no term in $\cos k_2 x$ in the outward solutions given by equations (4.27), the coefficients of this term, $\overline{w}_4^{(\nu)}$, in the matching equation must vanish. Applying this to equation (4.12b) we see that $\overline{R}_{21} = \overline{R}_{22} = 0$. It follows from the symmetry of the R-matrix that $\overline{R}_{12} = 0$. This is a further self-consistency numerical feature that the computer code exhibits correctly.

Starting with the above values for $G_i^{(\beta)}(r_A)$ we can generate the four solution vectors inward to $x = r_M$. The matching matrix equation (4.13) becomes:

$$\begin{bmatrix} F_1^{(1)}(x) & 0 & -G_1^{(1)}(x) & 0 & -G_1^{(3)}(x) & 0 \\ 0 & F_2^{(2)}(x) & 0 & -G_2^{(2)}(x) & 0 & -G_2^{(4)}(x) \\ F_1^{(1)\prime}(x) & 0 & -G_1^{(1)\prime}(x) & 0 & -G_1^{(3)\prime}(x) & 0 \\ 0 & F_2^{(2)\prime}(x) & 0 & -G_2^{(2)\prime}(x) & 0 & -G_2^{(4)\prime}(x) \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}_{x=r_M} \begin{bmatrix} \bar{u}_1 \\ \bar{u}_2 \\ \bar{w}_1 \\ \bar{w}_2 \\ \bar{w}_3 \\ \bar{w}_4 \end{bmatrix}^{(\nu)} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ k_1^{-\frac{1}{2}} \delta_{1\nu} \\ k_2^{-\frac{1}{2}} \delta_{2\nu} \end{bmatrix}$$

and $R_{11} = k_1^{\frac{1}{2}} \bar{w}_3^{(1)}$

Therefore the matched and normalised solution $F_i^{(\nu)}(x)$ to be used in the integral terms of equation (4.1) is:

$$F_i^{(\nu)}(x) = \begin{bmatrix} \bar{u}_1^{(\nu)} F_1^{(1)}(x) \\ \bar{u}_2^{(\nu)} F_2^{(2)}(x) \end{bmatrix} \quad \text{for} \qquad 4.28a$$

$$= \begin{bmatrix} \bar{w}_1^{(\nu)} G_1^{(1)}(x) + \bar{w}_2 G_1^{(2)}(x) \\ \bar{w}_3^{(\nu)} G_2^{(2)}(x) \end{bmatrix} \quad \text{for} \qquad 4.28b$$

To obtain the particular integral for the inhomogeneous equations, equations (4.28) are substituted into the integral terms of equations (4.1) and a single outward solution vector $\mathcal{F}_i^{(\nu)}(x)$ and a single

inward solution vector $\mathcal{J}_i^{(\nu)}(x)$ is generated for each value of $\nu = 1$ and 2. The boundary conditions are:

$$ {}^{n}\mathcal{Y}_i^{(\nu)}(x) = 0 \qquad \text{at } x = 0 $$

$$ \left[{}^{n}\mathcal{Y}_i^{(\nu)\prime}(x) \right]_{x=0} = \left[{}^{n-1}\mathcal{Y}_i^{(\nu)\prime}(x) \right]_{x=0} + \sum_{\alpha=1}^{2} {}^{n-1}u_\alpha^{(\nu)} \delta_{\alpha i} \qquad \text{for } n > 1 $$

$$ = \sum_{\alpha=1}^{2} \bar{u}_\alpha^{(\nu)} \delta_{\alpha i} \qquad \text{for } n = 1 $$

$$ \begin{bmatrix} {}^{n}\mathcal{Y}_i^{(\nu)}(x) \\ {}^{n}\mathcal{Y}_i^{(\nu)\prime}(x) \end{bmatrix}_{x=r_A} = \begin{bmatrix} k_i^{-\frac{1}{2}} \left(\sin k_i r_A \cdot \delta_{i\nu} + R_{i\nu}^{(n-1)} \cos k_i r_A \right) \\ k_i^{\frac{1}{2}} \left(\cos k_i r_A \cdot \delta_{i\nu} - R_{i\nu}^{(n-1)} \sin k_i r_A \right) \end{bmatrix} \qquad \text{for } n \geq 1 $$

where $R^{(0)} \equiv \bar{R}$, the matrix obtained from the homogeneous equations. Therefore the column matrix on the right hand side of equation (4.17) will be:

$$ \begin{bmatrix} \mathcal{Y}_1^{(\nu)}(x) - \mathcal{J}_1^{(\nu)}(x) \\ \mathcal{Y}_2^{(\nu)}(x) - \mathcal{J}_2^{(\nu)}(x) \\ \mathcal{Y}_1^{(\nu)\prime}(x) - \mathcal{J}_1^{(\nu)\prime}(x) \\ \mathcal{Y}_2^{(\nu)\prime}(x) - \mathcal{J}_2^{(\nu)\prime}(x) \\ 0 \\ 0 \end{bmatrix}_{x=r_M} $$

and $$ R_{\mu\nu}^{(n)} = R_{\mu\nu}^{(n-1)} + k_\mu^{\frac{1}{2}} \omega_{\mu+2}^{(\nu)} $$

The coefficients $u_1^{(\nu)}$, $u_2^{(\nu)}$ and $\omega_3^{(\nu)}$ ($\omega_1^{(\nu)} = \omega_2^{(\nu)} = 0$ from equation (4.16a) and $\omega_4^{(\nu)} = 0$ as explained previously) determine the matched solution vectors ${}^{n}F_i^{(\nu)}(x)$ given by:

$$ {}^{n}F_i^{(\nu)}(x) = \begin{bmatrix} {}^{n}J_1^{(\nu)}(x) + u_1^{(\nu)} F_1^{(1)}(x) \\ {}^{n}J_2^{(\nu)}(x) + u_2^{(\nu)} F_2^{(2)}(x) \end{bmatrix} \qquad \text{for } 0 \le x \le r_M \qquad 4.29a $$

$$ = \begin{bmatrix} {}^{n}g_1^{(\nu)}(x) \\ {}^{n}g_2^{(\nu)}(x) + \omega_3^{(\nu)} G_2^{(3)}(x) \end{bmatrix} \qquad \text{for } r_M \le x \le r_A \qquad 4.29b $$

To continue the iterative process the matched solutions given by equations (4.29) are substituted into the integral terms of equations (4.1) and the whole procedure repeated until the R-matrix converges.

4.2 Runga Kutta Method and Interpolation Formulae.

The Runga Kutta formula for integrating $\frac{dy}{dx} = f(x, y)$ subject to the starting condition $y = y_0$ at $x = x_0$ is:

$$ y_{n+1} \quad y_n + \frac{1}{6}\left(k_1 + 2k_2 + 2k_3 + k_4 \right) \qquad 4.30 $$

where
$$ k_1 = hf(x_n, y_n) $$
$$ k_2 = hf\left(x_n + \frac{h}{2}, y_n + \frac{k_1}{2}\right) $$
$$ k_3 = hf\left(x_n + \frac{h}{2}, y_n + \frac{k_2}{2}\right) $$
$$ k_4 = hf(x_n + h, y_n + k_3) $$

and $h = x_n - x_{n-1}$

With a second order differential equation $\frac{d^2y}{dx^2} = f(x,y)$ we substitute $y_1 = \frac{dy}{dx}$ and transform the original second order differential equation into two coupled first order differential equations given by:

$$\frac{dy}{dx} = y_1$$

$$\frac{dy_1}{dx} = f(x,y)$$

It can be seen that the initial values of y and $\frac{dy}{dx}$ at $x = x_0$ are required to start off the integration.

(a) Starting Values at the Origin For Equations (4.1).

We write equations (2.41a) and (2.48a) in the following form:

$$\frac{d^2}{dx^2} F_1(x) = -\left(k_1^2 + V(x)\right) F_1(x) - \int_0^\infty d\sigma . F_2(\sigma) K_{12}(x,\sigma) \qquad 4.31a$$

$$\frac{d^2}{dx^2} F_2(x) = -k_2^2 F_2(x) - \int_0^\infty d\sigma . F_1(\sigma) \tilde{K}_{12}(x,\sigma) - \int_0^\infty d\sigma . F_2(\sigma) K_{22}(x,\sigma) \qquad 4.31b$$

The system of homogeneous equations will be:

$$\frac{d^2}{dx^2} F_1^{(0)}(x) = -\left(k_1^2 + V(x)\right) F_1^{(0)}(x) \qquad 4.32a$$

$$\frac{d^2}{dx^2} F_2^{(0)}(x) = -k_2^2 F_2^{(0)}(x) \qquad 4.32b$$

The boundary conditions are specified by equations (4.20) and these ensure that $F_2^{(0)\,\prime\prime}(x=0) = 0$, where a double prime denotes the second derivative. To find the value of $F_1^{(0)\,\prime\prime}(x=0)$ we must calculate the Limit $F_1^{(0)}(x)V(x)$ since $V(x) \underset{x\to 0}{\sim} \frac{1}{x}$.

Using equation (2.36) we see that:

$$xV(x) = -4N^2\left[\frac{e^{-2ax}}{4a^2}\left(x+\frac{1}{a}\right) + \frac{C^2 e^{-2bx}}{4b^2}\left(x+\frac{1}{b}\right) + \frac{2Ce^{-(a+b)x}}{(a+b)^2}\left(x+\frac{2}{a+b}\right)\right]$$

Since $F_1^{(0)}(x) \underset{x\to 0}{\sim} x$ we have the following:

$$\underset{x\to 0}{\text{Limit}}\; F_1^{(0)}(x)V(x) = \underset{x\to 0}{\text{Limit}}\; xV(x) = -4N^2\left[\frac{1}{4a^3} + \frac{C^2}{4b^3} + \frac{4C}{(a+b)^3}\right]$$

$$= -4 \quad \text{since} \quad N^{-2} = \frac{1}{4a^3} + \frac{C^2}{4b^3} + \frac{4C}{(a+b)^3}$$

Therefore $F_1^{(0)\,\prime\prime}(x=0) = -4$

It has been shown in section 3.1 that $K_{12}(0,\sigma) \neq 0$ for $\sigma \neq 0$ therefore there will be a contribution to $F_1^{\prime\prime}(x=0)$ from the integral term in equation (4.31a). It was also shown in section 3.1

that $K_{22}(0,\sigma) = K_{22}(\sigma,0) = 0$ for all values of σ. Since $K_{12}(\sigma,0) = 0$ it follows that $\tilde{K}_{12}(0,\sigma) = K_{12}(\sigma,0) = 0$ for all values of σ therefore there is no contribution to $F_2''(x=0)$ from the integral terms in equation (4.31b).

It can be seen that we require values of $f(x)$ at $x=\frac{nh}{2}$ where n is a positive, odd integer. In the positron - Helium problem f consists of integrals that cannot be solved in closed form therefore they must be tabulated for set values of x. The required values at $x=\frac{nh}{2}$ can then be acquired through interpolation. We use Newton's forward Interpolation formula:

$$f(x) = f_0 + s\Delta f_0 + \frac{s(s-1)}{2!}\Delta^2 f_0 + \frac{s(s-1)(s-2)}{3!}\Delta^3 f_0 + \text{------}$$

where $f_0 \equiv f(x_0)$ and

$$\Delta f_0 = f_1 - f_0$$

$$\Delta^2 f_0 = \Delta f_1 - \Delta f_0 = f_2 - 2f_1 + f_0$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\Delta^n f_0 = \Delta^{n-1} f_1 - \Delta^{n-1} f_0$$

In particular Newton's forward quartic interpolation formula reduces to:

$$f(x_0+sh) = \frac{(s-1)(s-2)(s-3)(s-4)f_0}{4!} - \frac{s(s-2)(s-3)(s-4)f_1}{3!} +$$

$$s(s-1)(s-3)(s-4)\frac{\delta_{12}}{2!} - s(s-1)(s-2)(s-4)\frac{\delta_{13}}{3!} + s(s-1)(s-2)(s-3)\frac{\delta_{14}}{4!} \qquad 4.33$$

4.3 Numerical Checking Procedures.

The equations under consideration are:

$$\left[\frac{d^2}{dx^2} + V(x) + k_1^2\right] F_1(x) = D(x) \qquad 4.34a$$

$$\left[\frac{d^2}{dx^2} + k_2^2\right] F_2(x) = E(x) + H(x) \qquad 4.34b$$

where $$D(x) = -\int_0^\infty F_2(\sigma)\, K_{12}(x,\sigma).\, d\sigma \qquad 4.35a$$

$$E(x) = -\int_0^\infty F_1(\sigma)\, \tilde{K}_{12}(x,\sigma).\, d\sigma \qquad 4.35b$$

$$H(x) = -\int_0^\infty F_2(\sigma)\, K_{22}(x,\sigma).\, d\sigma \qquad 4.35c$$

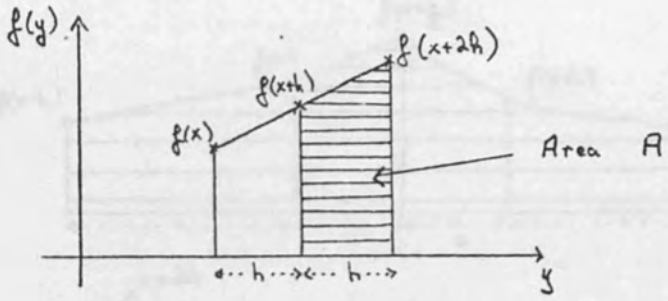
The integrands of D(x), E(x) and H(x) are discontinuous at well defined points which necessitate dividing the integration into several regions. Simpson's rule in the following two forms was used:

n even $$\int_x^{x+nh} f(y)\,dy = \frac{h}{3}\left(f_0 + 4f_1 + 2f_2 + \cdots\cdots + 4f_{n-1} + f_n\right) \qquad 4.36a$$

$$\underline{n \text{ odd}} \quad \int_{x}^{x+nh} f(y)\,dy = \frac{h}{24}\left(9f_0 + 28f_1 + 23f_2 + 24f_3 \cdots 24f_{n-3} + 23f_{n-2} + 28f_{n-1} + 9f_n\right) \qquad 4.36b$$

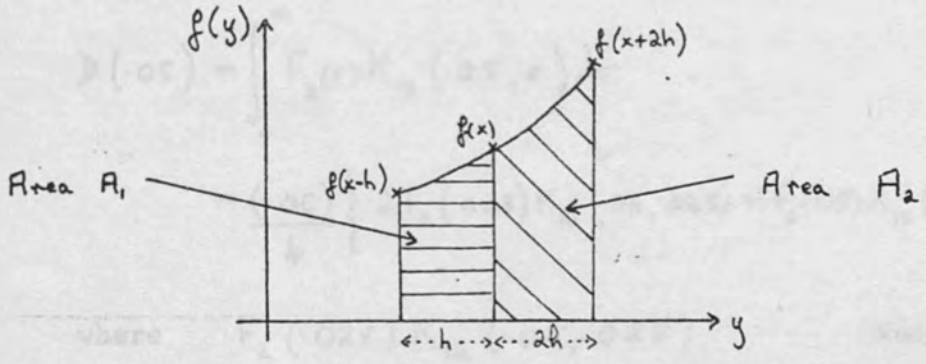
where $f_0 = f(x)$, $f_1 = f(x+h)$ etcetera.

At the beginning and end of the integration range it was necessary to use Simpson's rule of integration over one interval only as follows:



$$A = \int_{x+h}^{x+2h} f(y)\,dy = \frac{h}{12}\left(-f_0 + 8f_1 + 5f_2\right) \qquad 4.36c$$

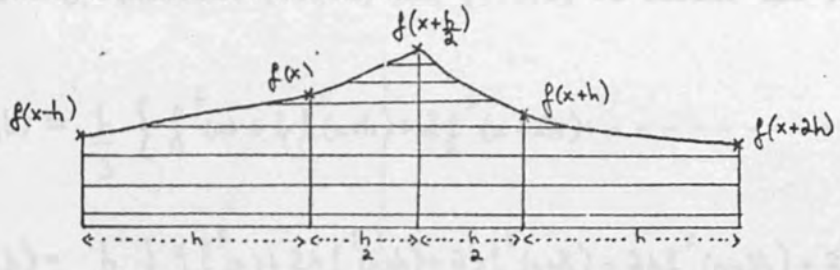
Because of the variation in step length of K_{12} and therefore $\tilde{K}_{12}$ (see Chapter III) the following single-interval formula was used:



$$A_1 = \int_{x-h}^{x} f(y)\,dy = \frac{h}{36}\left\{16f(x-h) + 21f(x) - f(x+2h)\right\} \qquad 4.36d$$

$$A_2 = \int_x^{x+2h} f(y)\,dy = \frac{h}{9}\left\{-4f(x-h) + 15f(x) + 7f(x+2h)\right\} \qquad 4.36e$$

The kernel $K_{12}(x,\sigma)$ is discontinuous at $\sigma = \frac{x}{2}$ (as well as at $\sigma = x$) and all of these half-values are not tabulated. The following formula was therefore derived:



$$\text{Total Area} = \int_{x-h}^{x+2h} f(y)\,dy = \frac{3h}{8}\left\{f(x-h) + 3f(x) + 3f(x+h) + f(x+2h)\right\} \qquad 4.36f$$

It is interesting to note that the value of the function at the half-value $(x+\frac{h}{2})$ is not required. The only value of x for which this could not be applied was $x = .05$. The value of $K_{12}(\cdot 05, \cdot 025)$ was calculated using a quartic interpolation formula, see section 4.2:

$$D(\cdot 05) = \int_0^{\infty} F_2(\sigma) K_{12}(\cdot 05, \sigma)\,d\sigma$$

$$= \frac{(\cdot 05)}{4}\left\{2F_2(\cdot 025)K_{12}(\cdot 05, \cdot 025) + F_2(\cdot 05)K_{12}(\cdot 05, \cdot 05)\right\} + \int_{\cdot 05}^{\infty} F_2(\sigma) K_{12}(\cdot 05, \sigma)\,d\sigma$$

where $F_2(\cdot 025)\,K_{12}(\cdot 05, \cdot 025)$ was calculated using $F_2(0)\,K_{12}(0, \cdot 5)$, $F_2(\cdot 2)\,K_{12}(\cdot 2, \cdot 1)$, $F_2(\cdot 4)K_{12}(\cdot 4, \cdot 2)$, $F_2(\cdot 6)K_{12}(\cdot 6, \cdot 3)$ and $F_2(\cdot 8)\,K_{12}(\cdot 8, \cdot 4)$.

(a) The Functions $D(x)$, $E(x)$ and $H(x)$.

By inspection of equations (4.35) it can be seen that the integrands of $D(x)$, $E(x)$ and $H(x)$ are discontinuous at the points $\sigma = \frac{x}{2}$ and x; $\sigma = x$ and $2x$; $\sigma = x$ respectively. Therefore three separate routines were written to calculate D, E and H.

Using equations (4.36a) and (4.36b) we define the following notation:

$$S_1^h(a,b) = \frac{h}{3}\left\{ f^F(a) + 4f^F(a+h) + 2f^F(a+2h) + \cdots + f^F(b) \right\}$$

$$S_2^h(a,b) = \frac{h}{24}\left\{ 9f^F(a) + 28f^F(a+h) + 23f^F(a+2h) + 24f^F(a+3h) + 24f^F(a+4h) + \cdots \right.$$

$$\left. \cdots + 24f^F(b-3h) + 23f^F(b-2h) + 28f^F(b-h) + 9f^F(b) \right\}$$

where F corresponds to either D, E or H and $f^F(\sigma)$ represents the integrand of the corresponding integral. For example $f^D(\sigma) = -F_2(\sigma)K_{12}(x,\sigma)$.

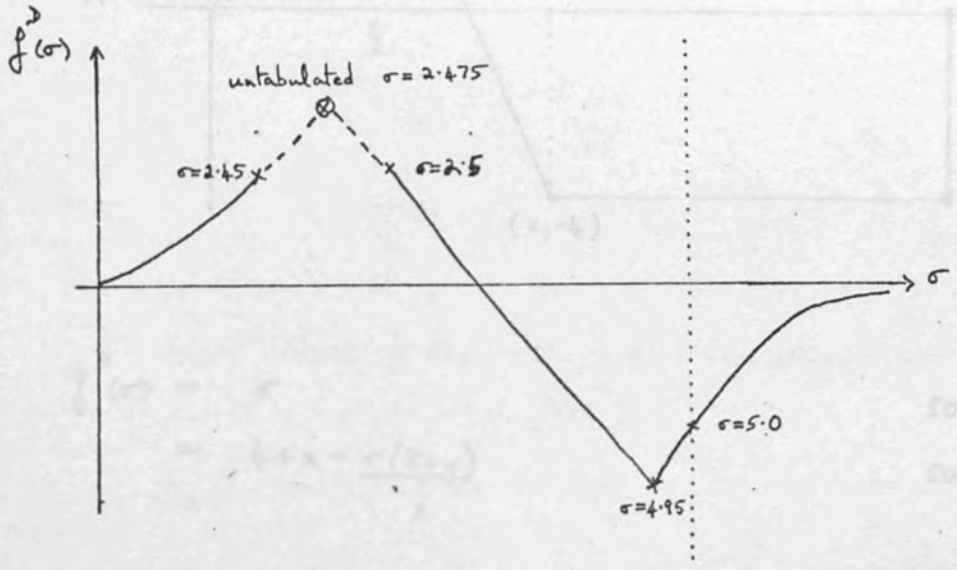
Consider the case of D(4.95). The integrand $f^D(\sigma) = -F_2(\sigma)K_{12}(4.95,\sigma)$ has singular first derivatives at the point $\sigma = 2.475$ (which is not tabulated) and the point $\sigma = 4.95$ (which is tabulated). As shown below, the integration must be split up into four sections, namely:

$$0 \leq \sigma \leq 2.475$$

$$2.475 \leq \sigma \leq 4.95$$

$$4.95 \leq \sigma \leq 5.0$$

$$5.0 \leq \sigma \leq 17.5$$



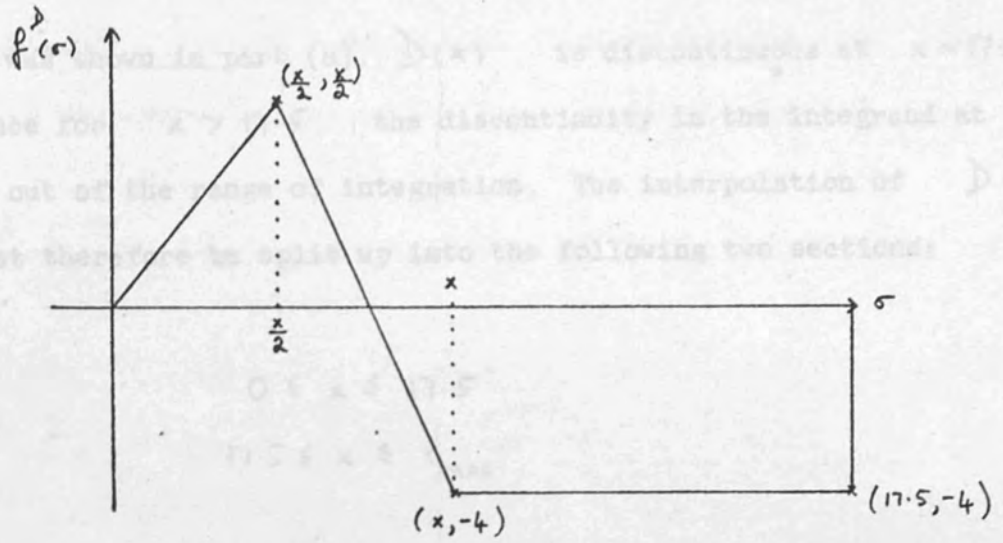
$x = 4.95$

The first two sections occur because of the singular first derivatives and the second two because of the change in step length at $\sigma=5$ from .05 to .1. Using equations (4.36a), (4.36b), (4.36c) and (4.36f) we may write the following:

$$D(4.95) = S_1^{.05}(0,2.4) + \frac{3}{8}(.05)\left\{ f^D(2.4) + 3f^D(2.45) + 3f^D(2.5) + f^D(2.55) \right\}$$

$$+ S_1^{.05}(2.55,2.95) + \frac{(.05)}{36}\left\{ 16f^D(4.95) + 21f^D(5.0) - f^D(5.1) \right\} + S_2^{.1}(5.0,17.5)$$

Similar formulae can be derived for E and H. Each integration routine was checked separately using a suitably discontinuous straight line graph. The case of $D(x)$ will now be illustrated:



$$f^D(\sigma) = \sigma \qquad \text{for} \quad 0 \le \sigma \le \frac{x}{2}$$

$$= 4 + x - \frac{\sigma(8+x)}{x} \qquad \text{for} \quad \frac{x}{2} < \sigma \le x$$

$$= -4 \qquad \text{for} \quad x < \sigma \le 17.5$$

Therefore the area $A(x)$ under the graph is given by:

$$A(x) = \frac{x^2}{4} + 3x - 70 \qquad \text{for} \quad 0 \le x \le 17.5$$

$$= -\frac{x^2}{4} - \frac{1225}{x} + \frac{33x}{2} - \frac{665}{8} \qquad \text{for} \quad 17.5 < x$$

and the discontinuity at $x = 17.5$ is clearly demonstrated. Exact agreement was obtained on these checks.

(b) The Interpolation of $D(x)$, $E(x)$ and $H(x)$.

The same tests as illustrated in part (a) were used. Because the upper integration limit r_{MAX} must necessarily be taken as finite, the numerical integration introduces a further discontinuity in D and E.

As was shown in part (a), $D(x)$ is discontinuous at $x = 17{\cdot}5$ since for $x > 17{\cdot}5$ the discontinuity in the integrand at $\sigma = x$ is out of the range of integration. The interpolation of $D(x)$ must therefore be split up into the following two sections:

$$0 \leq x \leq 17{\cdot}5$$

$$17{\cdot}5 \leq x \leq r_{MAX}$$

The code allowed r_{MAX} to take any value between 18 and 32.

$E(x)$ will be discontinuous at the point $x = \frac{r_{MAX}}{2}$ since for $x < \frac{r_{MAX}}{2}$ the integrand has two discontinuities and for $x > \frac{r_{MAX}}{2}$ it has only one. Since $\tilde{K}_{12}$ is tabulated for $r_{MAX} = 17{\cdot}4$ therefore the discontinuity is fixed at $x = 8{\cdot}7$. The interpolation of $E(x)$ is performed as follows:

$$0 \leq x \leq 8{\cdot}7$$

$$8{\cdot}7 \leq x \leq 17{\cdot}4$$

Since $K_{22}(x,\sigma)$ is discontinuous at $\sigma = x$ and is tabulated for x and $\sigma = {\cdot}1 \rightarrow 11{\cdot}6$, this discontinuity will always fall in the range of integration, thus $H(x)$ will be continuous for all x in the range $0 \leq x \leq 11{\cdot}6$.

(c) The Iteration Procedure for One Open and One Closed Channel.

We rewrite equations (4.1) in the following way:

$$\mathcal{L}_1 F_1^{(n)} = W_{12} F_2^{(n-1)} \qquad 4.37a$$

$$\mathcal{L}_2 F_2^{(n)} = W_{21} F_1^{(n-1)} + W_{22} F_2^{(n-1)} \qquad 4.37b$$

where $\mathcal{L}_i = \frac{d^2}{dx^2} + V(x).\delta_{i1} + k_i^2 \qquad i = 1,2$

and W_{12}, W_{21} and W_{22} are the appropriate integral operators as defined in equations (4.1) The superscript n denotes the nth. iterate and it can be seen that the (n-1)th. functions are substituted into the right hand side of equations (4.37) to produce the nth. iterated functions.

To start the iterative procedure we set all integral operators to zero and solve the following:

$$\mathcal{L}_1 F_1^{(0)} = 0 \qquad 4.38a$$

$$\mathcal{L}_2 F_2^{(0)} = 0 \qquad 4.38b$$

By inspection of equation (4.38b) we see that $F_2^{(0)} \equiv 0$.

The functions $F_1^{(0)}$ and $F_2^{(0)}$ are now substituted into the inhomogeneous terms of equations (4.37) giving the following:

$$\mathcal{L}_1 F_1^{(1)} = W_{12} F_2^{(0)} = 0 \qquad 4.39a$$

$$\mathcal{L}_2 F_2^{(1)} = W_{21} F_1^{(0)} + W_{22} F_2^{(0)} = W_{21} F_1^{(0)} \qquad 4.39b$$

It can be seen that equation (4.39b) is identical to equation (4.34a) so that $F_1^{(1)} = F_1^{(0)}$. We continue this process until the R-matrix (defined in Chapter II) has converged.

An interesting symmetry arises if W_{22} is set equal to zero. In this case equation (4.37b) reduces to:

$$\mathcal{L}_2 F_2^{(2)} = W_{21} F_1^{(1)} = W_{21} F_1^{(0)} \qquad \text{since} \quad F_1^{(1)} = F_1^{(0)}$$

and this equation is identical to equation (4.39b). Therefore $F_2^{(2)} = F_2^{(1)}$.

Continuing the iterative process we reach the following result:

$$F_1^{(n)} = F_1^{(n-1)} \qquad \text{for n odd}$$
$$F_2^{(n)} = F_2^{(n-1)} \qquad \text{for n even}$$

This feature of the iteration algorithm was displayed by the code.

Check on Equation (4.37a).

Setting $V(x) = 0$, equation (4.37a) was solved with an inhomogeneous term:

$$\frac{x}{36}(x-3)(6-x)e^{-Ax}$$

replacing $W_{12} F_2^{(n-1)}$. To ensure the same boundary conditions as in the positron-Helium case, A was taken as 3 . The particular integral $\mathcal{J}_1(x)$ for the equation is:

$$\mathcal{J}_1(x) = (a+bx+cx^2+dx^3)e^{-3x}$$

where $a = 2K^2\left(-\frac{7}{4}+10K-18K^2\right)$

$$b = K\left(-\frac{1}{2}+\frac{19K}{6}-6K^2\right)$$

$$c = K\left(\frac{1}{4}-\frac{K}{2}\right)$$

$$d = -\frac{K}{36}$$

$$K = \frac{1}{k_1^2+9}$$

The general solution is given by:

$$F_1(x) = k_1^{-\frac{1}{2}}\left(\sin k_1 x + R\cos k_1 x\right) + \mathcal{J}_1(x)$$

where R is the R-matrix which in this case is a scalar. The boundary condition $F_1(x=0) = 0$ gives $R = -k_1^{\frac{1}{2}} a$.

Therefore $F_1(x) = k_1^{-\frac{1}{2}} \sin k_1 x - a \cos k_1 x + {}^{4}f_1(x)$

Five figure agreement between the computed answer and this analytic answer was obtained.

Check on Equation (4.37b).

This equation was solved with an inhomogeneous term e^{-Bx} replacing $\left\{ W_{21} F_1^{(n-1)} + W_{22} F_2^{(n-1)} \right\}$. To ensure the same boundary conditions again, B was taken as 2. The particular integral ${}^{4}f_2(x)$ for the equation is:

$$ {}^{4}f_2(x) = \frac{e^{-2x}}{k_2^2 + 4} $$

and the general solution is given by:

$$ F_2(x) = A' e^{-|k_2|x} + \frac{e^{-2x}}{k_2^2 + 4} $$

The boundary condition $F_2(0) = 0$ gives $A' = \frac{-1}{k_2^2 + 4}$ therefore:

$$ F_2(x) = \frac{1}{k_2^2 + 4} \left(e^{-2x} - e^{-|k_2|x} \right) $$

Six figure agreement between the computed answer and this analytic answer was obtained:

(d) A Different Iteration Strategy.

In section 4.1 we described the iterative technique used for solving the system of equations (4.1). Instead of the boundary conditions specified by equations (4.15) we initially imposed the following conditions on the particular integral:

$$\text{n } f_i^{(\nu)}(x=0) = 0$$

$$\text{n } f_i^{(\nu)'}(x\ 0) = \delta_{i\nu}$$

$$\text{n } g_i^{(\nu)}(x\ r_A) = \begin{pmatrix} \sin k_\mu r_A \\ e^{-|k_\tau| r_A} \end{pmatrix}$$

$$\text{n } g_i^{(\nu)'}(x\ r_A) = \begin{pmatrix} k_\mu \cos k_\mu r_A \\ -|k_\tau| e^{-|k_\tau| r_A} \end{pmatrix}$$

It can be seen that equation (4.16) will be replaced by:

$$w_\mu^{(\nu)'} = k_\mu^{-\frac{1}{2}} \delta_{\mu\nu} - 1$$

and $$R_{\mu\nu} = k_\mu^{\frac{1}{2}} w_{\mu+N,A}^{(\nu)}$$

Therefore the right hand side matrix in equation (4.17) is replaced by:

$$\begin{bmatrix} \zeta_i^{(\nu)}(x) - \psi_i^{(\nu)}(x) \\ \hline \zeta_i^{(\nu)\prime}(x) - \psi_i^{(\nu)\prime}(x) \\ \hline k_\mu^{-\frac{1}{2}}\delta_{\mu\nu} - 1 \end{bmatrix} \begin{matrix} 1 \\ 2 \\ \vdots \\ M \\ M+1 \\ \vdots \\ 2M \\ 2M+1 \\ \vdots \\ 2M+\nu \\ \vdots \\ 2M+NA \end{matrix} \quad x = \tau_A$$

The iterated R-matrices produced from this set of boundary conditions were identical to eight significant figures to those produced using the method of section 4.1.

(e) Checking the Code Using Analytic Kernels.

Consider the following pair of coupled equations:

$$\left[\frac{d^2}{dx^2} + k_1^2\right] F_1(x) = \mu_1 x e^{-ax} \int_0^\infty \sigma e^{-b\sigma} F_2(\sigma) d\sigma \qquad 4.40a$$

$$\left[\frac{d^2}{dx^2} + k_2^2\right] F_2(x) = \mu_1 x e^{-bx} \int_0^\infty \sigma e^{-a\sigma} F_1(\sigma) d\sigma + \mu_2 x e^{-bx} \int_0^\infty \sigma e^{-b\sigma} F_2(\sigma) d\sigma \qquad 4.40b$$

These are of the same form as equations (4.34) with $V(x) = 0$ and:

$$K_{12}(x,\sigma) = \widehat{K}_{12}(\sigma,x) = -\mu_1 x\sigma e^{-ax-b\sigma}$$

$$K_{22}(x,\sigma) = -\mu_2 x\sigma e^{-b(x+\sigma)}$$

By taking the Laplace Transform of equations (4.40) and applying the positron-Helium asymptotic boundary conditions the solutions F_1 and F_2 are seen to be:

$$F_1(x) = k_1^{-\frac{1}{2}} \sin k_1 x + \mu_1 I_1 \left[B(a,k_1^2)\cos k_1 x + \left\{ C(a,k_1^2) + x D(a,k_1^2) \right\} e^{-ax} \right] \quad 4.41a$$

for $k_1^2 < 0$

$$F_2(x) = (\mu_1 I_2 + \mu_3 I_3) \left[B(b,-k_2^2) e^{-k_2 x} + \left\{ C(b,-k_2^2) + x D(b,-k_2^2) \right\} e^{-bx} \right] \quad 4.41b$$

for $k_2^2 > 0$ and $b >> |k_2|$

where $B(a,k^2) = -C(a,k^2) = \dfrac{-2a}{(a^2+k^2)^2}$, $D(a,k^2) = \dfrac{1}{a^2+k^2}$

$$I_{1,3} = \int_0^\infty \sigma e^{-b\sigma} F_2(\sigma)\, d\sigma \qquad \text{and} \qquad I_2 = \int_0^\infty \sigma e^{-a\sigma} F_1(\sigma)\, d\sigma \qquad 4.42$$

Numerically I_1 and I_3 differ since the upper limits will be 32 and 11.6 respectively to match up with the original code. The upper

limit for I_2 is taken as 17.4.

The phase shift δ is given by the expression:

$$\tan\delta = k_1^{\frac{1}{2}} \mu_1 I_1 B(a, k_1^2)$$

Equations (4.41) were solved iteratively by a separate check computer code. Table 4-1 presents the first few iterated phase shifts of each code for $a=b=3$, $\mu_1=100$, $\mu_2=10$ and $k_1^2=.5$. The zeroth iteration shows immediately that we can only expect four place accuracy in the code.

Although the analytic kernels do not possess the discontinuities of the true kernels some attempt was made to match the two sets for values of x and σ near the origin by choosing:

$$\mu_1 = 9980 \quad , \quad \mu_2 = 925 \quad , \quad a = 11 \quad , \quad b = 5$$

Since convergence was slow the check code was run keeping a and b fixed at these values but varying μ_1 and μ_2 by factors of 10. Table 4-2 clearly demonstrates the slower convergence for large μ_1 and μ_2 and also shows that the second kernel K_{22} affects the convergence to a larger extent than K_{12}.

4.4 Use of the Visual Display Device.

The size and shape of the functions D, E and H defined by equations (4.35) determine the behavior of the iterated functions F_1 and F_2. Their geometric characteristics have already

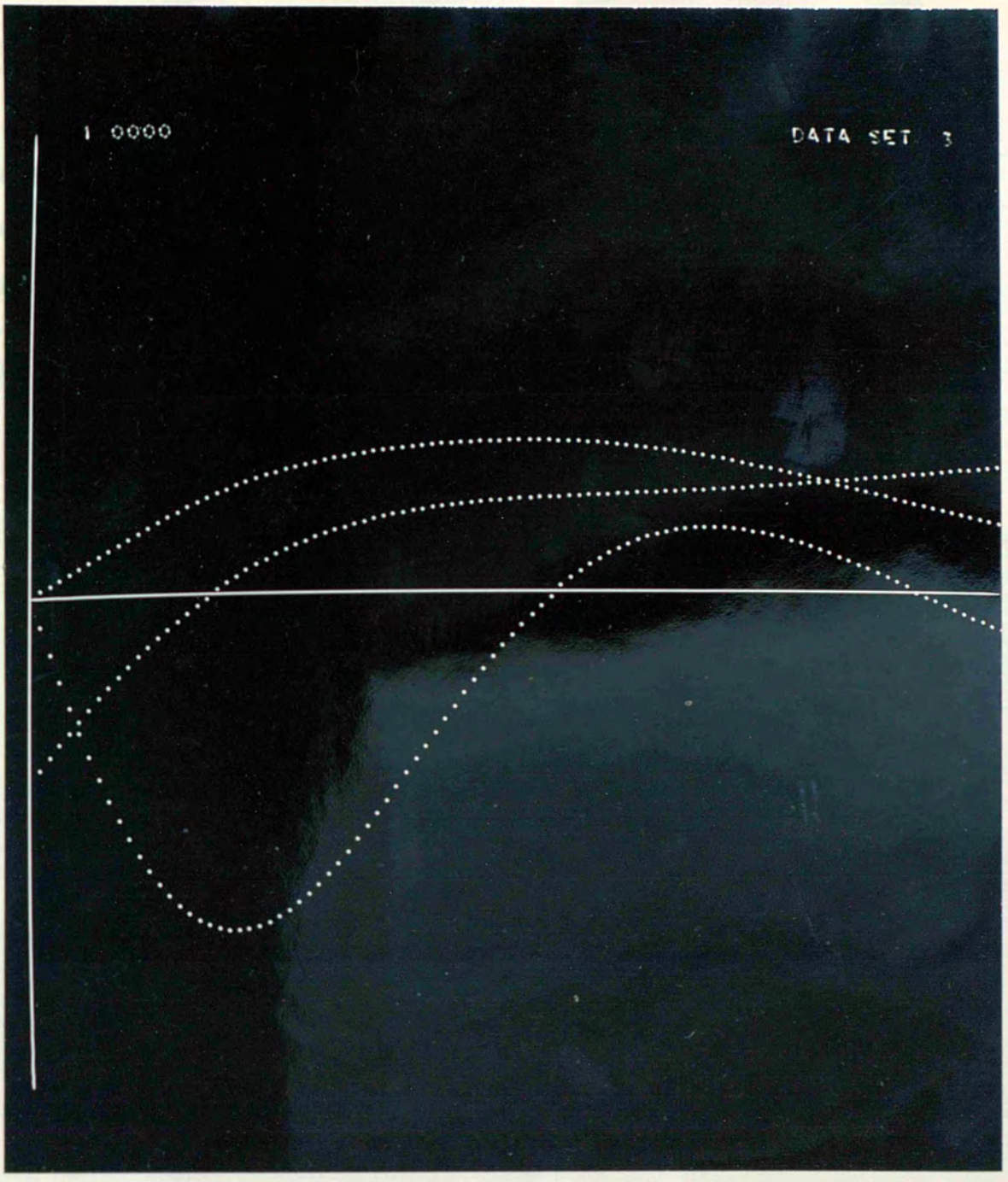


Figure 4-1 Photograph of a superimposition of D(x), E(x) and H(x) for x=0(.05)5 obtained from the Hylleraas Helium function at an energy k_1^2=1.0.

TABLE 4-1

A comparison of the "exact" iterated phase shifts of the check code and the "computed" phase shifts of the positron-Helium code for $a=b=3$, $\mu_1=100$, $\mu_2=10$ and $k_1^2=.5$.

Iteration	Exact Iterate	Computed Iterate
0	.0	$-.2252 \times 10^{-5}$
1	.05739	.05737
2	.05634	.05632
3	.05998	.05995
4	.05985	.05982
5	.06008	.06005
6	.06006	.
7	.06008	.

TABLE 4-2

A partial table of the number of iterations necessary for convergence in the check code for a = 11, b=5 and μ_1 and μ_2 as shown.

μ_1 \ μ_2	925.0	92.5	9.25	.925	.0925	.00925
9980.0	14	10	8	4	.	.
998.0	7	4	4	4	4	4
99.8	7	4	3	3	.	.
9.98	7	4	3	3	.	.
0.998	7	.	.	.	.	.
.0998	7	.	.	.	3	3
.00998	7	.	.	.	3	3

been discussed in Section 4.3(a) and (b) and Figure 4-1 presents a photograph of a superimposition of $D(x)$, $E(x)$ and $H(x)$ for $x = 0\,(.05)\,5$ obtained from the Hylleraas function at an energy $k_1^2 = 1.0$. Below is a sketch identifying the curves.

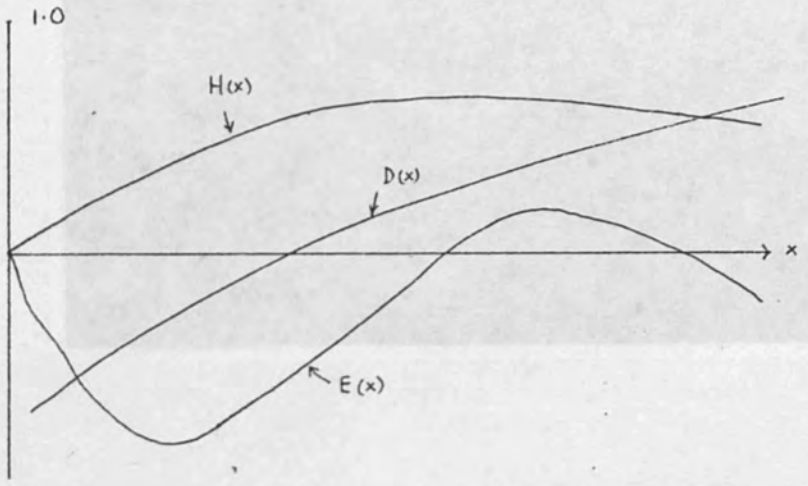
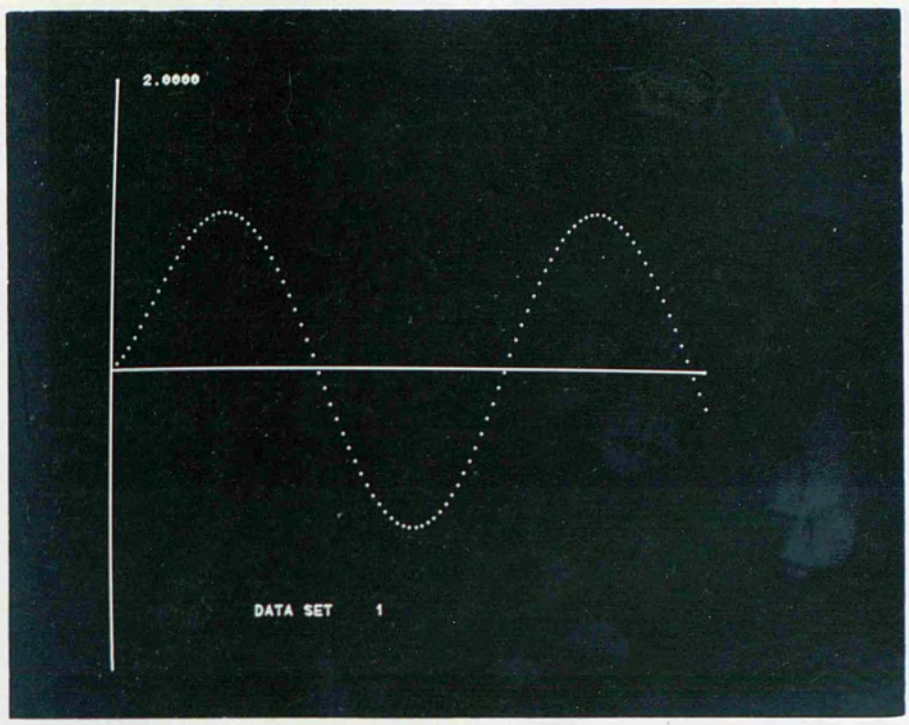


Figure 4-2 presents photographs of the first iterated $F_1(x)$ and $F_2(x)$ for $x = 0\,(.1)10$ and Figures 4-3 and 4-4 present a photograph of a superimposition of the first eight iterates of F_1 and F_2 respectively obtained from the Hylleraas function at an energy $k_1^2 = 1.0$. Below is a sketch identifying the iterates of F_2 in Figure 4-4.



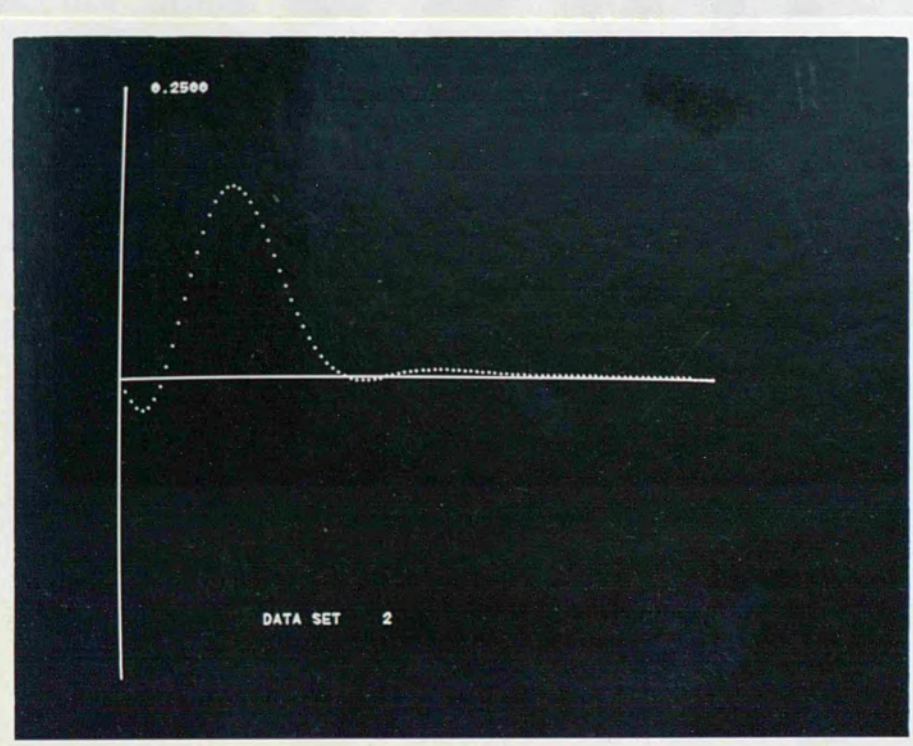


Figure 4-2 The upper photograph shows $F_1(x)$ for x=0(.1)10.
The lower photograph shows $F_2(x)$ for x=0(.1)10.

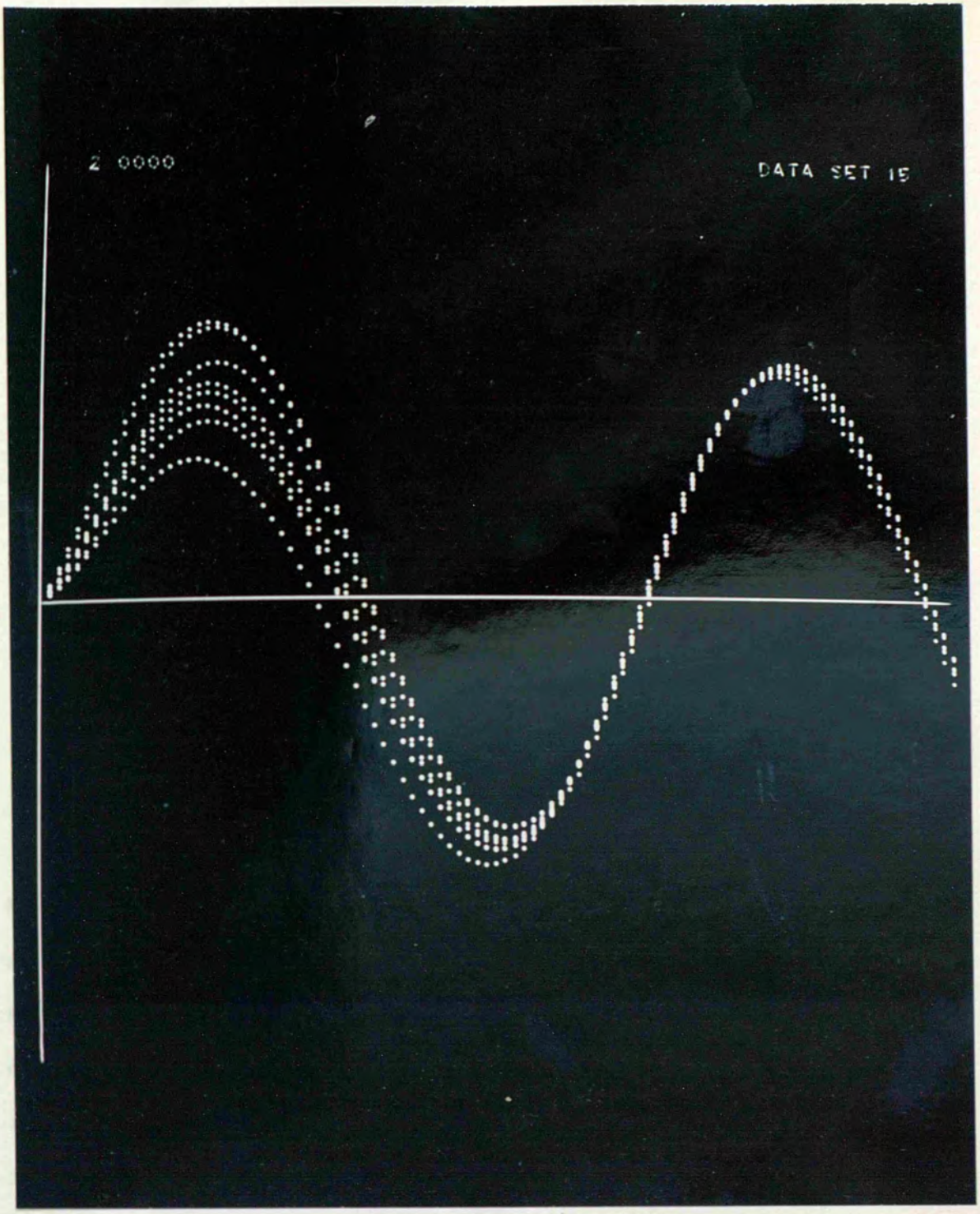
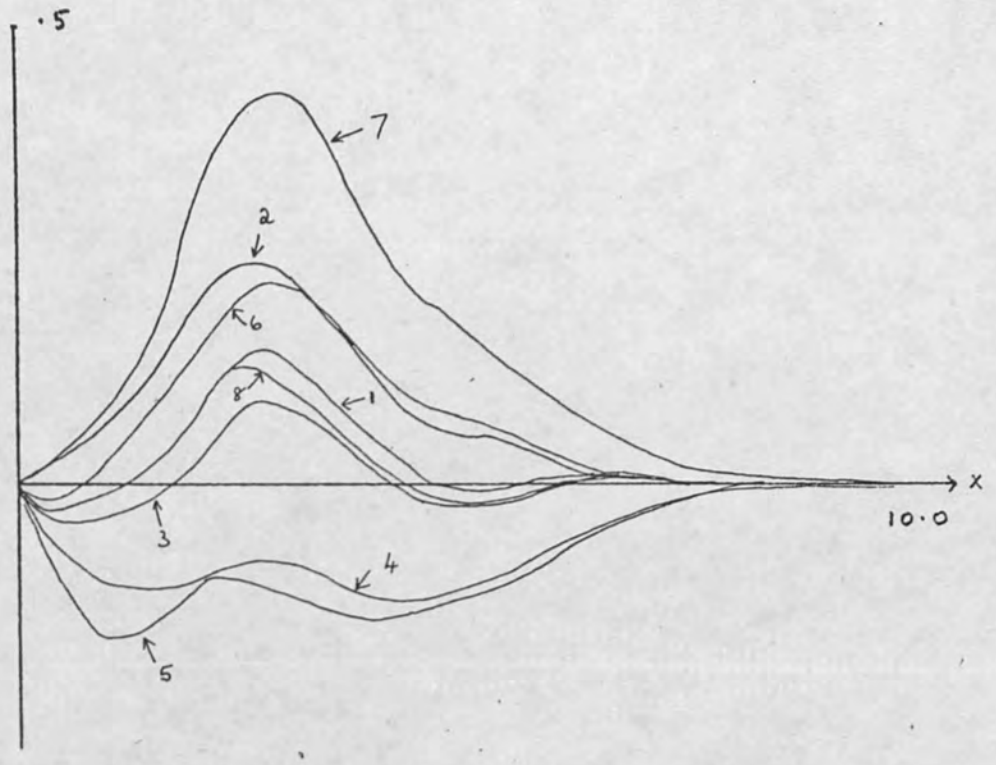


Figure 4-3 Photograph of the first 8 iterated F_1 functions obtained from the Hylleraas Helium function at an energy $k_1^a = 1.0$.



It is clear that F_1 and F_2 are displaying their correct asymptotic sinusoidal and exponentially decaying form respectively. All the functions mentioned can be seen to be continuous and have a first derivative at $x = 5$. A mismatch is easily detected as demonstrated in Figure 4-5 which shows photographs of $F_1(x)$ and $F_2(x)$ for x=0 (.)10 deliberately mismatched at x=5. A more subtle error is shown in Figure 4-6 which is a photograph of the first two iterates of E which were interpolated for midpoint values using a routine that had an incorrect minus sign. This is an excellent example of the usefulness of the graphical display since this error would be difficult to detect without laboriously drawing a graph by hand.

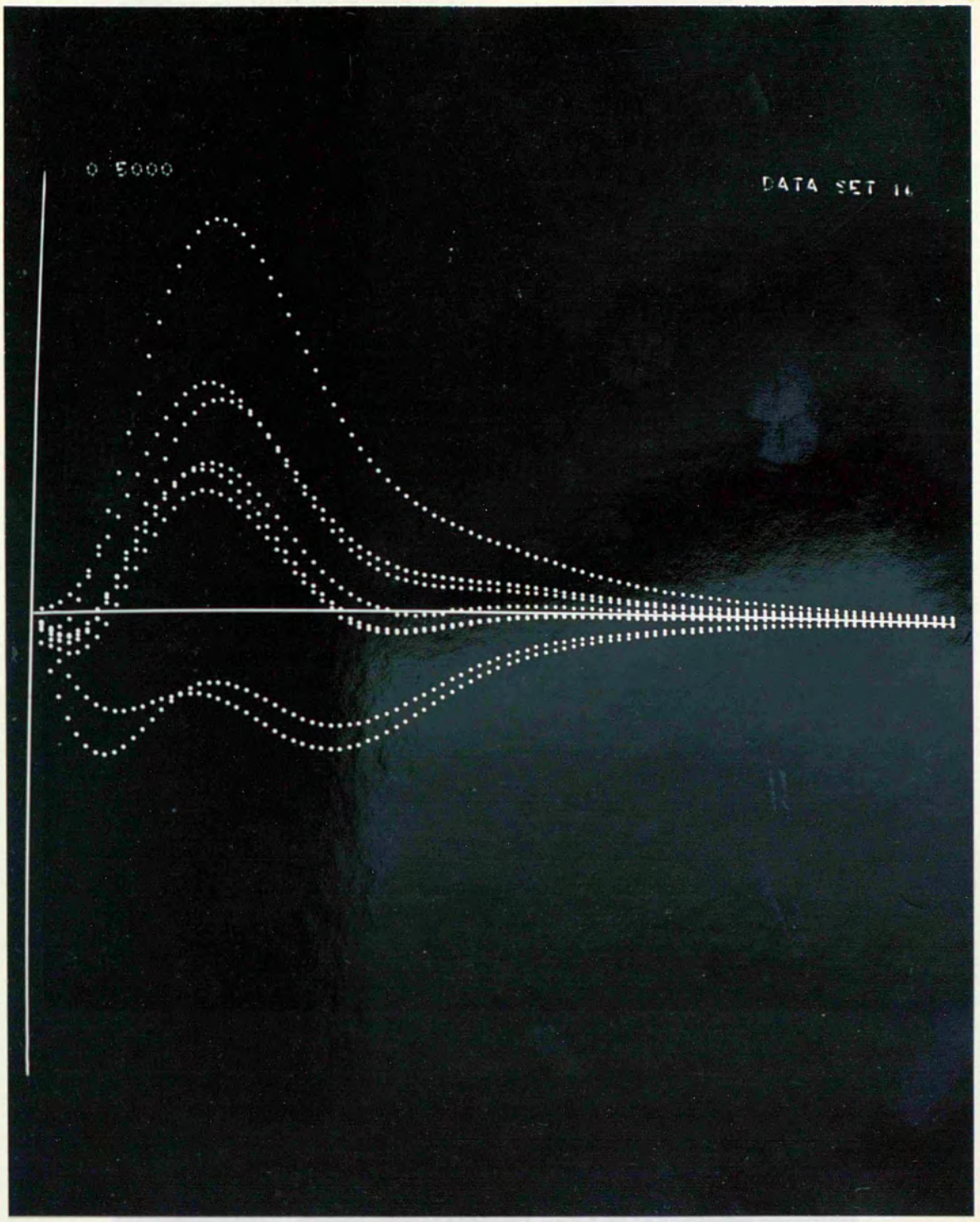
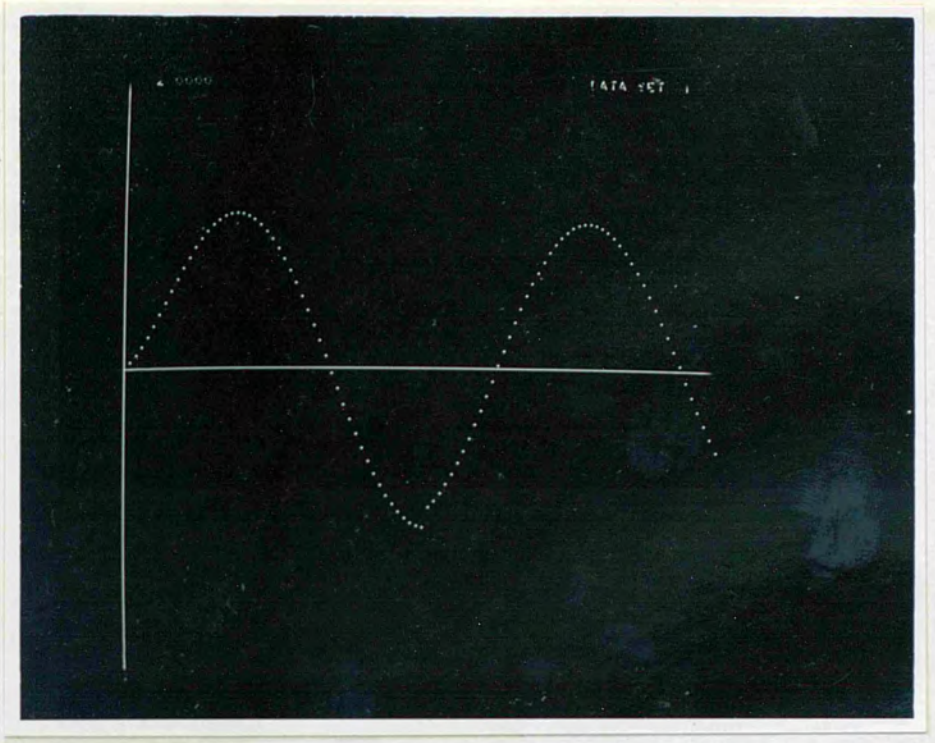


Figure 4-4 Photograph of the first 8 iterated F_a functions obtained from the Hylleraas Helium function at an energy $k_1^2 = 1.0$.



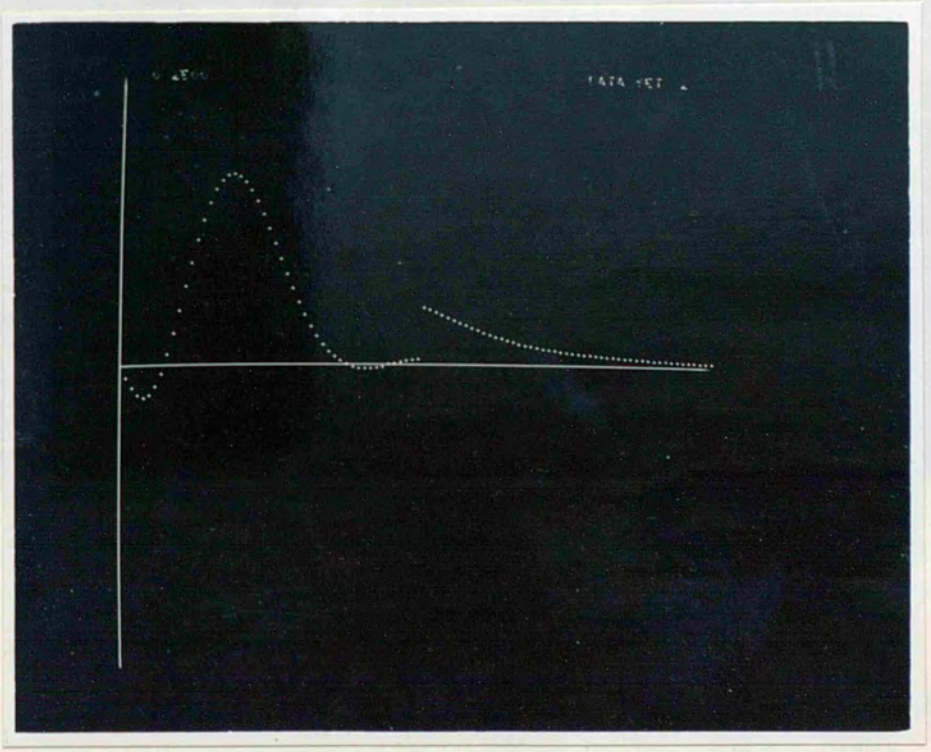


Figure 4-5 Photographs of F_1 (upper) and F_2 (lower) deliberately mismatched at x=5.

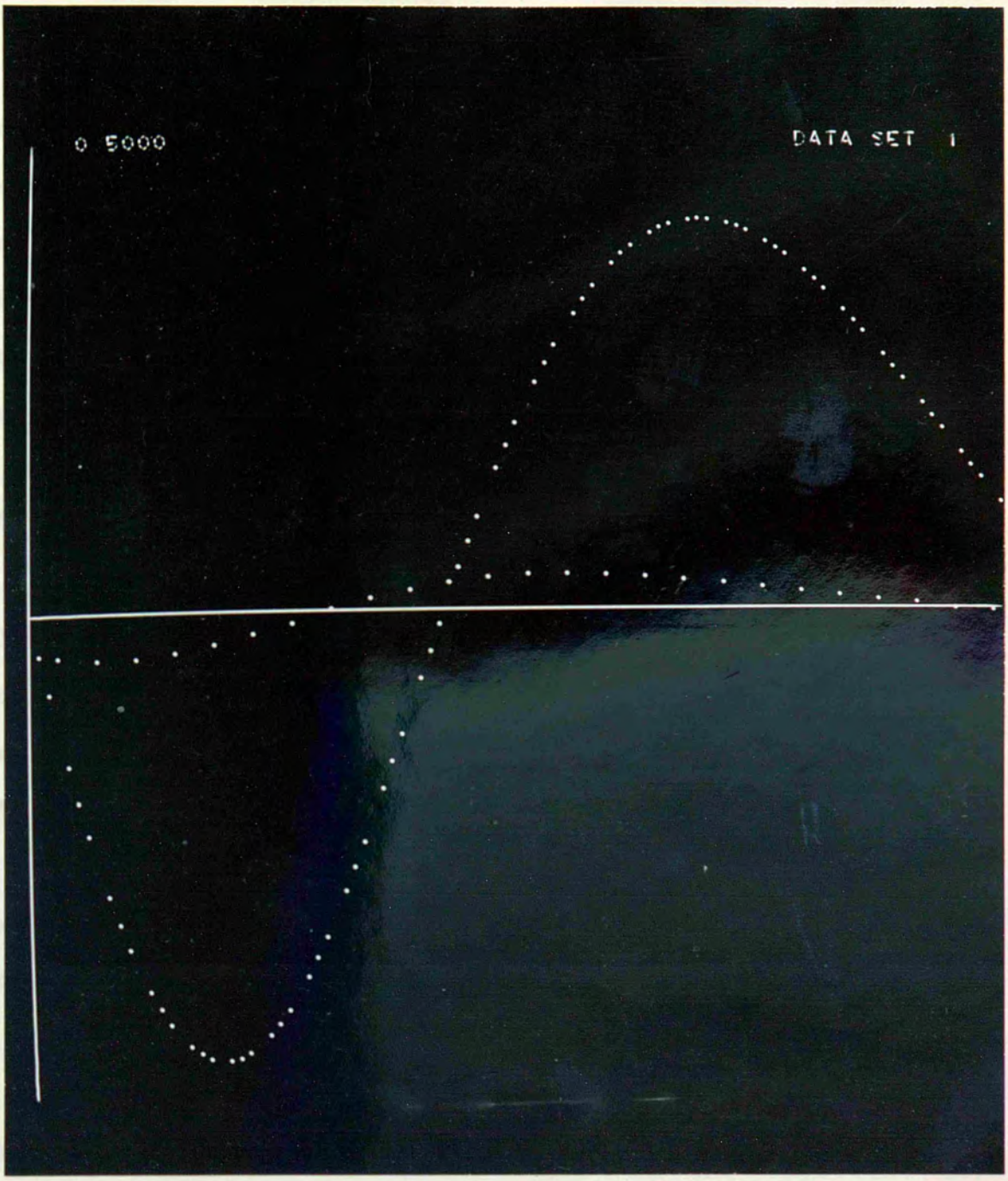


Figure 4-6 Photograph of the first 2 iterated E(x) functions interpolated for the midpoint values with a deliberate error in the interpolation routine.

In conclusion, it has been found that a graphical display device is a very effective tool for de-bugging a computer code whose elements possess distinct geometric characteristics. Although numerical checking must still be implemented, a visual display now replaces the drawn graph. The display is particularly useful for deciding upon the range and step size of integration and invaluable for comparing succeeding iterated solutions.

4.4. Review of Alternate Iteration Methods.

Alternate iteration methods fall into two broad categories. In the first, the actual iterative procedure is different to that of the matching procedure that has been described in section 4.1 and in the second, techniques of speeding up convergence are applied to an existing iteration procedure.

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In the first category, we have the method of Burke and Schey which is essentially that of the matching procedure but with a different set of equations replacing equations (4.12a) and (4.16a). NA integral conditions on the open channel functions F_μ for $\mu = 1, 2, \text{-----}, NA$ are specified as follows. Equation (4.11) is replaced by:

$$\sum_{\alpha=1}^{M} \bar{u}_\alpha^{(\nu)} \int_0^{r_M} F_\mu^{(\alpha)}(x)\,dx + \sum_{\beta=1}^{M+NR} \bar{\omega}_\beta^{(\nu)} \int_{r_M}^{r_0} G_\mu^{(\beta)}(x)\,dx = C_\mu$$

and equation (4.14a) is replaced by:

$$\int_0^{r_M} f_\mu^{(\nu)}(x)\,dx + \sum_{\alpha=1}^{M} u_\alpha^{(\nu)} \int_0^{r_M} F_\mu^{(\alpha)}(x)\,dx + \int_{r_M}^{r_0} g_\mu^{(\nu)}(x)\,dx + \sum_{\beta=1}^{M+NA} w_\beta^{(\nu)} \int_{r_M}^{r_0} G_\mu^{\beta}(x)\,dx = C_\mu$$

where the C_μ are arbitrary real constants and r_0 is also arbitrary and chosen so as to speed up convergence.

McEachran and Fraser (Smith, McEachran and Fraser;[88] McEachran and Fraser[23]) solved the following system of equations:

$$L_i F_i(r) = \sum_j W_{ij} F_j(r) \qquad 4.43$$

where $L_i = \frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k_i^2$

and the W_{ij} include short-range exponentially decaying potentials and integral operators.

In order to illustrate this method we will consider the case of one open channel and one closed channel only. The boundary conditions are:

$$F_i(r=0) = 0 \qquad \text{for } i = 1 \text{ and } 2$$

$$F_1(r) \underset{r\to\infty}{\sim} \sin\left(k_1 r - \frac{\ell\pi}{2}\right) + \tan\eta_\ell \cdot \cos\left(k_1 r - \frac{\ell\pi}{2}\right) \qquad 4.44$$

$$F_2(r) \underset{r\to\infty}{\sim} A e^{-|k_2| r}$$

where η_ℓ is the phase shift for the particular orbital angular momentum ℓ and A is a constant. Using these boundary conditions equations (4.48) can be converted into an integral equation as follows:

$$F_i(r) = u_\ell(k,r)\,\delta_{i1} - H_i(r) \qquad 4.45a$$

where $$H_i(r) = \int_0^\infty G_i(r,r') \sum_{j=1}^{2} W_{ij} F_j(r')\,dr' \qquad 4.45b$$

and $u_\ell(k,r)$ and the Green's function $G_i(r,r')$ are defined by Smith et al.(88)

The iterative procedure is started by evaluating $H_2(r)$ using the free wave solution $F_i(r) = u_\ell(k,r)\delta_{i1}$ obtained from solving $L_i u_\ell(k,r) = 0$. This value of $H_2(r)$ is substituted into the $i=2$ equation (4.45a) keeping $F_1(r)$ fixed, to yield a new $F_2(r)$ which in turn is used to recalculate $H_2(r)$. This process is repeated until $F_2(r)$ converges. $F_2(r)$ is now kept fixed and a similar process carried out for $F_1(r)$ using the $i=1$ equation (4.45a). The entire procedure is repeated until both $F_1(r)$ and $F_2(r)$ converge simultaneously.

For certain energies this method was found to give very slow convergence and sometimes no convergence at all so Kraidy and Fraser(89) used this same iterative procedure but imposed different asymptotic boundary conditions. They replaced equations (4.44) by:

$$F_i(r=0) = 0$$

$$F_1(r) \underset{r\to\infty}{\sim} \cot\eta_\ell \cdot \sin\left(k_1 r - \frac{\ell\pi}{2}\right) + \cos\left(k_1 r - \frac{\ell\pi}{2}\right) \qquad 4.46$$

$$F_2(r) \underset{r\to\infty}{\sim} A e^{-|k_2| r}$$

Therefore equations (4.43) are replaced by:

$$F_i(r) = \cot\eta_\ell \cdot u_\ell(k_1 r)\,\delta_{i1} - \mathcal{H}_i(r) \qquad 4.47$$

The boundary conditions specified by equations (4.46) impose a further condition:

$$-\int u_\ell(kr') \sum W_{1i} F_i(r')\,dr' = 1 \qquad 4.48$$

from which the phase shift η_ℓ may be calculated.

The iterative process is started with $F_1(r) = \cot\eta_\ell \cdot u_\ell(k_1 r) + (1-e^{-r}) v_\ell(k_1 r)$ and $F_2(r) = 0$ where the starting value of η_ℓ is obtained from equation (4.48) and $v_\ell(k_1 r)$ is the irregular solution of the free wave equation which is defined by Smith et al.[88] The same process as described previously was performed except that the nth. iterate $\cot\eta_\ell$ is calculated from equation (4.48).

It was found that this method produced convergence in most domains where the previous method did not and in general speeded up convergence.

The following methods fall into the second category. A very simple way of speeding up convergence was first introduced by Burke and Smith[22]. One replaces the mth. iterate $F_i^{(m)}(r)$ by a linear combination of the mth. and $(m-1)$th. iterates, $\alpha F_i^{(m)}(r) + (\alpha-1)F_i^{(m-1)}(r)$ where α is some predetermined constant. This new function is substituted into the integral terms of equations (4.45) or (4.47) and the appropriate iteration procedure continued. Burke and Smith[22] found that the choice of $\alpha > 1$ speeded up a slow, monotonically converging sequence, $\alpha = \frac{1}{2}$ reduced the number of iterations required for a converging oscillatory sequence and $\alpha < 0$ could sometimes avoid monotonically diverging sequences. Of course, extra computer time is required to find out which value of α is the best for a particular case.

Saraph and Seaton[90] showed that in the case of the anti-symmetric s-wave in electron-Hydrogen scattering, all iteration procedures gave slow convergence. This occurs because the Hydrogen ground state wave function $P(r) = 2re^{-r}$ also satisfies the electron-Hydrogen integro-differential equation and in a numerical calculation, the contribution of $P(r)$ to the iterated wave functions can become dominant so producing a loss of significant figures. To avoid this, an orthogonality condition can be imposed:

$$\int P(r)\,F(r)\,dr = 0 \quad , \qquad \lim_{n\to\infty} F^{(n)}(r) = F(r)$$

Again, this does not always produce convergence and so the

equivalent orthogonality condition can be applied to each iterate $F^{(n)}_{(r)}$. We re-write equation (4.43) as follows:

$$L F^{(n)} = W F^{(n-1)} \qquad 4.49$$

Let a solution be $f^{(n)}_{(r)}$ and choose a new function $y^{(n)}_{(r)} = f^{(n)}_{(r)} + \lambda^{(n)} Q$ where $y^{(n)}_{(r)}$ is to be orthogonal to $P_{(r)}$.

Therefore $$\int_0^\infty y^{(n)}_{(r)} P_{(r)} dr = 0 \qquad 4.50$$

Using equation (4.49) we have:

$$L y^{(n)}_{(r)} = W F^{(n-1)} + \lambda^{(n)} L Q$$

Choosing $LQ = -2P$ and using equation (4.50) we have the following:

$$L y^{(n)}_{(r)} = W F^{(n-1)} - 2\lambda^{(n)} P$$

and $$\lambda^{(n)} = - \frac{\int_0^\infty P_{(r)} f^{(n)}_{(r)} dr}{\int_0^\infty P_{(r)} Q_{(r)} dr}$$

If the sequence converges then $\underset{n\to\infty}{\text{Limit}}\ \lambda^{(n)} = 0$. John[91] has found that convergence could be obtained using this method but a relatively large number of iterations was required.

The various iteration-variation methods fall into the second category too. Saraph and Seaton [90] developed such a method for scattering problems with one open channel and Saraph [92] extended this to allow for multi-open channels. Equation (4.43) can be re-written in matrix form, with matrices of dimension equal to the total number of channels M, explicitly demonstrating the iterative process as follows:

$$L F_i^{(n)} = W F_i^{(n-1)} \qquad 4.51$$

where L is a diagonal matrix with elements $L_{ii} = \frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k_i^2$ and $F_i^{(n)}$ is a column vector having elements $F_{ij}^{(n)}$ which satisfy the following boundary conditions:

$$F_{ij}^{(n)}(r=0) = 0 \qquad 4.52a$$

$$F_{ij}^{(n)}(r) \underset{r\to\infty}{\sim} \sin\left(k_i r - \frac{\ell\pi}{2}\right)\delta_{ij} + R_{ij}^{(n)} \cos\left(k_i r - \frac{\ell\pi}{2}\right) \quad \text{for } k_i^2 > 0 \qquad 4.52b$$

$$F_{ij}^{(n)}(r) \underset{r\to\infty}{\sim} A_{ij}\, e^{-|k_i| r} \quad \text{for } k_i^2 < 0 \qquad 4.52c$$

where $R^{(n)}$ is the R-matrix obtained from the nth iterates $F_i^{(n)}$. The $n=0$ solution is the free wave solution $F_{ij}^{(0)} = u_\ell(k_i r)\,\delta_{ij}$ as defined previously.

Using the notation:

$$\left(\mathcal{Y}_i \left| L-W \right| \mathcal{Y}_j\right) = \int_0^\infty dr \left[\sum_{p,q} \mathcal{Y}_{ip}(r) \left\{ \lambda_p \delta_{pq} - W_{pq} \right\} \mathcal{Y}_{jq} \right] \qquad 4.53$$

the stationary expression of Kohn is:

$$R_{ij}^{K,n} = R_{ij}^{t,n} + \frac{1}{k_i} \left(\mathcal{Y}_i^t \left| L-W \right| \mathcal{Y}_j^t \right) \qquad 4.54$$

where $\mathcal{Y}^t$ is some trial function satisfying equations (4.52) and giving a trial R-matrix $R^{t,n}$. Saraph[92] chose for these trial functions a linear combination of the iterated wave functions $F^{(m)}$ for $m = 0, 1, ----, n$ as follows:

$$\mathcal{Y}_{ij}^t(r) = \left[1 - \sum_{\nu=1}^{n} C_{ij}^{(\nu)} \right] F_{ij}^{(0)}(r) + \sum_{\nu=1}^{n} C_{ij}^{(\nu)} F_{ij}^{(\nu)}(r) \qquad 4.55$$

It can be seen that $\mathcal{Y}_{ij}^t(r)$ has the correct asymptotic form if:

$$R_{ij}^{t,n} = \left[1 - \sum_{\nu=1}^{n} C_{ij}^{(\nu)} \right] R_{ij}^{(0)} + \sum C_{ij}^{(\nu)} R_{ij}^{(\nu)} \qquad 4.56$$

where the $C_{ij}^{(\nu)}$ are constants. Equation (4.55) is substituted into equation (4.54) and equations for the constants $C_{ij}^{(\nu)}$ are found by requiring that $R_{ij}^{K,n}$ be stationary with respect to the $C_{ij}^{(\nu)}$. That is:

$$\frac{\partial R_{ij}^{K,n}}{\partial C_{ij}^{(\nu)}} = 0 \qquad \text{for } \nu = 1, 2, ------, n$$

The $C_{ij}^{(\nu)}$ are then substituted into equation (4.54) to

obtain the stationary Kohn value of the R- matrix.

It was found that this iteration-variation method speeded up an already convergent sequence for the elements of the R-matrix and could produce convergence where ordinary iterative procedures gave diverging sequences.

McEachran et al.[23] developed a version of this method making use of recursion relations in order to simplify equation (4.54). They showed that the nth. Kohn R-matrix $R^{K,n}$ could be expressed in terms of the (n-1)th. R-matrix $R^{K,n-1}$ and the nth variational parameters $C_{ij}^{(n)}$.

Kraidy and Fraser[89] developed a simpler version of the iteration - variation method by using trial functions that were linear combinations of two iterates only. This trial function was then substituted into the integral terms of equations (4.51) to produce the next iterated solution. For example, equation (4.51) was solved for $F^{(n)}$ and R^{n}. The trial functions $F^{t(n)}$ were taken as follows:

$$F_{ij}^{t(n)}(r) = \left[1 - C^{(n)}\right] y_{ij}(r) + C^{(n)} F_{ij}^{(n)}(r)$$

where the functions y were taken either as $F^{(n-1)}$ or $F^{(1)}$. The corresponding expression for the R-matrix elements is:

$$R_{ij}^{t(n)} = \left[1 - C^{(n)}\right] b_{ij}^{t} + C^{(n)} R_{ij}^{(n)}$$

where $b^{t}_{ij} = R^{(n-1)}_{ij_{(1)}}$ if $y_{ij} = F^{(n-1)}_{ij}$

$= R_{ij}$ if $y_{ij} = F^{(1)}_{ij}$

It can be seen that there is only one variational parameter $C^{(n)}$ which is determined by solving $\frac{\partial R^{K,n}}{\partial C^{(n)}} = 0$ where $R^{K,n}$ is defined in equation (4.54).

Kraidy and Fraser[89] applied this technique to electron-atom scattering using both the tangent and cotangent asymptotic boundary conditions specified by equations (4.44) and (4.46). They found that convergence was generally faster if y_j was chosen to $= F^{(1)}$. In some cases, taking $y_j = F^{(n-1)}$ produced wrong answers because $F^{t(n-1)}$ approached $F^{t(n)}$ as the sequence converged and this caused numerical difficulties in the form of loss of significant figures. But in the majority of cases tried, the number of iterations required for convergence was less than that in an ordinary iteration scheme.

CHAPTER V

SCATTERING RESULTS

5.1 Convergence Problems.

For all energies below threshold the iterated phase shifts oscillated. The oscillations for the Hylleraas function are more pronounced and less symmetrical than those produced by the Hartree-Fock function. Table 5-1 presents the first 15 iterated values of the phase shift δ_n for each Helium function at an energy of $k_1^2 = \cdot 81$ and Figure 5-1 presents the equivalent graphical form.

By inspection of Figure 5-1 it can be seen that the Hartree-Fock phase shift has settled down to a symmetric oscillation which by the work of John [91] and Salmona and Seaton [93] should be averaged to give the required solution. No such symmetry is displayed by the Hylleraas phase shift which jumps about wildly even out as far as 30 iterations.

An averaging procedure was incorporated into the code that, after an assigned number of iterations n, would average the nth. and (n-1)th solutions and parameters to produce the (n + 1)th. iterate. Figure 5-2 presents the ordinary iterates $\delta_n^{H.F.}$ and averaged iterates $\eta_n^{H.F.}$ for the Hartree-Fock function at an energy $k_1^2 = \cdot 81$, averaged for $n = 7$ onwards. Figure 5-3 presents the equivalent first 20 iterates (δ_n^H, η_n^H) produced by the Hylleraas function. After the 11th iteration $\eta_n^{H.F.}$ increases

TABLE 5-1

The first 15 iterates of the phase shift δ_n for the Hartree-Fock and Hylleraas Helium functions at an energy $k_1^2 = .81$.

n	δ_n Hartree-Fock	δ_n Hylleraas
1	-.3090	-.3090
2	-.2748	-.2434
3	-.2770	-.2317
4	-.2713	-.2512
5	-.2843	-.2825
6	-.2697	-.2623
7	-.2741	-.2433
8	-.2630	-.2350
9	-.2746	-.2613
10	-.2649	-.2633
11	-.2730	-.2574
12	-.2618	-.2387
13	-.2716	-.2494
14	-.2624	-.2550
15	-.2719	-.2619

FIGURE 5-1

Phase shift iterates for the Hartree-Fock and Hylleraas Helium functions.

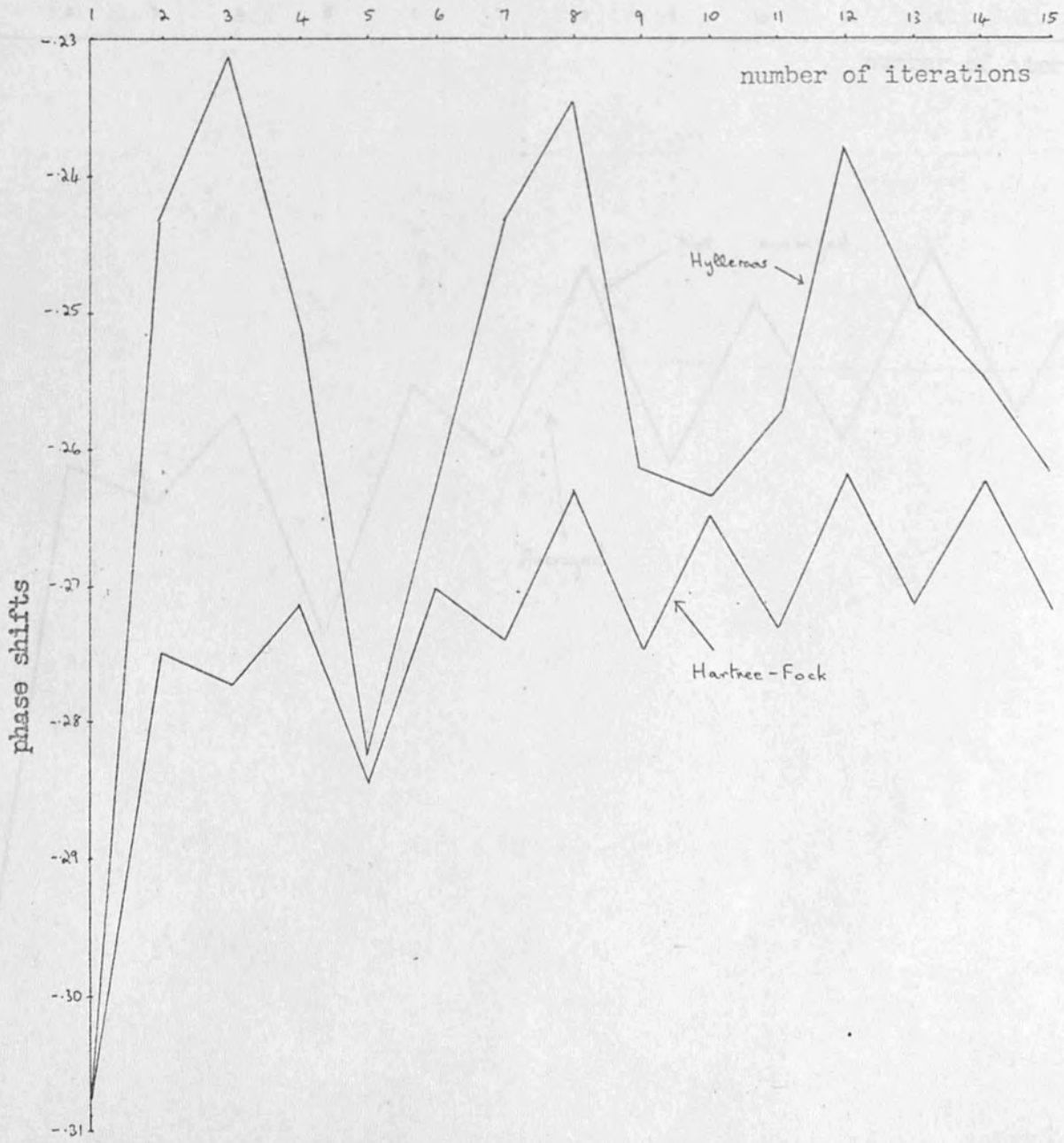


FIGURE 5-2

Averaged and non-averaged phase shift iterates for the Hartree-Fock Helium.

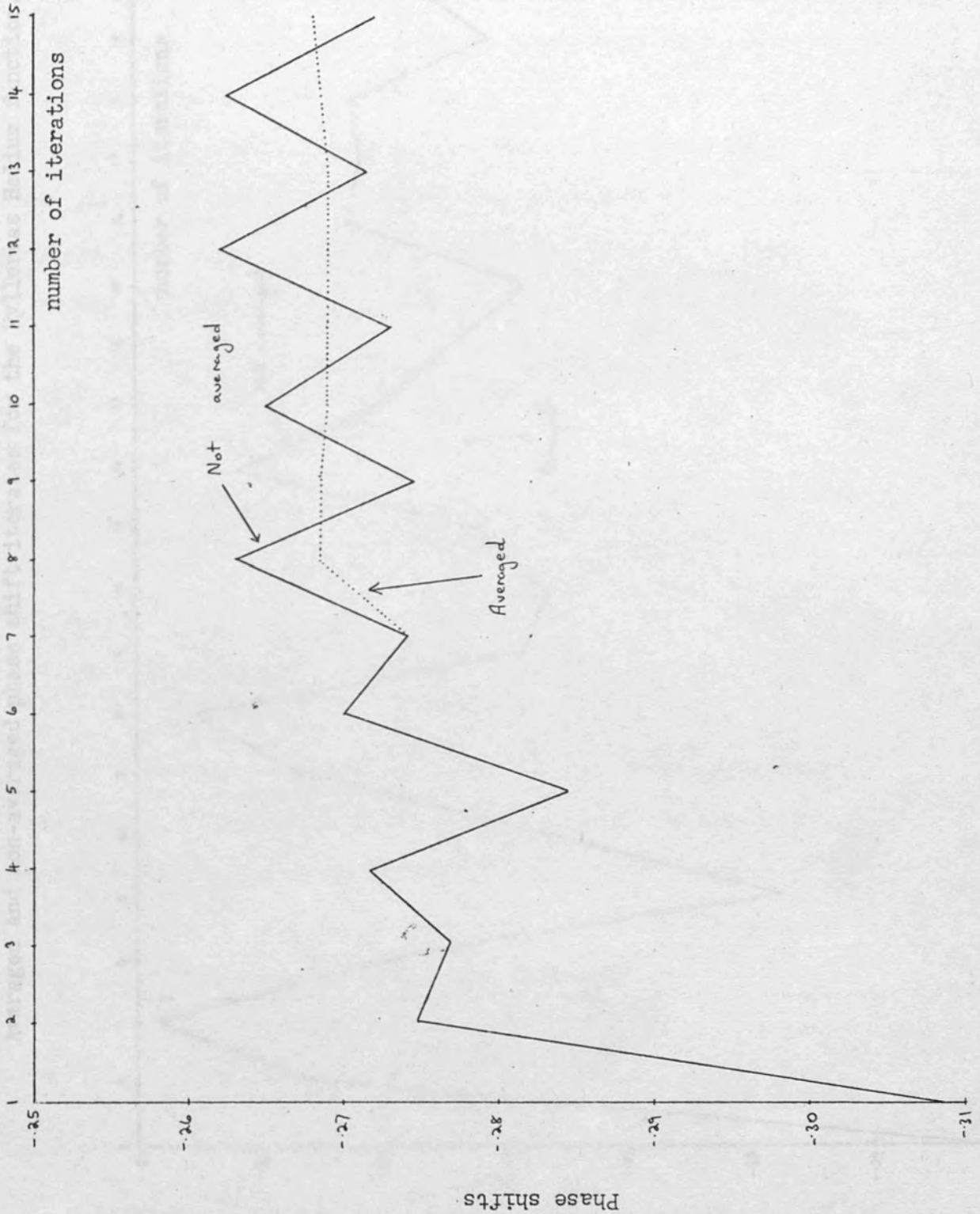
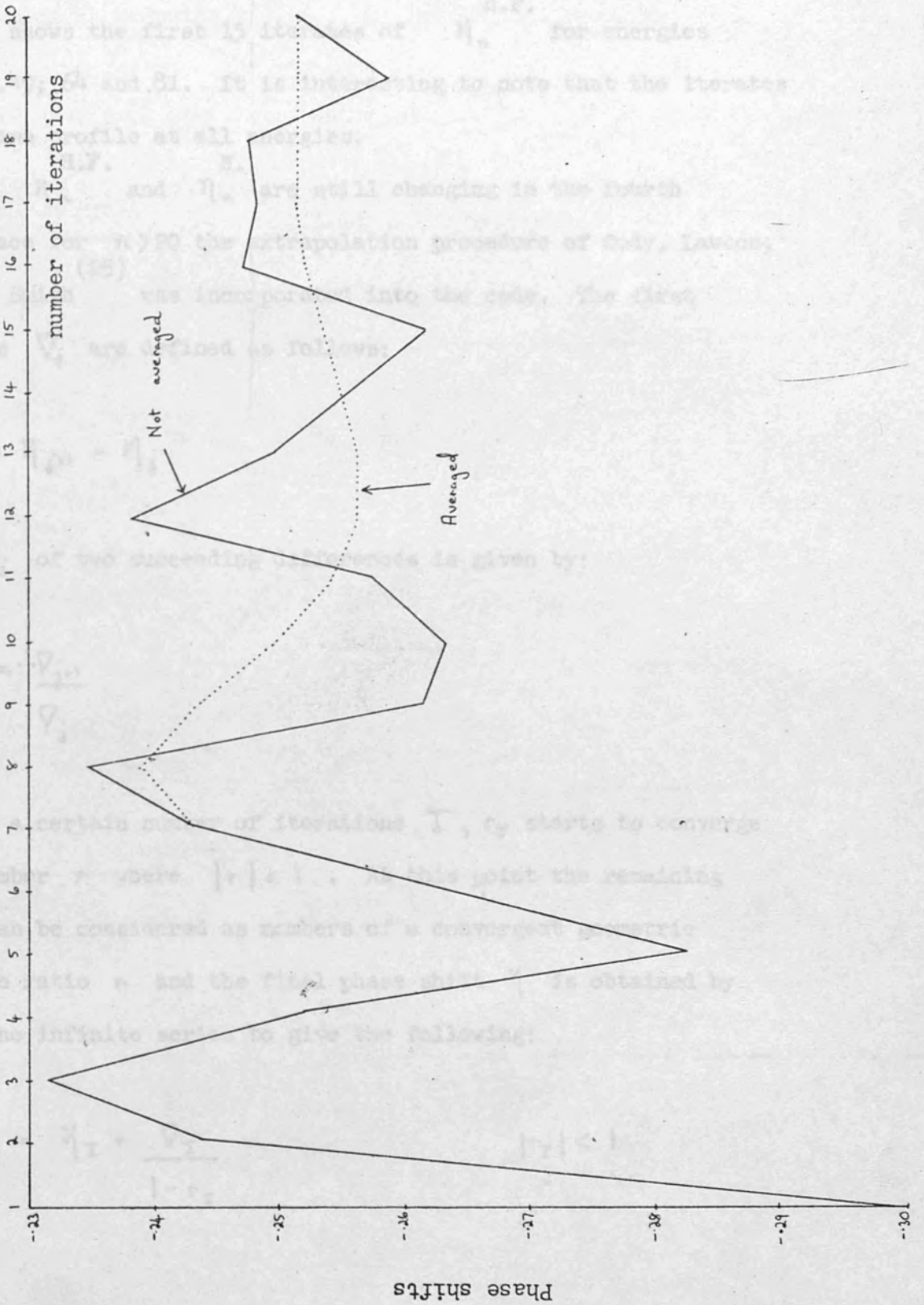


FIGURE 5-3

Averaged and non-averaged phase shift iterates for the Hylleraas Helium function.



steadily whereas η_n^H is still oscillating even after 50 iterations. Figure 5-4 shows the first 15 iterates of $\eta_n^{H.F.}$ for energies $k_1^2 = .36, .49; .64$ and $.81$. It is interesting to note that the iterates have the same profile at all energies.

Since $\eta_n^{H.F.}$ and η_n^H are still changing in the fourth decimal place for $n > 20$ the extrapolation procedure of Cody, Lawson, Massey and Smith[25] was incorporated into the code. The first differences ∇_j are defined as follows:

$$\nabla_j = \eta_{j+1} - \eta_j$$

A ratio r_j of two succeeding differences is given by:

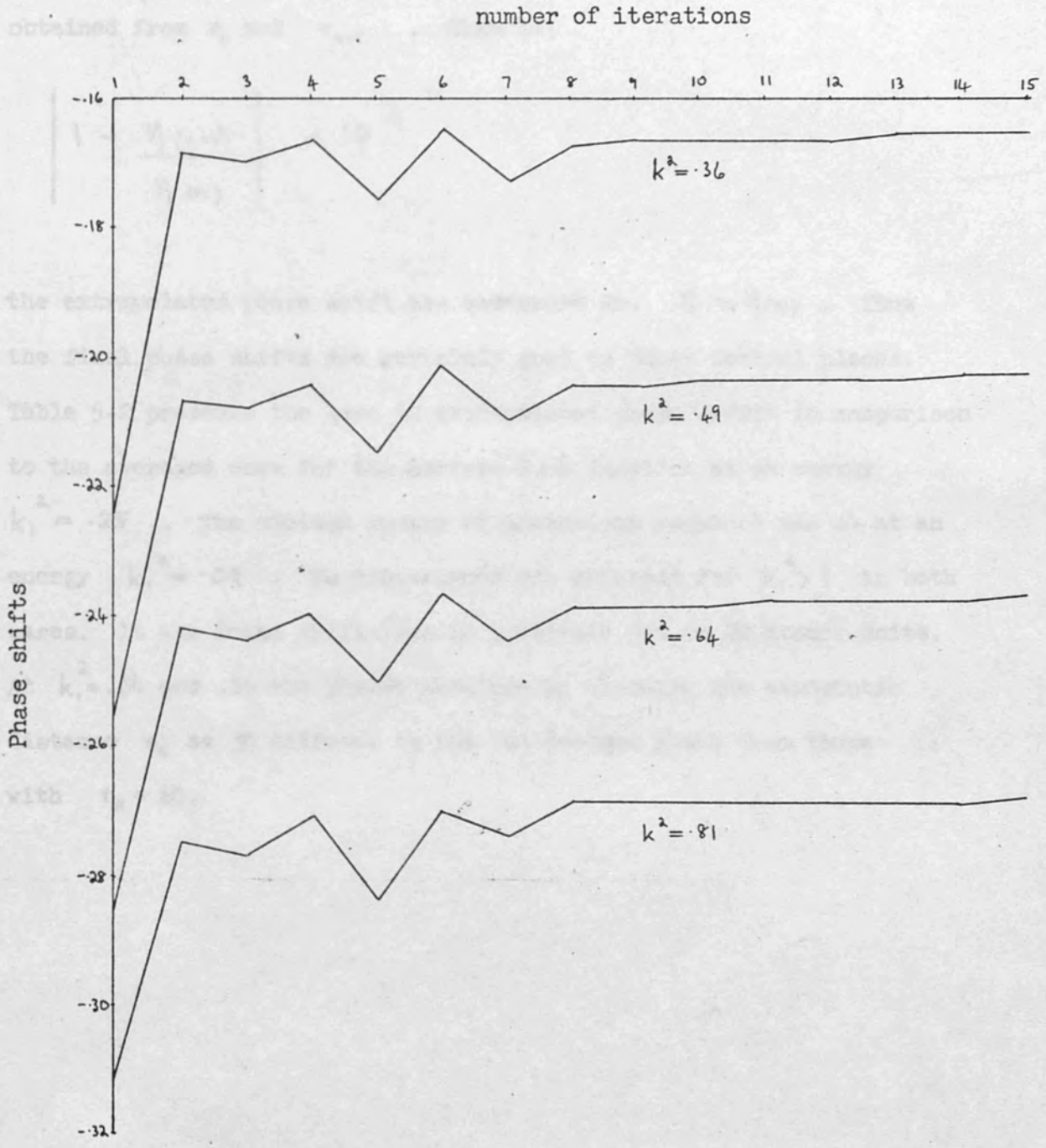
$$r_j = \frac{\nabla_{j+1}}{\nabla_j}$$

After a certain number of iterations J, r_J starts to converge to some number r where $|r| < 1$. At this point the remaining iterates can be considered as members of a convergent geometric series with ratio r and the final phase shift η is obtained by summing the infinite series to give the following:

$$\eta = \eta_J + \frac{\nabla_J}{1 - r_J} \qquad |r_J| < 1$$

FIGURE 5-4

Averaged phase shift iterates for the Hartree-Fock Helium function at energies k =.36, .49, .64 and .81 rydbergs.



Since the code can only be relied upon to give accuracy to 4 decimal places, the addition of the extrapolation procedure will reduce this further. The following convergence criterion was applied to η :

Let $\eta(n)$ and $\eta(n-1)$ be the extrapolated phase shifts obtained from r_n and r_{n-1} . Then if:

$$\left| 1 - \frac{\eta(n-1)}{\eta(n)} \right| < 10^{-4}$$

the extrapolated phase shift has converged and $\eta = \eta(n)$. Thus the final phase shifts are certainly good to three decimal places. Table 5-2 presents the last 12 extrapolated phase shifts in comparison to the averaged ones for the Hartree-Fock function at an energy $k_1^2 = .25$. The minimum number of iterations required was 14 at an energy $k_1^2 = .09$. No convergence was obtained for $k_1^2 > 1$ in both cases. It was found sufficient to integrate out to 20 atomic units. At $k_1^2 = .04$ and .16 the phases obtained by choosing the asymptotic distance r_A as 30 differed in the 7th decimal place from those with $r_A = 20$.

TABLE 5-2

Averaged and extrapolated phase shifts produced from the Hartree-Fock Helium function at an energy $k_1^2 = .25$ rydbergs.

Iteration	Averaged phase	Extrapolated phase
7	-.1329	-.1296
8	-.1281	-.1300
9	-.1280	-.1280
10	-.1278	-.1282
11	-.1276	-.1256
12	-.1274	-.1251
13	-.1272	-.1252
14	-.1270	-.1253
15	-.1269	-.1254
16	-.1267	-.1254
17	-.1266	-.1254
18	-.1265	-.1254

5.2 Results.

Phase shifts and cross sections for $0<k_1^2 \leq 1$ rydbergs were generated using both the Hartree-Fock and the Hylleraas Helium function.

(a) Mean Static Field Approximation (M.S.F.).

Table 5-3 presents the two sets of phase shifts together with those obtained by Kraidy (27) using the Hylleraas function. Figure 5-5 presents a graph of the phase shifts obtained from the Hartree-Fock function together with the Hylleraas results of Kraidy (27) when the dipole polarization term $\frac{\alpha}{r_p^2}$ was added to the M.S.F. equations. This attractive term is sufficient to make the phase shifts positive at low energies. Since the M.S.F. potential is repulsive the corresponding phase shifts are negative for all energies.

(b) Virtual Positronium Formation.

It is known that polarization in any form serves to make the atom more attractive and this is born out by the addition of virtual Positronium formation terms which can be thought of as a short-range polarization. Table 5-4 presents the two sets of phase shifts obtained here together with the Hylleraas results of Kraidy (27) and the variational results of Drachman (50). The phase shifts are plotted in Figure 5-6.

The three sets of elastic cross-sections below threhold are displayed in Table 5-5. Figure 5-7 shows Drachman's (50) variational

TABLE 5-3

S-wave phase shifts for positron-Helium scattering in the Mean Static Field Approximation.

ka_o	Hartree-Fock	Hylleraas	Hylleraas (Kraidy)
.05	-.01984	-.01908	.
.1	-.03961	-.03812	-.03815
.2	-.07875	-.07592	-.07593
.3	-.1170	-.1131	-.1131
.4	-.1538	-.1493	-.1493
.5	-.1890	-.1843	-.1843
.6	-.2222	-.2179	-.2180
.7	-.2534	-.2500	-.2500
.8	-.2823	-.2804	-.2803
.9	-.3090	-.3090	-.3089
1.0	-.3334	-.3358	-.3355

FIGURE 5-5

S-wave phase shifts in the M.S.F. approximation (Hartree-Fock) compared to a Hylleraas + dipole polarization term calculation of Kraidy[27].

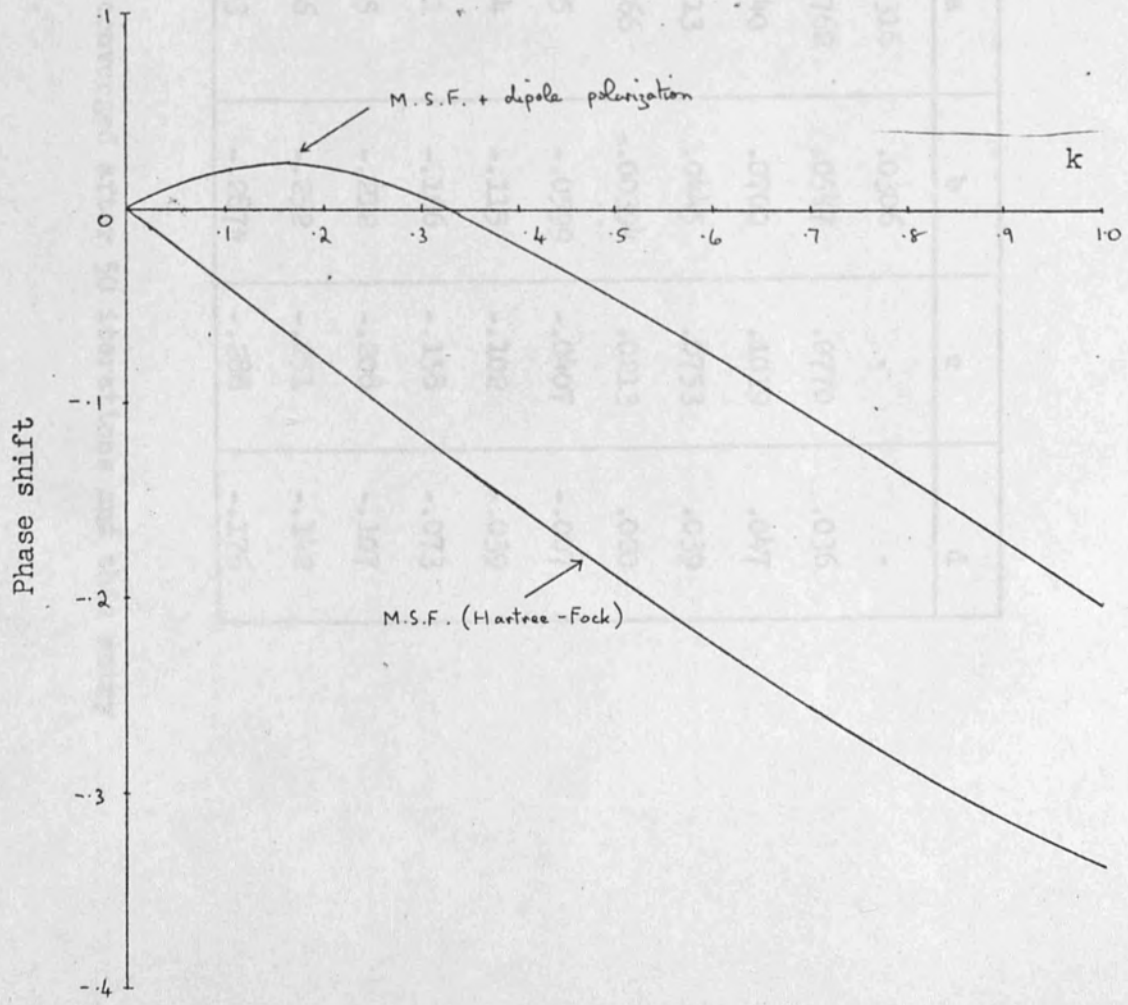


TABLE 5-4

S-wave phase shifts for positron-Helium scattering in the M.S.F. and virtual Positronium approximation. Column (a) Hartree-Fock Helium function, column (b) Hylleraas Helium function (this work); column (c) Hylleraas Helium function (Kraidy [27]), Column (d) gives Drachman's [50] variational results.

ka_0	a	b	c	d
.05	-.00316	.0306	.	.
.1	-.00762	.0547	.0770	.036
.2	-.0240	.0700	.1019	.047
.3	-.0513	.0445	.0753	.039
.4	-.0866	-.00394	.0213	.020
.5	-.125	-.0599	-.0407	-.007
.6	-.164	-.115	-.102	-.039
.7	-.201	-.166	-.158	-.073
.8	-.235	-.212	-.208	-.107
.9	-.266	-.252	-.251	-.142
1.0	-.293	-.287*	-.288	-.176

*This result had not converged after 50 iterations and this entry is an estimated value.

FIGURE 5-6

S-wave phase shifts in the virtual Positronium formation approximation.

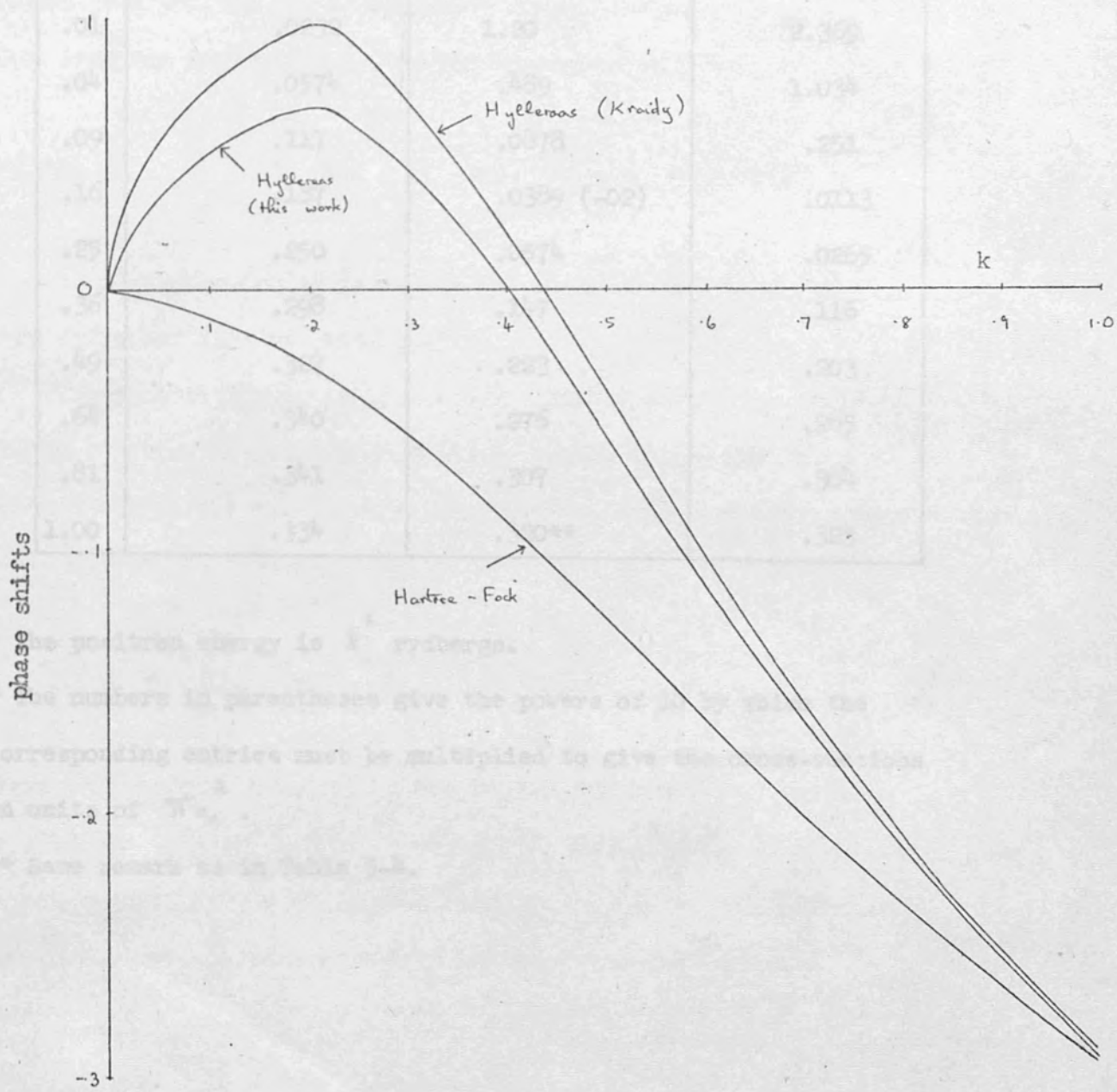


TABLE 5-5

Elastic cross-sections for positron-Helium scattering in the M.S.F. and virtual Positronium approximation. Column (a) Hartree-Fock Helium function; column (b) Hylleraas Helium function (this work); column (c) Hylleraas Helium function (Kraidy [27]).

k^2 †	a	b *	c
.01	.0232	1.20	2.369
.04	.0574	.489	1.034
.09	.117	.0878	.251
.16	.187	.0389 (-02)	.0113
.25	.250	.0574	.0265
.36	.298	.147	.116
.49	.327	.223	.203
.64	.340	.276	.265
.81	.341	.307	.304
1.00	.334	.320**	.323

† The positron energy is k^2 rydbergs.

* The numbers in parentheses give the powers of 10 by which the corresponding entries must be multiplied to give the cross-sections in units of πa_o^2.

** Same remark as in Table 5-4.

cross-sections plotted against those of this work. If there were an exact Helium function then Drachman's[50] phase shifts would be rigorous lower bounds and the Hartree-Fock results would be too small for all energies below threshold, and the Hylleraas too small for $k_1^2 > .3$ rydbergs.

It is evident that scattering results of this problem are extremely sensitive to the choice of ground state Helium function. It has been pointed out in Section 3.3. that to obtain the Hylleraas case from the Hartree-Fock code one merely substitutes:

$$C = 0 \quad , \quad a = \frac{27}{16} \qquad \text{and} \qquad E_{He} = 5.6953125$$

As a consequence of these trivial changes, we obtain the two very different sets of phase shifts.

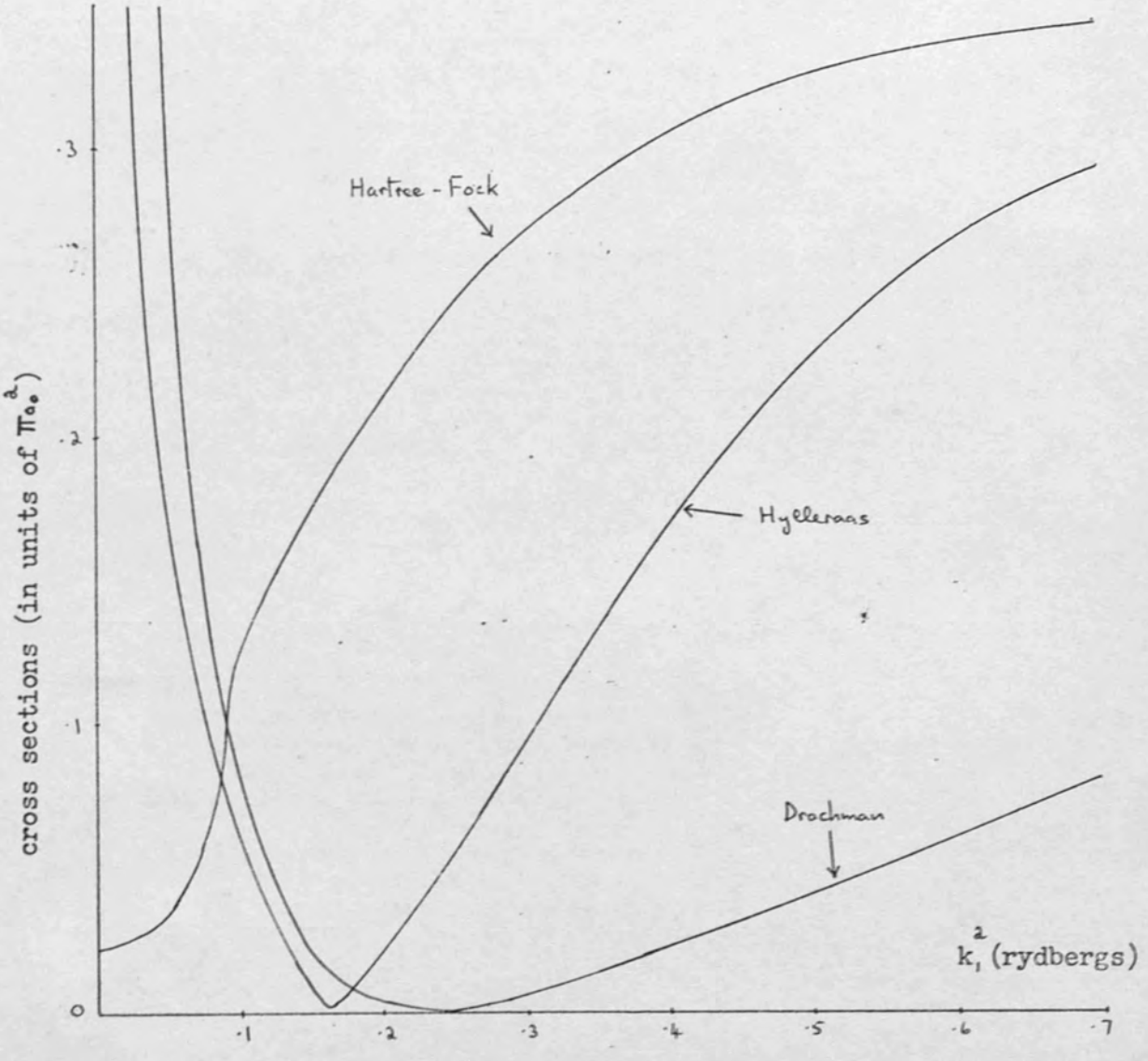
The sensitivity of the scattering results to the ground state Helium function has also been noted by Burke, Cooper and Ormonde[96] who considered the electron-Helium problem. They chose the ground-state Helium function as:

$$\Psi_0(\bar{12}) = \frac{1}{4\pi\sqrt{2}} (1 + P_{12}) \varphi_0(r_1) P_{1s}(r_2)$$

where φ_0 is the $1s$ state of the Helium ion defined by equation (2.23b) and $P_{1s}(r) = a\rho^{\frac{1}{2}} e^{-\rho r}$ where ρ is varied to minimize the total energy. It was found that allowing ρ to be less than the square root of the binding energy led to meaningless results.

FIGURE 5-7

Elastic cross-sections in the virtual Positronium formation approximation (this work) and a variational lower bound calculation (Drachman [50]).



Several ways of improving these results are described in Chapter VI. The most important of these is the addition of the 2_p states of Helium and Positronium since this will immediately introduce a large percentage of the attractive polarization effects. Short-range correlation terms are chosen so that the lower bound principle of Gailitis[41] can be applied.

CHAPTER VI

6.1 Higher Partial Waves.

Equations (2.34) define the set of coupled integro-differential equations resulting from allowing the total angular momentum to be ℓ and the Helium atom, ion and Positronium to remain in the ground state:

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + V(r) + k_1^2\right] f_\ell^{(\ell)}(r) = -\int_0^\infty d\sigma\, g_\ell^{(\sigma)} K_{12}^{(\ell)}(r,\sigma) \qquad 6.1a$$

$$\left[\frac{d^2}{d\sigma^2} - \frac{\ell(\ell+1)}{\sigma^2} + k_2^2\right] g_\ell^{(\sigma)}(\sigma) = -\int_0^\infty dr.\, f_\ell^{(\ell)}(r) K_{12}^{(\ell)}(r,\sigma) - \int_0^\infty d\sigma'.\, g_\ell^{(\sigma')}(\sigma') K_{22}^{(\ell)}(\sigma,\sigma') \qquad 6.1b$$

where $K_{12}^{(\ell)}$ and $K_{22}^{(\ell)}$ are defined by equations (2.44) and (2.52) respectively as:

$$K_{12}^{(\ell)}(r,\sigma) = \frac{64\pi}{2\ell+1}\left[S\left\{k_1^2 + 5 - E_{He} - \frac{2}{r} + \frac{2P^N(r)}{S}\right\} H_\ell^0(1)\right.$$

$$\left. + S\left\{-H_\ell^1(1) + 2H_\ell^2(1) + 4H_\ell^2(-a) - 2g_\ell^1(1) + 2H_\ell^0(a^2)\right\} - 2g_\ell^2(1)\right] \qquad 6.2a$$

$$K_{22}^{(\ell)}(r,\sigma) = \frac{1024\pi^2}{(2\ell+1)^2}(1+P_{12})\int_0^\infty dr_p\left[\left\{k_1^2 + 13 - \frac{4}{r_p} - E_{He}\right\} g_\ell^1(1) g_\ell^1(2)\right.$$

$$\left. + 4\left\{g_\ell^2(1) - g_\ell^3(1)\right\} g_\ell^1(2) - (2\ell+1)^3 \sum_{\lambda,q} \frac{\sigma_<^q}{\sigma_>^{q+1}} \frac{|C(q\ell\lambda;000)|^2}{(2\lambda+1)^2} g_\lambda^1(1) g_\lambda^1(2)\right. \qquad 6.2b$$

and all quantities are defined in Sections 2.3 and 2.4.

6.2 Correlation Terms.

(a) Derivation of the radial equations.

The total wave function for $L=0$ is now taken as:

$$\Psi(r_1, r_2, r_p) = \chi(p, \tilde{12}) \Big[\psi_0(\tilde{12}) F(p) + (1+P_{12}) \varphi_0(2) \omega(\rho_1) G(\sigma_1) + \sum_\nu C_\nu \Phi_\nu(r_1, r_2, r_p) \Big] \qquad 6.3$$

where ψ_0, φ_0 and χ are defined in Section 2.3 and Φ_ν is a correlation function. The terms of Φ_ν must vanish exponentially at large distances so that they do not contribute either to the long-range forces or to the scattered flux. Φ_ν is therefore chosen as follows:

$$\Phi_\nu(r_1, r_2, r_p) = r_p^{\,i} \left(r_{12}^{\,\ell} + \rho_1^{\,\ell} + \rho_2^{\,\ell} \right) e^{-\alpha(r_1+r_2+r_p)} (1+P_{jk}) r_1^{\,j} r_2^{\,k} \qquad 6.4$$

where P_{jk} is the operator interchanging j and k and C_ν is a variational parameter and $\nu = (i, j, k, \ell)$. The total wave function now contains terms explicitly dependent on the electron-electron and electron-positron coordinates. In order to define the number of linear parameters C_ν we introduce N:

$$N = i + j + k + \ell$$

i, j, k and ℓ are varied for N less than or equal to some specified number which in this work will be taken as four. α can

be chosen to help convergence.

Burke and Taylor (95) have shown that the phase shifts obtained from the wave function defined by equation (6.3) still satisfy a minimum principle even though the correlation terms are not orthogonal to the remaining terms. Therefore equation (6.3) is substituted into the variational principle to give the following:

$$\int \psi_0(\bar{12}) \left[H-E \right] \Psi(r_1, r_2, r_p)\, d\hat{r}_p\, d\underline{r}_1\, d\underline{r}_2 = 0 \qquad 6.5$$

$$\int \varphi_0(2)\, w(\rho_1) \left[H-E \right] \Psi(r_1, r_2, r_p)\, d\hat{\sigma}_1\, d\underline{\rho}_1\, d\underline{r}_2 = 0 \qquad 6.6$$

$$\int \Phi_\nu(r_1, r_2, r_p) \left[H-E \right] \Psi(r_1, r_2, r_p)\, d\underline{r}_1\, d\underline{r}_2\, d\underline{r}_p = 0 \qquad 6.7$$

Following the method of Appendix A equations (6.5) and (6.6) reduce to:

$$\left[\frac{d^2}{dr_p^2} + V_1(r_p) + k_1^2 \right] f(r_p) = - \int_0^\infty d\sigma_1\, g(\sigma_1)\, K_{12}(r_p, \sigma_1) + r_p \sum_\nu C_\nu \int \psi_0(\bar{12}) \left[H-E \right] \Phi_\nu\, d\hat{r}_p\, d\underline{r}_1\, d\underline{r}_2 \qquad 6.8$$

$$\left[\frac{d^2}{d\sigma_1^2} + k_1^2 \right] g(\sigma_1) = - \int_0^\infty dr_p\, f(r_p)\, K_{12}(r_p, \sigma_1) - \int_0^\infty d\sigma_2\, g(\sigma_2)\, K_{22}(\sigma_1, \sigma_2) + 2\sigma_1 \sum_\nu C_\nu \int \varphi_0(2)\, w(\rho_1) \left[H-E \right] \Phi_\nu\, d\hat{\sigma}_1\, d\underline{\rho}_1\, d\underline{r}_2 \qquad 6.9$$

Green's Theorem can be applied to equation (6.7) to give:

$$\int \Psi\,(r_1, r_2, r_p)\,[H-E]\;\Phi_\nu(r_1, r_2, r_p)$$

$$= \int dr_p\, f(r_p)\, p_\nu(r_p) + \int d\sigma_1\, g(\sigma_1)\, q_\nu(\sigma_1) + \sum_\mu C_\mu N_{\mu\nu} \qquad 6.10$$

where $$p_\nu(r_p) = \frac{r_p}{\sqrt{4\pi}} \int \psi_0(\bar{12})\,[H-E]\;\Phi_\nu\, d\hat{r}_p\, d\underline{r}_1\, d\underline{r}_2 \qquad 6.11a$$

$$q_\nu(\sigma_1) = \frac{2\sigma_1}{\sqrt{4\pi}} \int \psi_0(2)\,\omega(\rho_1)\,[H-E]\;\Phi_\nu\, d\hat{r}_1\, d\underline{r}_2\, d\rho_1 \qquad 6.11b$$

$$N_{\mu\nu} = \int \Phi_\nu\,[H-E]\,\Phi_\nu\, d\underline{r}_1\, d\underline{r}_2\, d\underline{r}_p \qquad 6.11c$$

From equation (6.10) we obtain:

$$C_\nu = -\sum_\mu M_{\nu\mu} \qquad 6.12a$$

where $$M_{\nu\mu} = (N^{-1})_{\nu\mu}\left[\int dr_p\, f(r_p)\, p_\nu(r_p) + \int d\sigma_1\, g(\sigma_1)\, q_\nu(\sigma_1)\right] \qquad 6.12b$$

Substituting equation (6.12a) into equations (6.8) and (6.9) produces the following system of integro-differential equations:

$$\left[\frac{d^2}{dr_p^2} + V_1(r_p) + k_1^2\right] f(r_p) = -\int_0^\infty d\sigma_1\, g(\sigma_1)\, K_{12}(r_p, \sigma_1)$$

$$-\sqrt{4\pi} \sum M_{\nu\mu}\, p_\nu(r_p) \qquad 6.13a$$

$$\left[\frac{d^2}{d\sigma_1^2}+k_2^2\right] g(\sigma_1) \quad - \int_0^\infty d\tau_\rho \, f(\tau_\rho) K_{12}(\tau_\rho, \sigma_1) - \int_0^\infty d\sigma_2 \, g(\sigma_2) K_{22}(\sigma_1, \sigma_2)$$

$$= \sqrt{4\pi} \sum_{\nu\mu} M_{\nu\mu} \, q_\nu(\sigma_1) \qquad 6.13b$$

(a) Simplification of $\not{p}_\nu$

A superscript ℓ will be affixed to Φ_ν and $\not{p}_\nu$ to denote which value of ℓ is under consideration. In this work ℓ will take the values 0, 1 and 2. Thus:

$$\Phi_\nu^0 = 3 X(\tau_\rho) Z(\tau_1, \tau_2) \qquad 6.14a$$

$$\Phi_\nu^1 = (\rho_1 + \rho_2 + \tau_{12}) X(\tau_\rho) Z(\tau_1, \tau_2) \qquad 6.14b$$

$$\Phi_\nu^2 = (\rho_1^2 + \rho_2^2 + \tau_{12}^2) X(\tau_\rho) Z(\tau_1, \tau_2) \qquad 6.14c$$

where $X(\tau_\rho) = \tau_\rho^i e^{-\alpha\tau_\rho}$

and $Z(\tau_1, \tau_2) = e^{-\alpha(\tau_1+\tau_2)} (1+\rho_{jk}) \tau_1^j \tau_2^k$

The expressions for $\not{p}_\nu^\ell$ can be simplified by use of the following formulae:

$$\int_0^{\tau_2} \tau^p e^{-q\tau} d\tau = \frac{p!}{q^{p+1}} - p! e^{-q\tau_2} \sum_{m=0}^{p} \frac{\tau_2^{p-m}}{(p-m)! \, q^{m+1}} \qquad 6.15a$$

$$\int_{r_2}^{\infty} r^p e^{-qr}\,dr = p!\,e^{-qr_2}\sum_{m=0}^{p}\frac{r_2^{\,p-m}}{(p-m)!\,q^{m+1}} \qquad 6.15b$$

After much detailed calculation, expressions for p_v^{ℓ} are obtained as follows:

$$p_v^{0}(r_p) = 3N^2 r_p (4\pi)^{\frac{3}{2}} X(r_p)\Bigg[2A^{j+3}A^{k+3}\left\{\frac{(i+1)}{r_p}\left(2\alpha-\frac{i}{r_p}\right) - 3\alpha^2 - E\right\}$$

$$+ (1+P_{jk})\Big\{ 2A^{j+2}A^{k+3}\left(2\alpha(j+1)-3\right) - 2j(j+1)\,A^{j+1}A^{k+3}$$

$$+ 4A^{k+3}(j+1)!\,r_p^{j+1}\sum_{m=1}^{j+1}\frac{m r_p^{-m}}{(j+2-m)!}\left[\frac{e^{-(a+\alpha)r_p}}{(a+\alpha)^{m+1}} + \frac{C e^{-(b+\alpha)r_p}}{(b+\alpha)^{m+1}}\right]$$

$$- \frac{(j+1)!}{2^{k+j+3}}\sum_{m\,1}^{j+2}\frac{m(k+j+3-m)!}{(j+2-m)!}\left[\frac{2^m}{(a+\alpha)^{k+j+5}} + \frac{2^m C^2}{(b+\alpha)^{k+j+5}} + \frac{2^{k+j+4} C\,B^{m+1}}{(a+b+2\alpha)^{k+j+4-m}}\right]\Big\}\Bigg] \qquad 6.16$$

where $$A^p = (p-1)!\left\{\frac{1}{(a+\alpha)^p} + \frac{C}{(b+\alpha)^p}\right\} \qquad 6.17a$$

and $$B^p = \left\{\frac{1}{(a+\alpha)^p} + \frac{1}{(b+\alpha)^p}\right\} \qquad 6.17b$$

$$p_v^{1}(r_p) = N^2(4\pi)^{\frac{3}{2}} r_p\, X(r_p)(1+P_{jk})\Bigg[4A^{j+3}A^{k+3}\left\{\alpha - 1 - \frac{(6+3i+3j+k)}{3r_p}\right\}$$

$$+ 8A^{j+3}A^{k+4}\frac{(\alpha-1)}{3r_p} + 4A^{j+3}A^{k+2}\left(r_p - 1 - \frac{j+k}{3}\right)$$

$$+\frac{4}{3r_p^2}A^{j+3}A^{k+5}\left(\frac{i}{r_p}-\alpha-1\right)-\frac{4}{3r_p}A^{j+5}A^{k+2}+\frac{8\alpha}{3}A^{j+4}A^{k+2}$$

$$+\frac{2A^{k+3}}{3}\Bigg\{-2(2\alpha+1)(j+3)!\sum_{m=0}^{j+3}\frac{D^{j+2-m}}{(j+3-m)!}+2(6+3i+j+k)(j+2)!\sum_{m=0}^{j+2}\frac{D^{j+1-m}}{(j+2-m)!}$$

$$-2i(j+4)!\sum_{m=0}^{j+4}\frac{D^{j+1-m}}{(j+4-m)!}+2(\alpha+1)(j+4)!\sum_{m=0}^{j+4}\frac{D^{j+2-m}}{(j+4-m)!}$$

$$-(4i+3j+3k+12)(j+1)!\sum_{m=0}^{j+1}\frac{D^{j+1-m}}{(j+1-m)!}+2(2\alpha-7)\sum_{m=0}^{j+1}\frac{D^{j+2-m}}{(j+1-m)!}$$

$$+(j+k)(j-1)!\sum_{m=0}^{j-1}\frac{D^{j+1-m}}{(j+1-m)!}+2(1-\alpha)j!\sum_{m=0}^{j}\frac{D^{j+2-m}}{(j-m)!}$$

$$+12(j+2)\sum_{m=0}^{j+2}\frac{D^{j+2-m}}{(j+2-m)!}+2(j+4)!\sum_{m=0}^{j+4}\frac{D^{j+2-m}}{(j+4-m)!}\Bigg\}$$

$$+\frac{4}{3}A^{k+5}\Bigg\{(j+2)!\sum_{m=0}^{j+2}\frac{D^{j-m}}{(j+2-m)!}-j!\sum_{m=0}^{j}\frac{D^{j-m}}{(j-m)!}\Bigg\}$$

$$+4\alpha(j+2)!\sum_{m=0}^{j+2}\frac{E^{k+j+5-m}}{(j+2-m)!}+\frac{4}{3}(j+k+3-r_p)(j+2)!\sum_{m=0}^{j+2}\frac{E^{k+j+4-m}}{(j+2-m)!}$$

$$-\frac{8}{3r_p}(j+2)!\sum_{m=0}^{j+2}\frac{E^{k+j+6-m}}{(j+2-m)!}+2(2r_p-2-j-k)(j+1)!\sum_{m=0}^{j+1}\frac{E^{k+j+4-m}}{(j+1-m)!}$$

$$+\frac{4}{3r_p}(j+4)!\sum_{m=0}^{j+1}\frac{E^{k+j+6-m}}{(j+4-m)!}-\frac{4\alpha}{3}j!\sum_{m=0}^{j}\frac{E^{k+j+5-m}}{(j-m)!}$$

$$+\frac{2}{3}(j+k)(j-1)!\sum_{m=0}^{j-1}\frac{E^{k+j+4-m}}{(j-1-m)!}-\frac{8\alpha}{3}(j+3)!\sum_{m=0}^{j+3}\frac{E^{k+j+5-m}}{(j+3-m)!}$$

$$-\frac{4}{r_p}(j+3)!\sum_{m=0}^{j+3}\frac{E^{k+j+6-m}}{(j+3-m)!}-4(j+2)!\sum_{r=0}^{j+2}\frac{D^{j+2-r}}{(j+2-r)!}\Bigg\{$$

$$\frac{(k+4)!}{3}\sum_{m=0}^{k+4}\frac{D^{k+2-m}}{(k+4-m)!}+(k+2)!\sum_{m=0}^{k+2}\frac{D^{k+2-m}}{(k+2-m)!}$$

$$-\frac{(k+1)!}{3}\sum_{m=0}^{k+1}\frac{D^{k+2-m}}{(k+1-m)!}-(k+3)!\sum_{m=0}^{k+3}\frac{D^{k+2-m}}{(k+3-m)!}\Bigg\}$$

$$+4(j+1)!\sum_{r=0}^{j+1}\frac{D^{j+1-r}}{(j+1-r)!}\Bigg\{\frac{(k+4)!}{3}\sum_{m=0}^{k+4}\frac{D^{k+3-m}}{(k+4-m)!}+(k+2)!\sum_{m=0}^{k+2}\frac{D^{k+3-m}}{(k+2-m)!}$$

$$-\frac{(k+1)!}{3}\sum_{m=0}^{k+1}\frac{D^{k+3-m}}{(k+1-m)!}-(k+3)!\sum_{m=0}^{k+3}\frac{D^{k+3-m}}{(k+3-m)!}\Bigg\}$$

$$-\frac{8}{3r_p^2}(k+2)!\sum_{m=0}^{k+2}\frac{(k+j+5-m)!}{(k+2-m)!}\sum_{r=0}^{k+j+5-m}F^{k+j+6-m-r}$$

$$+4(k+2)!\sum_{m=0}^{k+2}\frac{(k+j+3-m)!}{(k+2-m)!}\sum_{r=0}^{k+j+3-m}F^{k+j+4-m-r}$$

$$
\begin{aligned}
&-\frac{4r_p}{3}(k+2)!\sum_{m=0}^{k+2}\frac{(k+j+2-m)!}{(k+2-m)!}\sum_{r=0}^{k+j+2-m}F^{k+j+3-m-r}\\
&-4(k+1)!\sum_{m=0}^{k+1}\frac{(k+j+3-m)!}{(k+1-m)!}\sum_{r=0}^{k+j+3-m}F^{k+j+4-m-r}\\
&+\frac{4r_p}{3}(k+1)!\sum_{m=0}^{k+1}\frac{(k+j+2-m)!}{(k+1-m)!}\sum_{r=0}^{k+j+2-m}F^{k+j+3-m-r}\\
&+\frac{8}{3r_p}(k+1)!\sum_{m=0}^{k+1}\frac{(k+j+4-m)!}{(k+1-m)!}\sum_{r=0}^{k+j+4-m}F^{k+j+5-m-r}\\
&+\frac{4}{r_p^2}(k+3)!\sum_{m=0}^{k+3}\frac{(k+j+5-m)!}{(k+3-m)!}\sum_{r=0}^{k+j+5-m}F^{k+j+6-m-r}\\
&-\frac{4}{r_p}(k+3)!\sum_{m=0}^{k+3}\frac{(k+j+4-m)!}{(k+3-m)!}\sum_{r=0}^{k+j+4-m}F^{k+j+5-m-r}\\
&-\frac{4}{3r_p^2}(k+4)!\sum_{m=0}^{k+4}\frac{(k+j+5-m)!}{(k+4-m)!}\sum_{r=0}^{k+j+5-m}F^{k+j+6-m-r}\\
&+\frac{4}{3r_p}(k+1)!\sum_{m=0}^{k+4}\frac{(k+j+4-m)!}{(k+4-m)!}\sum_{r=0}^{k+j+4-m}F^{k+j+5-m-r}\Bigg]
\end{aligned}
\qquad 6.18
$$

where: $$D^{j+n-m} = D^{j+n-m}(r_p) = r_p^{\,j+n-m}\left[\frac{e^{-(a+\alpha)r_p}}{(a+\alpha)^{m+1}} + \frac{Ce^{-(b+\alpha)r_p}}{(b+\alpha)^{m+1}}\right] \qquad 6.19a$$

$$E^{k+j+n-m} = E^{k+j+n-m}_{(r_p)} = (k+j+n-m-1)!\left[\frac{1}{(a+\alpha)^{m+1}\left[2(a+\alpha)\right]^{k+j+n-m}}\right.$$

$$\left.+\frac{C^2}{(b+\alpha)^{m+1}\left[2(b+\alpha)\right]^{k+j+n-m}} + \frac{C.B^{m+1}}{(a+b+2\alpha)^{k+j+n-m}}\right] \qquad 6.19b$$

$$F^{k+j+n-m} = F^{k+j+n-m}_{(r_p)} = r_p^{k+j+n-m}\frac{E^{k+j+n-m}}{\left[(k+j+n-m-1)!\right]^2} \qquad 6.19c$$

$$P_v^2(r_p) = \frac{9}{2}(4\pi)^{\frac{3}{2}} N^2 r_p X(r_p) A^{j+3} A^{k+3}\left[-r_p^2(E+3\alpha^2)\right.$$

$$\left.+2\alpha r_p(i+3) - i(i+5) - j(j+5) - k(k+5) - 18\right]$$

$$+(4\pi)^{\frac{3}{2}} N^2 r_p X(r_p)(1+P_{jk})\left[4A^{j+3}A^{k+5}\left\{\frac{2}{r_p}\left[2+\alpha(i+1)\right]\right.\right.$$

$$\left.\left.-\frac{i(i+1)}{r_p^2} - E - 3\alpha^2\right\} + 4A^{j+3}A^{k+4}\left\{\alpha(k+j+6)-3\right\}\right.$$

$$+4r_p^2 A^{j+3}A^{k+2}\left\{\alpha(k+j+2)-3\right\}$$

$$-2A^{k+1}\left(r_p^2 A^{j+3} + A^{j+5}\right)\left\{j(j+1)+k(k+1)\right\} + 4A^{j+5}A^{k+2}\left\{\alpha(j+k+2)\right.$$

$$\left.-\frac{10}{3}\right\} + 8A^{k+3}\left\{(j+2)!\sum_{m=0}^{j+2}\frac{D^{j+3-m}}{(j+2-m)!}\right.$$

$$+\frac{2}{3}(j+4)!\sum_{m=0}^{j+4}\frac{D^{j+3-m}}{(j+4-m)!}-\frac{2}{3}(j+1)!\sum_{m=0}^{j+1}\frac{D^{j+3-m}}{(j+3-m)!}$$

$$-(j+3)!\sum_{m=0}^{j+3}\frac{D^{j+3-m}}{(j+3-m)!}\Bigg\}+8A^{k+5}(j+1)!\sum_{m=1}^{j+2}\frac{m\,D^{j+1-m}}{(j+2-m)!}$$

$$+4(j+2)!\sum_{m=1}^{j+3}\frac{m\,E^{k+j+6-m}}{(j+3-m)!}-4r_p^2(j+1)!\sum_{m=1}^{j+2}\frac{m\,E^{k+j+4-m}}{(j+2-m)!}$$

$$+\frac{8}{3}(j+1)!\sum_{m=0}^{j+1}\frac{E^{k+j+6-m}}{(j+1-m)!}-\frac{8}{3}(j+4)!\sum_{m=0}^{j+4}\frac{E^{k+j+6-m}}{(j+4-m)!}\Bigg] \qquad 6.20$$

It can be seen that p_ν' is the most complicated of the three expressions and this is on account of the factors ρ_1, ρ_2 and r_{12} appearing linearly.

(b) Simplification of q_ν.

q_ν is more complicated than p_ν because of the coordinate system $(\underline{\sigma}_1, \underline{\rho}_1, \underline{r}_2)$ which will be changed to $(\underline{\sigma}_1, \underline{\sigma}_2, \underline{r}_p)$ as was done for the second kernel K_{22}. The three expressions are as follows:

$$q_\nu^0(\sigma_1) = 3(16)^3\pi^{\frac{3}{2}}(1+P_{jk})\int d\sigma_2\, dr_p\, r_p\, X(r_p)\,\sigma_1\sigma_2^2\Bigg[\mathcal{L}_0^k(2)\mathcal{M}_0^j(1)\Big\{E$$

$$-3\alpha^2+\frac{4}{r_p}+\frac{1}{r_p}\left(2\alpha-\frac{i}{r_p}\right)(i+1)\Big\}+\mathcal{L}_0^k(2)\mathcal{M}_0^{j-1}(1)\{2\alpha(j+1)-4\}-\mathcal{L}_0^k(2)\mathcal{M}_0^{j-2}(1)\,j(j+1)$$

$$+\mathcal{L}_0^{k-1}(2)\mathcal{M}_0^j(1)\{2\alpha(k+1)-4\}-k(k+1)\mathcal{L}_0^{k-2}(2)\mathcal{M}_0^j(1)-\mathcal{L}_0^k(2)\sum_\lambda\frac{\mathcal{M}_\lambda^j(1)}{2\lambda+1}\cdot\gamma_\lambda$$

$$-\mathcal{M}_0^j(2)\sum_\lambda\frac{\mathcal{L}_\lambda^k(1)}{2\lambda+1}\cdot\gamma_\lambda'+\sum_\lambda\frac{\mathcal{L}_\lambda^k(2)\mathcal{M}_\lambda^j(1)}{(2\lambda+1)^2}\cdot\gamma_\lambda''\Bigg] \qquad 6.21$$

where $$\mathcal{L}_\lambda^k(1) = \mathcal{L}_\lambda^k(\sigma_1, r_p) = \frac{2\lambda+1}{2}\int_{-1}^{+1} r_1^k e^{-\alpha r_1} P_\lambda(\eta)\, d\eta \qquad 6.22a$$

and $$\mathcal{M}_\lambda^k(1) = \mathcal{M}_\lambda^k(\sigma_1, r_p) = \frac{2\lambda+1}{2}\int_{-1}^{+1} r_1^k e^{-\alpha r_1 - \beta r_2} P_\lambda(\eta)\, d\eta \qquad 6.22b$$

where $\eta = \hat{\sigma}_1 \cdot \hat{r}_p$.

$\gamma_\lambda = \dfrac{r_<^\lambda}{r_>^{\lambda+1}}$ where $r_<$ is the smaller of σ_1 and r_p and $r_>$ is the greater. γ_λ' and γ_λ'' are defined similarly except that σ_1 and r_p are replaced by σ_2 and r_p, σ_1 and σ_2 respectively.

$$q_\nu^i(\sigma_1) = 64\pi^{\frac{3}{2}} \sigma_1 \int d\sigma_2\, dr_p\, \sigma_2^2\, r_p^{i+2}\, e^{-\alpha r_p} (1+P_{jk}) \Big[$$

$$\left(\frac{4}{r_p} - E - 3\alpha^2 + \frac{2\alpha(i+1)}{r_p} - \frac{i(i+1)}{r_p^2}\right) \Big\{ \mathcal{N}_o^j(1)\, \mathcal{L}_o^k(2)$$

$$+ \mathcal{M}_o^j(1)\, \varphi_o^k(2) + 2\mathcal{M}_o^j(1)\, \mathcal{L}_o^k(2) \cdot A(\sigma_1, \sigma_2) + 2\sum_{\lambda=1}^{\infty} B_\lambda^{jk} \Big\}$$

$$+ 2\{\alpha(j+1) - 2\} \Big\{ \mathcal{N}_o^{j-1}(1)\, \mathcal{L}_o^k(2) + \mathcal{M}_o^{j-1}(1)\, \varphi_o^k(2)$$

$$+ 2\mathcal{M}_o^{j-1}(1)\, \mathcal{L}_o^k(2) \cdot A(\sigma_1, \sigma_2) + 2\sum_{\lambda=1}^{\infty} B_\lambda^{j-1,k} \Big\}$$

$$+ 2\{\alpha(k+1)-2\}\{ N_0^{j}(1)\, L_0^{k-1}(2) + M_0^{j}(1)\, \varphi_0^{k-1}(2)$$

$$+ 2 M_0^{j}(1)\, L_0^{k-1}(2).A(\sigma_1,\sigma_2) + 2\sum_{\lambda=1}^{\infty} B_\lambda^{j,k-1}\Big\}$$

$$- j(j+1)\Big\{ N_0^{j-2}(1)\, L_0^{k}(2) + M_0^{j-2}(1)\, \varphi_0^{k}(2) + 2 M_0^{j-2}(1)\, L_0^{k}(2) A(\sigma_1,\sigma_2)$$

$$+ 2\sum_{\lambda=1}^{\infty} B_\lambda^{j-2,k}\Big\} - k(k+1)\Big\{ N_0^{j}(1)\, L_0^{k-2}(2) + M_0^{j}(1)\, \varphi_0^{k-2}(2)$$

$$+ 2 M_0^{j}(1)\, L_0^{k-2}(2) A(\sigma_1,\sigma_2) - 2 M_0^{j}(1)\, L_0^{k}(2) - 2 R_0^{j}(1)\, \varphi_0^{k}(2)$$

$$- 4 R_0^{j}(1)\, L_0^{k}(2).A(\sigma_1,\sigma_2) - 4\sum_{\lambda=1}^{\infty} C_\lambda^{jk}$$

$$- 2 S_0^{k}(1)\Big\{ N_0^{j}(2) + 2 M_0^{j}(2).A(\sigma_1,\sigma_2)\Big\} - 4\sum_{\lambda=1}^{\infty} D_\lambda^{jk}$$

$$- 4\left(R_0^{j}(1)\, L_0^{k}(2) + M_0^{j}(1)\, S_0^{k}(2)\right) - 4(i-\alpha r_p)\left(R_0^{j}(1)\, L_0^{k}(2)\right.$$

$$\left. + M_0^{j}(1)\, S_0^{k}(2)\right) - 4j\left(2\sigma_1^2 + r_p^2\right) R_0^{j-2}(1)\, L_0^{k}(2)$$

$$- 4\alpha\left(2\sigma_1^2 + r_p^2\right) R_0^{j-1}(1)\, L_0^{k}(2) - 4k\left(2\sigma_2^2 + r_p^2\right) M_0^{j}(1)\, S_0^{k-2}(2)$$

$$+ 4\alpha\left(2\sigma_2^2 + r_p^2\right) M_0^{j}(1)\, S_0^{k-1}(2) + \sum_{\lambda=0}^{\infty} \gamma_\lambda^{*}\left[\frac{N_\lambda^{j}(1) L_\lambda^{k}(2) + M_\lambda^{j}(1)\varphi_\lambda^{k}(2)}{(2\lambda+1)^2}\right.$$

$$- \frac{2 M_\lambda^{j}(1)\, L_\lambda^{k}(2)}{(2\lambda+1)^2} \qquad - \frac{4\sigma_1^2\left\{j M_\lambda^{j-2}(1) - \alpha M_\lambda^{j-1}(1)\right\} L_\lambda^{k}(2)}{(2\lambda+1)^2}$$

$$- 4\sigma_2^2 \left\{ \frac{k\, \mathcal{L}_\lambda^{k-2}(1) - \alpha\, \mathcal{L}_\lambda^{k-1}(1)}{(2\lambda+1)^2} M_\lambda^j(2) \right\} \Bigg]$$

$$- \frac{4}{3}\sigma_1 \gamma_0'' \Bigg[\left\{ \left(\alpha - \frac{i}{r_p}\right) R_1^j(1) + 3\alpha r_p R_1^{j-1}(1) - 3j r_p R_1^{j-2}(1) \right\} \mathcal{L}_0^k(2)$$

$$+ \frac{r_p}{2} \left\{ \left(\alpha M_1^{j-1}(1) - j M_1^{j-2}(1)\right) \mathcal{L}_0^k(2) + \left(k \mathcal{L}_0^{k-2}(1) - \alpha \mathcal{L}_0^{k-1}(1)\right) M_1^j(2) \right\} \Bigg]$$

$$- \frac{4\sigma_2 \gamma_0''}{3} \Bigg[\left\{ \left(\alpha - \frac{i}{r_p}\right) S_1^k(1) + 3\alpha r_p S_1^{k-1}(1) - 3k r_p S_1^{k-2}(1) \right\} M_0^j(2)$$

$$+ \frac{r_p}{2} \left\{ \left(\alpha \mathcal{L}_1^{k-1}(1) - k \mathcal{L}_1^{k-2}(1)\right) M_0^j(2) + \left(j M_0^{j-2}(1) - \alpha M_0^{j-1}(1)\right) \mathcal{L}_1^k(2) \right\} \Bigg]$$

$$- \frac{4}{9}\sigma_1\sigma_2 \gamma_0'' \left\{ \left(\alpha M_1^{j-1}(1) - j M_1^{j-2}(1)\right) \mathcal{L}_1^k(2) \right.$$

$$\left. + \left(\alpha \mathcal{L}_1^{k-1}(1) - k \mathcal{L}_1^{k-2}(1)\right) M_1^j(2) \right\} - 4\sigma_1 r_p \sum_{\lambda=1}^{\infty} \frac{\gamma_{\lambda-1}''}{2\lambda+1} \left\{ \right.$$

$$\left(\frac{\alpha}{r_p} - \frac{i}{r_p^2} \right) R_\lambda^j(1) + 3\alpha R_\lambda^{j-1}(1) - 3j R_\lambda^{j-2}(1) \Big\} \left\{ \frac{\mathcal{L}_{\lambda+1}^k(2)}{(2\lambda+3)} \cdot \frac{\sigma_c^2}{\sigma_>^2} \right.$$

$$\left. + \frac{\mathcal{L}_\lambda^k(2)}{(2\lambda+1)} \cdot \frac{\sigma_c}{\sigma_>} + \frac{\mathcal{L}_{\lambda-1}^k}{(2\lambda-1)} \right\} - 4\sigma_2 r_p \sum_{\lambda=1}^{\infty} \frac{\gamma_{\lambda-1}''}{2\lambda+1} \left\{ \right.$$

$$\left\{ \left(\frac{\alpha}{r_p} - \frac{i}{r_p}_2 \right) S_\lambda^k(1) + 3\alpha S_\lambda^{k-1}(1) - 3k S_\lambda^{k-2}(1) \right\} \Bigg\{$$

$$\frac{M_{\lambda+1}^{j}(2)}{(2\lambda+3)} \cdot \frac{\sigma_<^2}{\sigma_>^2} + \frac{M_\lambda^{j}(2)}{(2\lambda+1)} \cdot \frac{\sigma_<}{\sigma_>} + \frac{M_{\lambda-1}^{j}(2)}{(2\lambda-1)} \Bigg\}$$

$$- 4\sigma_1\sigma_2 \sum_{\lambda 1}^{\infty} \frac{\gamma''_{\lambda-1}}{(2\lambda+1)^2} \left\{ \left(\alpha M_\lambda^{j-1}(1) - j M_\lambda^{j-2}(1) \right) \mathcal{L}_\lambda^k(2) \right.$$

$$\left. + M_\lambda^{j}(1) \left(\alpha \mathcal{L}_\lambda^{k-1}(2) - k \mathcal{L}_\lambda^{k-2}(2) \right) \right\} \left(\frac{\sigma_<^2}{\sigma_>^2} + \frac{\sigma_<}{\sigma_>} + 1 \right) \Bigg] \qquad 6.23$$

where $\mathcal{L}_\lambda^k$ and M_λ^k are defined in eqations (6.22).

$$N_\lambda^k(1) = N_\lambda^k(\sigma_1, r_p) = \frac{2\lambda+1}{2} \int_{-1}^{+1} r_1^k \rho_1 e^{-\alpha r_1 - \frac{\rho_1}{2}} P_\lambda(\eta)\, d\eta \qquad 6.24a$$

$$\varphi_\lambda^k(1) = \varphi_\lambda^k(\sigma_1, r_p) = \frac{2\lambda+1}{2} \int_{-1}^{+1} r_1^k \rho_1 e^{-(\alpha+2) r_1} P_\lambda(\eta)\, d\eta \qquad 6.24b$$

$$R_\lambda^k(1) = R_\lambda^k(\sigma_1, r_p) = \frac{2\lambda+1}{2} \int_{-1}^{+1} \frac{r_1}{\rho_1}^k e^{-\alpha r_1 - \frac{\rho_1}{2}} P_\lambda(\eta)\, d\eta \qquad 6.24c$$

$$S_\lambda^k(1) = S_\lambda^k(\sigma_1, r_p) = \frac{2\lambda+1}{2} \int_{-1}^{+1} \frac{r_1}{\rho_1}^k e^{-(\alpha+2) r_1} P_\lambda(\eta)\, d\eta \qquad 6.24d$$

$$A(\sigma_1,\sigma_2) = \frac{1}{\sigma_>}\left(\sigma_1^2+\sigma_2^2 - \frac{\sigma_<}{\sigma_>}\frac{2\sigma_1\sigma_2}{3}\right) \qquad 6.25a$$

where $\sigma_<$ is the smaller of σ_1 and σ_2 and $\sigma_>$ is the greater.

$$B_\lambda^{jk}(\sigma_1,\sigma_2) = \frac{M_\lambda^{j}{}_{(1)}\, L_\lambda^{k}{}_{(2)}}{(2\lambda+1)^2}\,\gamma_{\lambda-1}''\left\{(\sigma_1^2+\sigma_2^2)\frac{\sigma_<}{\sigma_>} - \left[\frac{\lambda}{2\lambda-1} + \frac{\lambda+1}{2\lambda+3}\left(\frac{\sigma_<}{\sigma_>}\right)^2\right]2\sigma_1\sigma_2\right\} \qquad 6.25b$$

where $\gamma_\lambda'' = \left(\frac{\sigma_<}{\sigma_>}\right)^{\lambda}_{\lambda+1}$

$$C_\lambda^{jk}(\sigma_1,\sigma_2) = \frac{R_\lambda^{j}{}_{(1)}\, L_\lambda^{k}{}_{(2)}}{(2\lambda+1)^2}\,\gamma_{\lambda-1}''\left\{(\sigma_1^2+\sigma_2^2)\frac{\sigma_<}{\sigma_>} - \left[\frac{\lambda}{2\lambda-1} + \frac{\lambda+1}{2\lambda+3}\left(\frac{\sigma_<}{\sigma_>}\right)^2\right]2\sigma_1\sigma_2\right\} \qquad 6.25c$$

$$D_\lambda^{jk}(\sigma_1,\sigma_2) = \frac{M_\lambda^{j}{}_{(1)}\, S_\lambda^{k}{}_{(2)}}{(2\lambda+1)^2}\,\gamma_{\lambda-1}''\left\{(\sigma_1^2+\sigma_2^2)\frac{\sigma_<}{\sigma_>} - \left[\frac{\lambda}{2\lambda-1} + \frac{\lambda+1}{2\lambda+3}\left(\frac{\sigma_<}{\sigma_>}\right)^2\right]2\sigma_1\sigma_2\right\} \qquad 6.25d$$

And finally:

$$q_v^2(\sigma_1) = 64\pi^{\frac{3}{2}}\sigma_1 \int d\sigma_2 dr_p\, \sigma_2^2 r_p^{i+2} e^{-\alpha r_p} \Bigg[-\frac{8}{3}\Big\{ \sigma_1 r_p \textcircled{H}_{1,0}$$

$$+ \sigma_2 r_p \textcircled{H}_{0,1} + \frac{\sigma_1\sigma_2}{3} \textcircled{H}_{1,1} \Big\} + 8(\sigma_1^2+\sigma_2^2+r_p^2)\textcircled{H}_{0,0}$$

$$+ 4(4\alpha r_p - 4i - 9) M_0^j(1)\, L_0^k(2) + 8 M_0^j(1) \Big\{ -\frac{\sigma_2 r_p}{3\sigma_>} L_1^k(2)$$

$$- \frac{\sigma_2}{3}\left(\alpha - \frac{i}{r_p}\right) L_1^k(2) - (4\sigma_2^2+r_p^2)\left(k L_0^{k-2}(2) - \alpha L_0^{k-1}(2)\right)$$

$$+ \frac{4\sigma_2 r_p}{3}\left(k L_1^{k-2}(2) - \alpha L_1^{k-1}(2)\right)\Big\} + 8 L_0^k(1) \Big\{ -\frac{\sigma_1 r_p}{3\sigma_>} M_1^j(2)$$

$$- \frac{\sigma_1}{3}\left(\alpha - \frac{i}{r_p}\right) M_1^j(2) - (4\sigma_1^2+r_p^2)\left(j M_0^{j-2} - \alpha M_0^{j-1}(2)\right)$$

$$+ \frac{4\sigma_1 r_p}{3}\left(j M_1^{j-2}(2) - \alpha M_1^{j-1}(2)\right) + \frac{8}{3} L_1^k(1) \Big\{$$

$$\frac{2}{3}\sigma_1\sigma_2\left(j M_1^{j-2}(2) - \alpha M_1^{j-1}(2)\right) - \sigma_2 r_p\left(j M_0^{j-2}(2) - \alpha M_0^{j-1}(2)\right)$$

$$- \frac{\sigma_1\sigma_2}{3\sigma_>} M_1^j(2) \Big\} + \frac{8}{3} M_1^j(1) \Big\{ \frac{2}{8}\sigma_1\sigma_2\left(k L_1^{k-2}(2) - \alpha L_1^{k-1}(2)\right)$$

$$- \sigma_1 r_p \left(k \mathcal{L}_0^{k-2}(2) - \alpha \mathcal{L}_0^{k-1}(2) \right) \Big\}$$

$$+ \gamma \sum_{\lambda} \Bigg[\frac{\mathcal{M}_\lambda^j(1)\, \mathcal{L}_\lambda^k(2)}{(2\lambda+1)^2} \gamma''_{\lambda-1} \Big\{ \left(\sigma_1^2 + \sigma_2^2 + r_p^2 \right) \frac{\sigma_<}{\sigma_>} - \sigma_1 \sigma_2 \left(1 + \frac{\sigma_<}{\sigma_>} + \frac{\sigma_<^2}{\sigma_>^2} \right) \Big\}$$

$$- \frac{r_p}{2\lambda+1} \frac{\sigma_<}{\sigma_>} \Big\{ \sigma_1 \mathcal{M}_\lambda^j(1) \Big[\frac{\mathcal{L}^k_{\lambda-1}(2)}{2\lambda-1} + \frac{\mathcal{L}^k_\lambda(2)}{2\lambda+1} \cdot \frac{\sigma_<}{\sigma_>} + \frac{\mathcal{L}^k_{\lambda+1}}{2\lambda+3} \cdot \frac{\sigma_<^2}{\sigma_>^2} \Big]$$

$$+ \sigma_2 \mathcal{L}_\lambda^k(1) \Big[\frac{\mathcal{M}^j_{\lambda-1}(2)}{2\lambda-1} + \frac{\mathcal{M}^j_\lambda(2)}{2\lambda+1} \cdot \frac{\sigma_<}{\sigma_>} + \frac{\mathcal{M}^j_{\lambda+1}(2)}{2\lambda+3} \cdot \frac{\sigma_<^2}{\sigma_>^2} \Big] \Big\} \Bigg] \qquad 6.26$$

where $$\textcircled{H}_{\lambda,\lambda'} = \frac{4}{r_p} \mathcal{M}_\lambda^j(1)\, \mathcal{L}_{\lambda'}^k(2) - 4 \mathcal{M}_\lambda^{j-1}(1)\, \mathcal{L}_{\lambda'}^k(2)$$

$$- 4 \mathcal{M}_\lambda^j(1)\, \mathcal{L}_{\lambda'}^{k-1}(2) - 2 R_\lambda^j(1)\, \mathcal{L}_{\lambda'}^k(2) - 2 \mathcal{M}_\lambda^j(1)\, S_{\lambda'}^k(2)$$

$$- (E + 3\alpha^2) \mathcal{M}_\lambda^j(1)\, \mathcal{L}_{\lambda'}^k(2) + 2\alpha(j+1) \mathcal{M}_\lambda^{j-1}(1)\, \mathcal{L}_{\lambda'}^k(2)$$

$$+ 2\alpha(k+1) \mathcal{M}_\lambda^j(1)\, \mathcal{L}_{\lambda'}^{k-1}(2) + \frac{2\alpha}{r_p}(i+1) \mathcal{M}_\lambda^j(1)\, \mathcal{L}_{\lambda'}^k(2)$$

$$- j(j+1) \mathcal{M}_\lambda^{j-2}(1)\, \mathcal{L}_{\lambda'}^k(2) - k(k+1) \mathcal{M}_\lambda^j(1)\, \mathcal{L}_{\lambda'}^{k-2}(2)$$

$$- \frac{i}{r_p}(i+2) \mathcal{M}_\lambda^j(1)\, \mathcal{L}_{\lambda'}^k(2) \qquad 6.27$$

The various values of ν are shown below:

ν	l	i	j	k
1	0	0	0	0
2	0	1	0	0
3	0	0	1	0
4	0	1	1	0
5	0	1	1	1
6	1	0	0	0
7	1	1	0	0
8	1	1	1	0
9	1	1	1	1
10	2	0	0	0
11	2	1	0	0
12	2	1	1	0

6.3 Addition of the 2P states of Helium and Positronium.

The radial equations will be derived assuming that the Helium ion remains in its ground state and the Helium atomic states considered are the $(1s\,n\ell)^{(2S+1)}\ell$. The total wave function with angular and spin quantum numbers L and S respectively, describing the scattering of a positron by a Helium atom is given by:

$$\Psi^{LS}(1,2,\rho) = \sum_{\nu} \Phi^{LS}_{\nu}(\underline{\xi}\, S_s; \underline{r}_p S_p) + (1+P_{12}) \sum_{\mu} \Phi^{LS}_{\mu}(\underline{\eta}\, S_\eta; \underline{r}_1 S_2) \qquad 6.28$$

where $\underline{\xi} = (\underline{r}_1, \underline{r}_2)$ and $\underline{\eta} = (\underline{r}_2, \underline{r}_1)$

$\nu = (n_s k_s \ell_s \ell_p)$ and $\mu = (n_\eta k_\eta \ell_\eta \ell_3)$ where $n_\eta = (n_2, n_4)$ and $\ell_\eta = (\ell_2\ \ell_4)$

Thus the two electrons are labelled by angular and spin quantum numbers $(\ell_1 m_1 S_1 m_{s_1})$ and $(\ell_2 m_2 S_2 m_{s_2})$ and the positron by $(\ell_p m_p S_p m_{s_p})$. The components of equation (6.28) are expanded as follows:

$$\Phi^{LS}_{\nu}(\underline{\xi}\, S_s; \underline{r}_p S_p) = \sum_{\substack{m_s m_{s_s} \\ m_p m_{s_p}}} \varphi_\gamma(\underline{\xi}, S_s)\, C(\ell_p \ell_s L; m_p m_s M_L)$$

$$\times C\left(\tfrac{1}{2} S_s S; m_{s_p} m_{s_s} M_S\right) \frac{F^{LS}_{\nu}(r_p)}{r_p}\, Y_{\ell_p m_p}(\hat{r}_p)\, \chi_{\frac{1}{2} m_{s_p}}(p) \qquad 6.29$$

where $\gamma = (n_s \ell_s m_s S_s m_{s_s})$ and the C's are Clebsch-Gordon coefficients. χ is the normalized single-particle spin function and φ_γ is the Helium atomic function. Following Burke, Cooper and Ormonde[96] we write the wave function for the $(1s\,n\ell)^{(2S_f+1)}\ell_f$ state of Helium in the form:

$$\varphi_\gamma(\underline{\xi}, S_s) = \chi^{m_{s_s}}_{S_s}(1,2)\left[1 + (-1)^{S_s} P_{12}\right] \varphi_{n_s \ell_s m_s}(\underline{\xi}) \qquad 6.30a$$

where $\varphi_{n_s l_s m_s}(\underline{\rho}) = \frac{\varphi_0(r_1)}{\sqrt{8\pi}} u_{n_s l_s}(r_2) Y_{l_s m_s}(\hat{r}_2)$ 6.30b

and φ_0 is the 1s radial wave function of the Helium ion defined in equation (2.23b). The radial function u_{nl} is determined variationally by solving:

$$\delta \int \varphi_\gamma(\underline{\rho}, S_s)\left[H_{He} - E_\gamma^{He} \right] \varphi_\gamma(\underline{\rho}, S_s) d\tau_1 d\tau_2 = 0 \qquad 6.31a$$

subject to : $$\int \varphi_\gamma \varphi_{\gamma'} d\tau_1 d\tau_2 = \delta_{\gamma\gamma'} \qquad 6.31b$$

where $d\tau$ includes a summation over the spins and :

$$H_{He} = -(\nabla_1^2 + \nabla_2^2) - \frac{4}{r_1} - \frac{4}{r_2} + \frac{4}{r_{12}} \qquad 6.32$$

The second term in equation (6.28) can be expanded as follows:

$$\Phi_\mu^{LS}(\underline{\eta} S_\eta ; \underline{\sigma}_1 S_2) = \sum_{\substack{m_3 m_{s_2} \\ m_\eta m_{s_\eta}}} \varphi_\lambda(\underline{\eta}, S_\eta)\, C(l_3 l_\eta L ; m_3 m_\eta M_L) Y_{l_3 m_3}(\hat{\sigma}_1) \times C\left(\tfrac{1}{2} S_\eta S ; m_{s_2} m_{s_\eta} M_S\right) \underline{\underline{G_\mu^{LS}(\sigma_1)}}_{\sigma_1} \chi_{\frac{1}{2} m_{s_2}}(2) \qquad 6.33$$

where $\lambda = (n_\eta l_\eta m_\eta S_\eta m_{s_\eta})$. φ_λ is defined as follows:

$$\varphi_\lambda(\underline{\eta}, S_\eta) = \varphi_0(r_2)\, \omega_{n_\eta l_\eta}(\rho_1) Y_{l_\eta m_\eta}(\hat{\rho}_1)\, \chi_{S_\eta}^{m_{s_\eta}}(1,\rho) \qquad 6.34$$

where $\omega_{n_\eta l_\eta}$ is the radial Positronium function. H_{ps} and H_2 are

defined as follows:

$$H_{ps} = -2\nabla_p^2 - \frac{2}{\rho} \qquad \left[H_{ps} - E_{n\ell}^{ps}\right] \omega_{n\ell m}(\underline{\rho}) = 0 \qquad 6.35a$$

$$H_2 = -\nabla_2^2 - \frac{4}{r_2} \qquad \left[H_2 + 4\right] \varphi_0(r_2) = 0 \qquad 6.35b$$

and $\omega_{n\ell m}(\underline{\rho}) = \omega_{n\ell}(\rho)\, Y_{\ell m}(\hat{\rho})$

Referring to equation (2.17) the general expression for $A_{LS}^{(1)}$ is:

$$A_{LS}^{(1)}(r_p) = \int \sum_{\substack{m_\ell' m_{s_\ell}' \\ m_p' m_{s_p}'}} \varphi_{\gamma'}(\underline{r}, S_\ell)\, C(\ell_p' \ell_\ell' L; m_p' m_\ell' M_L)\, C(\tfrac{1}{2} S_\ell' S; m_{s_p}' m_{s_\ell}' M_s)$$

$$\times Y_{\ell_p' m_p'}(\hat{r}_p)\, \chi_{\frac{1}{2} m_{s_p}'}(p) \left[H - E\right] \Psi^{LS}(1,2,p)\, d\hat{r}_p\, d\underline{r}_1 d\underline{r}_2 \qquad 6.36$$

The following formula is used to simplify the spin expressions:

$$\sum_{\substack{\text{spin} \\ \text{components}}} \chi_{SM_S}(1)\, \chi_{S'M_S'}(1) = \delta_{SS'}\, \delta_{M_S M_S'} \qquad 6.37$$

One type of spin product in equation (6.36) is:

$$\chi_{S_3'}^{m_{s_3}'}(1,2)\, \chi_{\frac{1}{2} m_{s_p}'}(p)\, \chi_{S_\ell}^{m_{s_\ell}}(1,2)\, \chi_{\frac{1}{2} m_{s_p}}(p) = \delta_{S_3 S_3'}\, \delta_{m_{s_\ell} m_{s_\ell}'}\, \delta_{m_{s_p} m_{s_p}'}$$

A second type of spin product is :

$$\chi_{S_3'}^{m_{s_2}'}(1,2)\, \chi_{\frac{1}{2} m_{s_p}'}(p)\, \chi_{S_\eta}^{m_{s_\eta}}(1,p)\, \chi_{\frac{1}{2} m_{s_2}}(2) = \sum_{\substack{m_{s_1}' m_{s_2}' \\ m_{s_1}'' m_{s_p}''}} C(\tfrac{1}{2}\,\tfrac{1}{2}\, S_3'; m_{s_1}' m_{s_2}' m_{s_3}')$$

$$\times C(\tfrac{1}{2}\,\tfrac{1}{2}\, S_\eta; m_{s_1}'' m_{s_p}'' m_{s_\eta})\, \chi_{\frac{1}{2} m_{s_1}'}(1)\, \chi_{\frac{1}{2} m_{s_2}'}(2)\, \chi_{\frac{1}{2} m_{s_p}'}(p)\, \chi_{\frac{1}{2} m_{s_1}''}(1)\, \chi_{\frac{1}{2} m_{s_p}''}(p)\, \chi_{\frac{1}{2} m_{s_2}}(2)$$

$$= \sum_{m_{s_1}' m_{s_p}'} C(\tfrac{1}{2}\,\tfrac{1}{2} S_3'; m_{s_1}' m_{s_2}' m_{s_3}')\, C(\tfrac{1}{2}\,\tfrac{1}{2} S_\eta; m_{s_1}' m_{s_p}' m_{s_\eta})\, \delta_{m_{s_1}' m_{s_1}''}\, \delta_{m_{s_2} m_{s_2}'}\, \delta_{m_{s_p}' m_{s_p}''}$$

Therefore equation (6.36) reduces to:

$$A^{(\omega}_{LS}(r_p) = \int \sum_{m_s' m_p'} \left[1 + (-1)^{S_s'} P_{12}\right] \varphi_{n_s' \ell_s' m_s'}(\underline{\xi}) C(\ell_p' \ell_s' L; m_p' m_s' M_L)$$

$$\times Y_{\ell_p' m_p'}(\hat{r}_p) \left[H - E\right] \Bigg[\sum \left\{1 + (-1)^{S_s} P_{12}\right\} \varphi_{n_s \ell_s m_s}(\underline{\xi}) \delta_{S_s S_s'}$$

$$\times C(\ell_p \ell_s L; m_p m_s M_L) \frac{F_\nu^{LS}(r_p)}{r_p} Y_{\ell_p m_p}(\hat{r}_p) + \frac{(1 + P_{12})}{\sqrt{4\pi}} \sum_{\substack{m_s m_\eta \\ \mu}} \varphi_0(r_2)$$

$$\times \omega_{n_\eta \ell_\eta}(\rho_1) Y_{\ell_\eta m_\eta}(\hat{\rho}_1) C(\ell_3 \ell_\eta L; m_3 m_\eta M_L) \overline{J}^{S}_{S_s' S_\eta} \frac{G^{LS}_{\mu}(\sigma_1)}{\sigma_1}$$

$$\times Y_{\ell_3 m_3}(\hat{\sigma}_1) \Bigg] d\hat{r}_p \, d\underline{r}_1 \, d\underline{r}_2$$

where $$\overline{J}^{S}_{S_s' S_\eta} = \sum_{\substack{m_{s_1} m_{s_2} \\ m_{s_p'} m_{s_\eta} \\ m_{s_s'}}} C\left(\tfrac{1}{2} S_s' S; m_{s_p'} m_{s_s'} M_S\right) C\left(\tfrac{1}{2} S_\eta S; m_{s_2} m_{s_\eta} M_S\right)$$

$$\times C\left(\tfrac{1}{2}\tfrac{1}{2} S_s'; m_{s_1} m_{s_2} m_{s_s'}\right) C\left(\tfrac{1}{2}\tfrac{1}{2} S_\eta; m_{s_1} m_{s_p'} m_{s_\eta}\right)$$

$$= -\left[(2S_s' + 1)(2S_\eta + 1)\right] \begin{Bmatrix} \frac{1}{2} & S_s' & S \\ \frac{1}{2} & S_\eta & \frac{1}{2} \end{Bmatrix} \qquad 6.38$$

where $\begin{Bmatrix} \end{Bmatrix}$ denotes a 6-j coefficient as defined by Rotenberg, Bivins, Metropolis and Wooten[97]. The 6-j coefficient can be defined in terms of the 3-j coefficients as follows:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix} = \sum_{\substack{\text{all } m \\ \text{and } n}} (-1)^{\ell_1 + \ell_2 + \ell_3 + n_1 + n_2 + n_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

$$\times \begin{pmatrix} j_1 & \ell_2 & \ell_3 \\ m_1 & n_2 & -n_3 \end{pmatrix} \begin{pmatrix} \ell_1 & j_2 & \ell_3 \\ -n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & j_3 \\ n_1 & -n_2 & m_3 \end{pmatrix} \qquad 6.39$$

where $\begin{pmatrix} & & \end{pmatrix}$ represents a 3-j coefficient which is directly related to the Clebsch-Gordan coefficients as follows:

$$C(\ell_1 \ell_2 \ell_3; m_1 m_2 m_3) = (2\ell_3+1)^{\frac{1}{2}}(-1)^{-\ell_1+\ell_2-m_3} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} \qquad 6.40$$

$A_{LS}^{(1)}$ is now written as follows:

$$A_{LS}^{(1)}(r_p) = B_{LS}^{(1)}(r_p) + B_{LS}^{(2)}(r_p)$$

where $$B_{LS}^{(1)}(r_p) = \sum_{\substack{m_s' m_p' \\ m_s m_p \nu}} \int \left[1+(-1)^{S_s} P_{12}\right] \varphi_{n_s' \ell_s' m_s'}(\underline{\xi}) \, Y_{\ell_p' m_p'}(\hat{r}_p)$$

$$\times C(\ell_p' \ell_s' L; m_p' m_s' M_L) \, C(\ell_p \ell_s L; m_p m_s M_L) \left[H-E\right] \left[1+(-1)^{S_s} P_{12}\right] \varphi_{n_s \ell_s m_s}(\underline{\xi})$$

$$\times Y_{\ell_p m_p}(\hat{r}_p) \, \frac{F_\nu^{LS}(r_p)}{r_p} \, d\hat{r}_p \, d\underline{r}_1 d\underline{r}_2 \qquad 6.41$$

and $$B_{LS}^{(2)}(r_p) = \frac{2}{\sqrt{4\pi}} \sum_{\substack{m_s' m_p' \\ m_3 m_n \mu}} \int \left[1+(-1)^{S_s'} P_{12}\right] \varphi_{n_s' \ell_s' m_s'}(\underline{\xi}) \, T^{S}_{S_s' S_n}$$

$$\times C(\ell_p' \ell_s' L; m_p' m_s' M_L) \, C(\ell_3 \ell_n L; m_3 m_n M_L) \, Y_{\ell_p' m_p'}(\hat{r}_p) \left[H-E\right] \varphi_0(r_2)$$

$$\times \omega_{n_n \ell_n}(\rho_1) \, Y_{\ell_n m_n}(\hat{\rho}_1) \, Y_{\ell_3 m_3}(\hat{\sigma}_1) \, \frac{G_\mu^{LS}(\sigma_1)}{\sigma_1} \, d\hat{r}_p \, d\underline{r}_1 d\underline{r}_2 \qquad 6.42$$

Applying equations (2.33) and (6.31) to (6.41) results in:

$$B_{LS}^{(1)}(r_p) = \sum_{\substack{m_p m_p' \\ m_s}} C(\ell_p' \ell_s L; m_p' m_s M_L) \, C(\ell_p \ell_s L; m_p m_s M_L) \int Y_{\ell_p' m_p'}(\hat{r}_p)$$

$$\times \left[-\nabla_\rho^2 - k_{\nu'}^2 \right] Y_{\ell_\rho m_\rho}(\hat{r}_\rho) \frac{F^{LS}_{\nu'}(r_\rho)}{r_\rho} d\hat{r}_\rho + \sum_\nu V_{\nu'\nu}(r_\rho) \frac{F^{LS}_{\nu}(r_\rho)}{r_\rho}$$

where $k_{\nu'}^2 = E - E^{He}_{\gamma'}$

and $$V_{\nu'\nu}(r_\rho) = - \sum_{\substack{m_\rho m_\rho' \\ m_s m_s'}} C(\ell_\rho' \ell_s' L; m_\rho' m_s' M_L)\, C(\ell_\rho \ell_s L; m_\rho m_s M_L)$$

$$\times \int Y_{\ell_\rho' m_\rho'}(\hat{r}_\rho)\, Y_{\ell_\rho m_\rho}(\hat{r}_\rho) \left\{ \left[1 + (-1)^{S_2} P_{12} \right] \varphi_{n_s' \ell_s' m_s'}(\underline{\xi}) \right\} \left\{ \left[1 + (-1)^{S_2} P_{12} \right] \varphi_{n_s \ell_s m_s}(\underline{\xi}) \right\}$$

$$\times \left[\frac{2}{\rho_1} + \frac{2}{\rho_2} - \frac{4}{r_\rho} \right] d\hat{r}_\rho\, d\underline{\xi}_1\, d\underline{\xi}_2 \qquad 6.43$$

Performing the angular integration over r_ρ gives:

$$\beta^{(1)}_{LS}(r_\rho) = -\frac{1}{r_\rho} \left[\frac{d^2}{dr_\rho^2} - \frac{\ell_\rho(\ell_\rho+1)}{r_\rho^2} \right] F^{LS}_{\nu'}(r_\rho) + \frac{1}{r_\rho} \sum_\nu V_{\nu'\nu}(r_\rho) F^{LS}_{\nu}(r_\rho) \qquad 6.44$$

The second integral $\beta^{(2)}_{LS}$ simplifies to the following:

$$\beta^{(2)}_{LS}(r_\rho) = \frac{8}{\sqrt{4\pi}} \sum_{\substack{m_s' m_\rho' \\ m_3 m_\eta \\ \mu}} C(\ell_\rho' \ell_s' L; m_\rho' m_s' L)\, C(\ell_3 \ell_\eta L; m_3 m_\eta M_L)$$

$$\times \mathcal{J}^{S}_{s_s' s_\eta} \int \left[1 + (-1)^{S_s'} \right] \varphi_{n_s' \ell_s' m_s'}(\underline{\xi})\, Y_{\ell_\rho' m_\rho'}(\hat{r}_\rho)\, \varphi_0(r_2)\, \omega_{n_\eta \ell_\eta}(\rho_1)\, Y_{\ell_\eta m_\eta}(\hat{\rho}_1)$$

$$\times \left[-\nabla_{\sigma_1}^2 + \frac{8}{r_\rho} - \frac{8}{r_1} + \frac{4}{r_{12}} - \frac{4}{\rho_2} - k_\mu^2 \right] Y_{\ell_3 m_3}(\hat{\sigma}_1)\, \mathcal{G}^{LS}_{\mu}(\sigma_1)\, d\hat{r}_\rho\, d\underline{\sigma}_1\, d\underline{\xi}_2$$

where $\frac{1}{2} k_\mu^2 = E + 4 - E^{ps}_{n_\eta \ell_\eta}$ 6.45

Applying Green's Theorem results in:

$$B^{(2)}_{LS}(r_p) = \frac{8}{\sqrt{4\pi}} \sum_{\substack{m_s' m_p' \\ m_3 m_n \\ \mu}} C(\ell_p' \ell_s' L; m_p' m_s' M_L)\, C(\ell_3 \ell_n L; m_3 m_n M_L)$$

$$\times J^{S}_{s_s' s_n} \int_{\sigma_1} \varphi_0(r_2)\, G^{LS}_{\mu}(\sigma_1)\, Y_{\ell_3 m_3}(\hat{\sigma}_1)\, Y_{\ell_p' m_p'}(\hat{r}_p) \left[-\nabla_{\sigma_1}^2 + \frac{8}{r_p} - \frac{8}{r_1} \right.$$

$$\left. + \frac{4}{r_{12}} - \frac{4}{\rho_2} - k_\mu^2 \right] \left[1 + (-1)^{S_s'} P_{12} \right] \varphi_{n_s' \ell_s' m_s'}(\underline{\rho})\, \omega_{n_n \ell_n}(\rho_1)$$

$$\times Y_{\ell_n m_n}(\hat{\rho}_1)\, d\hat{r}_p\, d\underline{\sigma}_1\, d\underline{r}_2$$

$$= \frac{1}{r_p} \sum_{\mu} \int_0^\infty G^{LS}_{\mu}(\sigma_1)\, K^{LS}_{\nu'\mu}(r_p, \sigma_1)\, d\sigma_1 \qquad 6.46$$

where: $$K_{\nu'\mu}(r_p, \sigma_1) = \frac{8 \sigma_1 r_p}{\sqrt{4\pi}} \sum_{\substack{m_s' m_p' \\ m_3 m_n}} C(\ell_p' \ell_s' L; m_p' m_s' M_L)$$

$$\times C(\ell_3 \ell_n L; m_3 m_n M_L)\, J^{S}_{s_s' s_n} \int \varphi_0(r_2)\, Y_{\ell_3 m_3}(\hat{\sigma}_1)$$

$$\times Y_{\ell_p' m_p'}(\hat{r}_p) \left[-\nabla_{\sigma_1}^2 + \frac{8}{r_p} - \frac{8}{r_1} + \frac{4}{r_{12}} - \frac{4}{\rho_2} - k_\mu^2 \right] \left[1 + (-1)^{S_s'} P_{12} \right]$$

$$\times \varphi_{n_s' \ell_s' m_s'}(\underline{\rho})\, \omega_{n_n \ell_n}(\rho_1)\, Y_{\ell_n m_n}(\hat{\rho}_1)\, d\hat{r}_p\, d\hat{\sigma}_1\, d\underline{r}_2 \qquad 6.47$$

Combining equations (6.45),(6.46) and omitting the superscripts L and S we obtain:

$$\left[\frac{d^2}{dr_p^2} - \frac{\ell_p(\ell_p+1)}{r_p^2} + k_\nu^2\right] F_\nu(r_p) = \sum_{\nu'} V_{\nu\nu'}(r_p)\, F_{\nu'}(r_p)$$

$$+ \sum_{\mu'} \int_0^\infty G_{\mu'}(\sigma_1) K_{\nu\mu'}(r_p,\sigma_1) d\sigma_1 \qquad 6.48$$

For the second equation we define $A^{(2)}_{LS}$ as follows:

$$A^{(2)}_{LS}(\sigma_1) = \sum_{\substack{m_3' m_{s_2}' \\ m_4' m_{s_4}'}} C(\ell_3'\ell_4' L; m_3' m_4' M_L)\, C\left(\tfrac{1}{2}, S_4' S; m_{s_2}' m_{s_4}' M_S\right)$$

$$\times \int \varphi_{\lambda'}(\underline{r}_4, S_4)\, Y_{\ell_3' m_3'}(\hat{\sigma}_1)\, \chi_{\frac{1}{2} m_{s_2}'}(2)\, [H-E]\, \Psi^{LS}(1,2,p)\, d\hat{\sigma}_1\, d\underline{r}_1\, d\underline{r}_2$$

$$= \sum_{m_3' m_4'} C(\ell_3'\ell_4' L; m_p' m_4' M_L) \int \frac{\varphi_0(r_2)}{\sqrt{4\pi}} w_{n_4'\ell_4'}(\rho_1)$$

$$\times Y_{\ell_4' m_4'}(\hat{\rho}_1)\, Y_{\ell_3' m_3'}(\hat{\sigma}_1)\, [H-E] \sum_{\substack{m_p m_s \\ \nu}} C(\ell_p \ell_s L; m_p m_s M_L)$$

$$\times \bar{J}^S_{s_s s_4'} \left[1 + (-1)^{S_s}\right] \varphi_{n_s \ell_s m_s}(\underline{r}_s) \frac{F^{LS}_\nu(r_p)}{r_p} Y_{\ell_p m_p}(\hat{r}_p) +$$

$$(1+P_{12}) \sum_{\substack{m_3 m_4 \\ \mu}} \delta_{s_4 s_4'}\, C(\ell_3 \ell_4 L; m_3 m_4 M_L) \frac{\varphi_0(r_2)}{\sqrt{4\pi}} w_{n_4\ell_4}(\rho_1)$$

$$\times Y_{\ell_4 m_4}(\hat{\rho}_1)\, Y_{\ell_3 m_3}(\hat{\sigma}_1) \frac{G^{LS}_\mu(\sigma_1)}{\sigma_1}\Bigg] d\hat{\sigma}_1\, d\rho_1\, d\underline{r}_2$$

$$= B^{(3)}_{LS}(\sigma_1) + B^{(4)}_{LS}(\sigma_1) + B^{(5)}_{LS}(\sigma_1)$$

where: $$B_{LS}^{(3)}(\sigma_1) = \sum_{\substack{m_3'm_n' \\ m_p m_s \\ \nu}} C(\ell_3'\ell_n' L; m_3'm_n' M_L)\, C(\ell_p \ell_s L; m_p m_s M_L)$$

$$\times \overline{J}^{S}_{s_3 s_n'} \int \frac{\varphi_0(r_2)}{\sqrt{4\pi}}\, \omega_{n_3\ell_n'}(\rho_1)\, Y_{\ell_n' m_n'}(\hat{\rho}_1)\, Y_{\ell_3' m_3'}(\hat{\sigma}_1)\, [H-E]$$

$$\left[1+(-1)^{S_s}\right] \varphi_{n_s\ell_s m_s}(\underline{\xi})\, Y_{\ell_p m_p}(\hat{r}_p)\, \frac{\underline{F_\nu^{LS}(r_p)}}{r_p}\, d\hat{\sigma}_1\, d\underline{\rho}_1\, d\underline{r}_2$$

$$= 2^3 \sum C(\ell_3'\ell_n' L; m_3'm_n' M_L)\, C(\ell_p \ell_s L; m_p m_s M_L)$$

$$\times \frac{\overline{J}^{S}_{s_s s_n'}}{\sqrt{4\pi}} \int \left[1+(-1)^{S_s}\right] \varphi_{n_s\ell_s m_s}(\underline{\xi})\, Y_{\ell_p m_p}(\hat{r}_p)\, [H-E]\, \varphi_0(r_2)$$

$$\times \omega_{n_n\ell_n'}(\rho_1')\, Y_{\ell_n' m_n'}(\hat{\rho}_1)\, Y_{\ell_3' m_3'}(\hat{\sigma}_1)\, \frac{\underline{F_\nu^{LS}(r_p)}}{r_p}\, d\hat{\sigma}_1\, d\underline{r}_p\, d\underline{r}_2$$

$$= \frac{1}{2\sigma_1} \sum_{\nu} \int_0^\infty F_\nu^{LS}(r_p)\, K_{\mu'\nu}(r_p, \sigma_1)\, dr_p \qquad 6.49$$

$$B_{LS}^{(4)}(\sigma_1) = \sum_{\substack{m_3'm_n' \\ m_3 m_n \\ \mu}} C(\ell_3'\ell_n' L; m_3'm_n' M_L)\, C(\ell_3 \ell_n L; m_3 m_n M_L$$

$$\times \int \frac{\varphi_0(r_2)}{\sqrt{4\pi}}\, \omega_{n_n'\ell_n'}(\rho_1)\, Y_{\ell_n' m_n'}(\hat{\rho}_1)\, Y_{\ell_3' m_3'}(\hat{\sigma}_1)\, [H-E]\, \frac{\varphi_0(r_2)}{\sqrt{4\pi}}$$

$$\times \omega_{n_n\ell_n}(\rho_1)\, Y_{\ell_n m_n}(\hat{\rho}_1)\, Y_{\ell_3 m_3}(\hat{\sigma}_1)\, \frac{\underline{G_\mu^{LS}(\sigma_1)}}{\sigma_1}\, d\hat{\sigma}_1\, d\underline{\rho}_1\, d\underline{r}_2$$

$$= \sum_{\substack{m_3' m_4' \\ m_3 m_4 \\ \mu}} C(\ell_3' \ell_4' L; m_3' m_4' M_L) C(\ell_3 \ell_4 L; m_3 m_4 M_L)$$

$$\times \int \frac{\{\varphi_0(r_2)\}^2}{4\pi} w_{n_3 \ell_3'}(\rho_1) w_{n_4' \ell_4'}(\rho_1) Y_{\ell_4 m_4}(\hat{\rho}_1) Y_{\ell_4' m_4'}(\hat{\rho}_1)$$

$$\times Y_{\ell_3' m_3'}(\hat{\sigma}_1) \left[-\frac{1}{2}\nabla_{\sigma_1}^2 + \frac{4}{r_p} - \frac{4}{r_1} - \frac{2}{\rho_2} + \frac{2}{r_{12}} - \frac{1}{2}k_\mu^2 \right] Y_{\ell_3 m_3}(\hat{\sigma}_1)$$

$$\times \frac{G_\mu^{LS}(\sigma_1)}{\sigma_1} d\hat{\sigma}_1 d\rho_1 d\underline{r}_2$$

$$= \frac{1}{2\sigma_1}\left[\frac{d^2}{d\sigma_1^2} - \frac{\ell_3(\ell_3+1)}{\sigma_1^2} + k_{\mu'}^2 \right] G_{\mu'}^{LS}(\sigma_1) + \frac{1}{2\sigma_1} \sum_\mu V_{\mu'\mu}(\sigma_1) G_\mu^{LS}(\sigma_1) \qquad 6.50$$

where: $$V_{\mu'\mu}(\sigma_1) = \frac{1}{\pi} \sum_{\substack{m_3 m_4 \\ m_3' m_4'}} C(\ell_3' \ell_4' L; m_3' m_4' M_L)$$

$$\times C(\ell_3 \ell_4 L; m_3 m_4 M_L) \int \{\varphi_0(r_2)\}^2 w_{n_4 \ell_4}(\rho_1)$$

$$\times w_{n_4' \ell_4'}(\rho_1) Y_{\ell_4 m_4}(\hat{\rho}_1) Y_{\ell_4' m_4'}(\hat{\rho}_1) Y_{\ell_3' m_3'}(\hat{\sigma}_1) Y_{\ell_3 m_3}(\hat{\sigma}_1)$$

$$\times \left[\frac{2}{r_p} - \frac{2}{r_1} - \frac{1}{\rho_2} + \frac{1}{r_{12}} \right] d\hat{\sigma}_1 d\rho_1 d\underline{r}_2 \qquad 6.51$$

And finally: $$B_{LS}^{(S)}(\sigma_1) = \sum_{\substack{m_3' m_4' \\ m_3 m_4 \\ \mu}} C(\ell_3' \ell_4' L; m_3' m_4' M_L)$$

$$\times C(\ell_3 \ell_4 L; m_3 m_4 M_L) \int \frac{\varphi_0(r_2) w_{n_4' \ell_4'}(\rho_1) Y_{\ell_4' m_4'}(\rho_1) Y_{\ell_3' m_3'}(\hat{\sigma}_1) \times}{4\pi}$$

$$\times \left[H-E \right] \varphi_0(r_1)\, \omega_{n_1 \ell_n}(\rho_2)\, Y_{\ell_n m_n}(\hat{\rho}_2)\, Y_{\ell_3 m_3}(\hat{\sigma}_2)\, \frac{G^{LS}_{\mu}(\sigma_2)}{\sigma_2}\, d\hat{\sigma}_1\, d\rho_1\, d\underline{r}_2$$

$$= \frac{16}{\pi} \sum_{\substack{m_3 m_n \\ m_3' m_n' \\ \mu}} C(\ell_3' \ell_n' L; m_3' m_n' M_L)\, C(\ell_3 \ell_n L; m_3 m_n M_L)$$

$$\times \int \varphi_0(r_2)\, \omega_{n_1' \ell_n'}(\rho_1)\, Y_{\ell_n' m_n'}(\hat{\rho}_1)\, Y_{\ell_3' m_3'}(\hat{\sigma}_1)\, \varphi_0(r_1)\, \omega_{n_1 \ell_n}(\rho_2)$$

$$\times Y_{\ell_n m_n}(\hat{\rho}_2)\, Y_{\ell_3' m_3'}(\hat{\sigma}_1) \left[-\frac{1}{2}\nabla_{\sigma_2}^2 + \frac{4}{r_p} - \frac{4}{r_2} - \frac{2}{\rho_1} + \frac{2}{r_{12}} - \frac{1}{2}k_\mu^2 \right] Y_{\ell_3 m_3}(\hat{\sigma}_2)$$

$$\times \frac{G^{LS}_{\mu}(\sigma_2)}{\sigma_2}\, d\hat{\sigma}_1\, d\underline{\sigma}_2\, d\underline{r}_p$$

$$= -\frac{8}{\pi} \sum_{\substack{m_3' m_n' \\ m_3 m_n \\ \mu}} C(\ell_3' \ell_n' L; m_3' m_n' M_L)\, C(\ell_3 \ell_n L; m_3 m_n M_L)$$

$$\times \int Y_{\ell_3 m_3}(\hat{\sigma}_2)\, Y_{\ell_3' m_3'}(\hat{\sigma}_1)\, \frac{G^{LS}_{\mu}(\sigma_2)}{\sigma_2} \left[\nabla_{\sigma_2}^2 - \frac{8}{r_p} + \frac{8}{r_2} + \frac{4}{\rho_1} - \frac{4}{r_{12}} + k_\mu^2 \right]$$

$$\times \varphi_0(r_2)\, \varphi_0(r_1)\, \omega_{n_1' \ell_n'}(\rho_1)\, \omega_{n_1 \ell_n}(\rho_2)\, Y_{\ell_n' m_n'}(\hat{\rho}_1)\, Y_{\ell_n m_n}(\hat{\rho}_2)\, d\hat{\sigma}_1\, d\underline{\sigma}_2\, d\underline{r}_p$$

$$= \frac{1}{2\sigma_1} \sum \int_0^\infty G^{LS}_{\mu}(\sigma_2)\, K_{\mu'\mu}(\sigma_1, \sigma_2)\, d\sigma_2 \qquad 6.52$$

where:

$$K_{\mu'\mu}(\sigma_1, \sigma_2) = -\frac{16\sigma_1\sigma_2}{\pi} \sum_{\substack{m_3' m_n' \\ m_3 m_n}} C(\ell_3' \ell_n' L; m_3' m_n' M_L)$$

$$\times C(\ell_3 \ell_n L; m_3 m_n M_L) \int Y_{\ell_3 m_3}(\hat{\sigma}_2)\, Y_{\ell_3' m_3'}(\hat{\sigma}_1) \left[\nabla_{\sigma_2}^2 - \frac{8}{r_p} + \frac{8}{r_2} + \frac{4}{\rho_1} - \frac{4}{r_{12}} + k_\mu^2 \right]$$

$$\times \varphi_0(r_1)\varphi_0(r_2)\, w_{n_4\ell_4}(\rho_1)\, w_{n_4'\ell_4'}(\rho_1)\, Y_{\ell_4 m_4}(\hat{\rho}_1)\, Y_{\ell_4' m_4'}(\hat{\rho}_1)\, d\hat{\sigma}_1 d\hat{\sigma}_2 d\underline{r}_p \qquad 6.53$$

Combining equations (6.49),(6.50) and (6.52) gives:

$$\left[\frac{d^2}{d\sigma_1^2} - \frac{\ell_3(\ell_3+1)}{\sigma_1^2} + k_\mu^2\right] G_\mu(\sigma_1) = \sum_{\mu'} V_{\mu\mu'}(\sigma_1)\, G_{\mu'}(\sigma_1)$$

$$+ \sum_{\nu'} \int_0^\infty F_{\nu'}^{LS}(r_p)\, K_{\mu\nu'}(r_p,\sigma_1)\, dr_p + \sum_{\mu'} \int_0^\infty G_{\mu'}^{LS}(\sigma_2)\, K_{\mu\mu'}(\sigma_1,\sigma_2)\, d\sigma_2 \qquad 6.54$$

(a) The Direct Interactions V.

The interaction V between the positron and the Helium atom which is given by equation (6.43) can be written as follows:

$$V_{\nu'\nu}(r_p) = -2 \sum_{\substack{m_p m_p' \\ m_s m_s'}} C(\ell_p'\ell_s' L; m_p' m_s' M_L)\, C(\ell_p \ell_s L; m_p m_s M_L)$$

$$\times \int Y_{\ell_p m_p}(\hat{r}_p)\, Y_{\ell_p' m_p'}(\hat{r}_p) \left\{1+(-1)^{S_s} P_{12}\right\} \varphi_{n_s'\ell_s' m_s'}(\underline{\xi}) \left\{1+(-1)^{S_s} P_{12}\right\}$$

$$\times \varphi_{n_s \ell_s m_s}(\underline{\xi}) \left[\frac{1}{\rho_1} - \frac{1}{r_p}\right] d\hat{r}_p\, d\underline{r}_1 d\underline{r}_2$$

$$= \frac{4}{r_p}\delta_{\nu\nu'} - 2\sum \Big[\Delta(u_{n_s\ell_s}, u_{n_s'\ell_s'})\, y_0(\varphi_0, \varphi_0; r_p)\, \delta_{\ell_s\ell_s'}\delta_{\ell_p\ell_p'}\delta_{\alpha 0}$$

$$+ \Delta(\varphi_0, \varphi_0)\, y_\alpha(u_{n_s\ell_s}, u_{n_s'\ell_s'}; r_p)\, g_\alpha(\ell_s \ell_p \ell_p' \ell_s'; L)$$

$$+ (-1)^{S_s}\, \delta_{\alpha\ell_s'}\, \delta_{\ell_p L}\, \delta_{\ell_s 0} \left[\frac{(2\ell_p'+1)}{(2L+1)(2\ell_s'+1)}\right]^{\frac{1}{2}} C(\ell_p'\ell_s' L; 000) \times$$

$$\times \Delta(\varphi_0, u_{n_s} \ell_s)\, y_{\ell_s'}(\varphi_0, u_{n_s'} \ell_s'; r_p) + (-1)^{S_2'} \delta_{\alpha \ell_s} \delta_{\ell_p' L} \delta_{\ell_s' 0}$$

$$\times \left[\frac{(2\ell_p+1)}{(2L+1)(2\ell_s+1)}\right]^{\frac{1}{2}} C(\ell_p \ell_s L; 000)\, \Delta(\varphi_0, u_{n_s'} \ell_s')\, y_{\ell_s}(\varphi_0, u_{n_s} \ell_s; r_p) \qquad 6.55$$

where $$\Delta(A,B) = \int_0^\infty A(r')\, B(r')\, r'^2\, dr' \qquad 6.56$$

and $$y_\lambda(A,B,r) = \frac{1}{r^{\lambda+1}} \int_0^r r'^\lambda A(r') B(r') r'^2 dr' + r^\lambda \int_r^\infty \frac{A(r') B(r') r'^2 dr'}{r'^{\lambda+1}} \qquad 6.57$$

$$g_\lambda(\ell_1 \ell_2 \ell_2' \ell_1'; L) = (-1)^{\ell_1+\ell_2-L} f_\lambda(\ell_1 \ell_2 \ell_1' \ell_2'; L) \qquad 6.58$$

where $$f_\lambda(\ell_1 \ell_2 \ell_1' \ell_2'; L) = (-1)^{\ell_2+\ell_2'-L} \left[\frac{(2\ell_1+1)(2\ell_1'+1)(2\ell_2+1)(2\ell_2'+1)}{2\lambda+1}\right]^{\frac{1}{2}}$$

$$\times C(\ell_1 \ell_1' \lambda; 000)\, C(\ell_2 \ell_2' \lambda; 000) \begin{Bmatrix} \ell_1 & \ell_2 & L \\ \ell_2' & \ell_1' & \lambda \end{Bmatrix} \qquad 6.59$$

and the 6-j coefficient has already been defined in equation (6.39).

The interaction $V_{\mu\mu'}$ of the Positronium with the residual Helium ion is given by equation (6.51). Before being able to perform the angular integrations, the spherical harmonic functions with arguments $(\hat{r}_1 \hat{r}_2)$ must first be expanded using a theorem by Moshinsky (98) which states:

Given $\underset{\sim}{r} = \underset{\sim}{x} + \underset{\sim}{y}$ then:

$$r^L Y_{LM}(\hat{r}) = \sum_{p,q} \left[\frac{4\pi (2L+1)!}{(2L-2p+1)!\,(2p+1)!} \right]^{\frac{1}{2}} \times x^p y^{L-p}$$

$$\times C(p, L-p, L; q, M-q, M)\, Y_{pq}(\hat{x})\, Y_{L-p,M-q}(\hat{y}) \qquad 6.60$$

As was shown for the L=0 case in Appendix B the direct interaction $V_{\mu'\mu}$ vanishes if only S-states of Positronium are taken into account. In general:

$$V_{\mu'\mu}(\sigma_1) = -16 \sum_{\alpha} \delta_{\alpha,\text{odd}}\, f_\alpha(\ell_3 \ell_4 \ell_3' \ell_4'; L) \left[2\Delta(\varphi_0, \varphi_0) \right.$$

$$* y_\alpha(\omega_{n_4\ell_4}, \omega_{n_4'\ell_4'}; 2\sigma_1) + \sum_{p} \frac{\sigma_1^{\alpha-p-1}(-1)^p}{2p+1}$$

$$\left. \times \left\{ \frac{(2\alpha)!}{(2\alpha-2p)!\,(2p)!} \right\}^{\frac{1}{2}} C(p, \alpha-p, \alpha; 000)\, K_\alpha^p(\sigma_1) \right] \qquad 6.61$$

where $$K_\alpha^p(\sigma_1) = \int \left\{ \varphi_0(2) \right\}^2 \mathcal{Y}_\alpha^p(r_2, \sigma_1) r_2^{p+1} dr_2 \qquad 6.62a$$

and $$\mathcal{Y}_\alpha^p(r_2, \sigma_1) = \frac{2r_2\sigma_1}{2\alpha+1} \int_{-1}^{+1} y_\alpha(\omega_{n_4\ell_4}, \omega_{n_4'\ell_4'}; 2|\underline{r}_2 - \underline{\sigma}_1|) P_\alpha(\eta)\, d\eta \qquad 6.62b$$

where $\eta = \hat{r}_2 \cdot \hat{\sigma}_1$

(b) Simplification of the Kernels.

In order to simplify products of Clebsch-Gordon coefficients appearing in both kernels, the following two formulae have been used:

$$\sum_{m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & j_3 \\ n_1 & n_2 & -m_3 \end{pmatrix}$$

$$= \sum_{\ell_3 n_3} (-1)^{j_3+\ell_3+m_1+n_1} (2\ell_3+1) \begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix} \times \begin{pmatrix} \ell_1 & j_2 & \ell_3 \\ n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} j_1 & \ell_2 & \ell_3 \\ m_1 & n_2 & -n_3 \end{pmatrix} \qquad 6.63$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix}$$

$$= \sum_{n_1 n_2 n_3} (-1)^{\ell_1+\ell_2+\ell_3+n_1+n_2+n_3} \begin{pmatrix} j_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & -n_3 \end{pmatrix} \times \begin{pmatrix} \ell_1 & j_2 & \ell_3 \\ -n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & j_3 \\ n_1 & -n_2 & m_3 \end{pmatrix} \qquad 6.64$$

After repeated applications of equations (6.39), (6.40), (6.60), (6.63) and (6.64) $K_{\nu'\mu}$, defined by equation (6.47) finally reduces down to:

$$K_{\nu'\mu}(r_p,\sigma_i) = -8\,\bar{J}^{s}_{s_s's_\eta}\,\delta_{\ell_p'L}\,\delta_{\ell_s'0}\sum_{\alpha}\sum_{p=0}^{\ell_\eta} C(\alpha\,p\,\ell_3;000)$$

$$\times C(\alpha,\ell_\eta-p,L;000)\left\{\frac{(2\ell_\eta)!}{2(2\ell_\eta-2p)!\,(2p)!\,(2L+1)}\right\}^{\frac{1}{2}}$$

$$\times\frac{(2\ell_\eta+1)(2r_p)^{\ell_\eta-p}}{(2\ell_\eta-2p+1)}(-1)^{L+p+\alpha}\begin{Bmatrix}\ell_3 & \ell_\eta & L\\ \ell_\eta-p & \alpha & p\end{Bmatrix}$$

$$\times\Big[\Delta(\varphi_0,u_{n_s'0})\left\{\frac{d^2}{d\sigma_1^2}-\frac{\ell_3(\ell_3+1)}{\sigma_1^2}-\frac{8}{r_p}+k_\mu^2\right\}\mathcal{H}^{\alpha}_{n_\eta\ell_\eta}(1)$$

$$+8\,\Delta(\varphi_0,u_{n_s'0})\,\mathcal{G}^{\alpha}_{n_\eta\ell_\eta}(1)\Big](2\sigma_1)^p$$

$$-32\,\frac{\bar{J}^{s}_{s_s's_\eta}}{(2\ell_s'+1)}\sum_{\alpha}\sum_{p=0}^{\ell_\eta}\frac{(2\ell_\eta+1)}{(2\ell_\eta-2p+1)}\left\{\frac{(2\ell_s'+1)(2\ell_p'+1)(2\ell_\eta)!}{(2\ell_\eta-2p)!\,(2p)!}\right\}^{\frac{1}{2}}$$

$$\times(2\sigma_1)^p(2r_p)^{\ell_\eta-p}\Big[y_{\ell_s'}(\varphi_0,u_{n_s'\ell_s'};r_p)\,\frac{\mathcal{H}^{\alpha}_{n_\eta\ell_\eta}(1)}{2L+1}$$

$$\times(-1)^{L+\alpha-p}\,C(\alpha\,p\,\ell_3;000)\,C(\ell_s'\ell_p'L;000)$$

$$\times C(\alpha,\ell_\eta-p,L;000)\begin{Bmatrix}\ell_3 & \ell_\eta & L\\ \ell_\eta-p & \alpha & p\end{Bmatrix}$$

$$-K^{\alpha}_{n_\eta\ell_\eta n_s'\ell_s'\ell_s'}(1)\sum_{\mathcal{L}\mathcal{L}'}\sum_{p'=0}^{\ell_s'}\left[\frac{(2\ell_s'+1)!\,(2\ell_3+1)}{(2\ell_s'-2p')!\,(2p')!}\right]^{\frac{1}{2}}\frac{(2\sigma_1)^{p'}r_p^{\ell_s'-p'}}{(2\ell_s'-2p'+1)}$$

$$\times C(\alpha\,p\,\mathcal{L};000)\,C(p'\,\ell_3\,\mathcal{L};000)\,C(\ell_p',\ell_s'-p',\mathcal{L}';000)\times$$

$$\times C(\alpha, \ell_\eta - p, \ell'; 000) \begin{Bmatrix} p & \ell' & L \\ \ell_p' & \ell_s' & \ell_s' - p \end{Bmatrix}.$$

$$\times \begin{Bmatrix} \ell_\eta & \ell & \ell' \\ \alpha & \ell_\eta - p & p' \end{Bmatrix} \begin{Bmatrix} \ell_\eta & \ell & \ell' \\ p' & L & \ell_3 \end{Bmatrix} (-1)^{\ell_\eta + \ell_p' + \alpha + \ell_3 + L + p + p'}$$

$$- 8 (-1)^{s_s'} J^{s}_{s_s' s_\eta} \sum_{\substack{\alpha \ell \\ \ell' \ell}} \sum_{p=0}^{\ell_\eta} \sum_{p'=0}^{\ell_s'} C(\alpha, \ell_\eta - p, \ell; 000)$$

$$\times C(\ell_p', \ell_s' - p', \ell; 000) C(p\, p'\, \ell'; 000) C(\ell_3\, \alpha\, \ell'; 000)$$

$$\times \frac{(2\ell+1)(2\ell_s'+1)(2\ell_\eta+1)}{(2\ell+1)(2\ell'+1)(2\ell_3'-2p'+1)(2\ell_\eta-2p+1)} \left[\frac{(2\ell_\eta)!\,(2\ell_s')!\,(2\ell_3+1)(2\ell_p'+1)}{2(2\ell_\eta-2p)!\,(2p)!\,(2\ell_s'-2p')!\,(2p')!} \right]$$

$$\times r_p^{\ell_s'-p'} (2r_p)^{\ell_\eta - p} (-1)^{\ell_\eta + \ell_p' + \ell_3 + \ell + \ell'} \begin{Bmatrix} L & p' & \ell' \\ \ell_s' - p' & \ell_p' & \ell_s' \end{Bmatrix}$$

$$\times \begin{Bmatrix} \ell & L & p' \\ \ell' & p & \ell \end{Bmatrix} \begin{Bmatrix} \alpha & \ell_\eta & \ell \\ p & \ell & \ell_\eta - p \end{Bmatrix} \begin{Bmatrix} \ell_3 & \ell_\eta & L \\ \ell & \ell' & \alpha \end{Bmatrix}$$

$$\times \Big[\Big\{ \Delta(\varphi_0, \varphi_0) \Big(\frac{d^2}{d\sigma_1^2} - \frac{\ell_3(\ell_3+1)}{\sigma_1^2} - \frac{\delta}{r_p} + k_\mu^2 \Big)$$

$$+ 4 y_0(\varphi_0, \varphi_0; r_p) \Big\} g^{\alpha}_{n_s' \ell_s' n_\eta \ell_\eta}(1) - 4 A^{\alpha}_{n_s' \ell_s' n_\eta \ell_\eta}(1)$$

$$+ 8 \Delta(\varphi_0, \varphi_0) B^{\alpha}_{n_s' \ell_s' n_\eta \ell_\eta}(1) \Big] (2\sigma_1)^{p+p'} \qquad 6.65$$

where $H(1) \equiv H(r_p, \sigma_1)$ etcetera.

$$\frac{\varphi_0(r_1)\,\omega_{n\ell}(\rho_1)}{\rho_1^{\ell}} = \frac{1}{r_p\sigma_1}\sum_{\alpha} H^{\alpha}_{n\ell}(r_p,\sigma_1)\,P_{\alpha}(\hat{r}_p\cdot\hat{\sigma}_1) \qquad 6.66a$$

$$\frac{\varphi_0(r_1)\,\omega_{n\ell}(\rho_1)}{r_1\rho_1^{\ell}} = \frac{1}{r_p\sigma_1}\sum_{\alpha} G^{\alpha}_{n\ell}(r_p,\sigma_1)\,P_{\alpha}(\hat{r}_p\cdot\hat{\sigma}_1) \qquad 6.66b$$

$$\frac{\varphi_0(r_1)\,\omega_{n\ell}(\rho_1)\,y_{\lambda}(\varphi_0,u_{n'\ell'};r_1)}{r_1^{\lambda}\rho_1^{\ell}} = \frac{1}{r_p\sigma_1}\sum_{\alpha} K^{\alpha}_{n\ell n'\ell'\lambda}(r_p,\sigma_1)\,P_{\alpha}(\hat{r}_p\cdot\hat{\sigma}_1) \qquad 6.66c$$

$$\frac{u_{n\ell}(r_1)\,\omega_{n'\ell'}(\rho_1)}{r_1^{\ell}\,\rho_1^{\ell'}} = \frac{1}{r_p\sigma_1}\sum_{\alpha} g^{\alpha}_{n\ell n'\ell'}(r_p,\sigma_1)\,P_{\alpha}(\hat{r}_p\cdot\hat{\sigma}) \qquad 6.66d$$

$$\frac{u_{n\ell}(r_1)\,\omega_{n'\ell'}(\rho_1)\,y_0(\varphi_0,\varphi_0;r_1)}{\rho_1^{\ell'}} = \frac{1}{r_p\sigma_1}\sum A^{\alpha}_{n\ell n'\ell'}(r_p,\sigma_1)\,P_{\alpha}(\hat{r}_p\cdot\hat{\sigma}_1) \qquad 6.66e$$

$$\frac{u_{n\ell}(r_1)\,\omega_{n'\ell'}(\rho_1)}{r_1^{\ell+1}\,\rho_1^{\ell'}} = \frac{1}{r_p\sigma_1}\sum B^{\alpha}_{n\ell n'\ell'}(r_p,\sigma_1)\,P_{\alpha}(\hat{r}_p\cdot\hat{\sigma}_1) \qquad 6.66f$$

$K_{\mu'\mu}$ is defined by equation(6.53) and reduces to:

$$K_{\mu'\mu}(\sigma_1,\sigma_2) = -64 \sum_{\substack{\alpha\alpha' \\ \mathcal{L}''}} \sum_{p=0}^{\ell_n} \sum_{p'=0}^{\ell_n'} C(\alpha,\ell_n-p,\mathcal{L}'';000)$$

$$\times C(\alpha',\ell_n'-p',\mathcal{L}'';000)(-1)^{\ell_n+\ell_n'+\ell_3+\ell_3'+\alpha+\alpha'+p+p'}$$

$$\times \frac{(2\sigma_1)^{p'}(2\ell_n+1)(2\ell_n'+1)}{(2\mathcal{L}''+1)(2\ell_n-2p+1)(2\ell_n'-2p'+1)} \left[\frac{(2\ell_n)!\,(2\ell_n')!}{(2\ell_n-2p)!\,(2p)!\,(2\ell_n'-2p')!\,(2p')!}\right]^{\frac{1}{2}}$$

$$\times \int (2r_p)^{\ell_n+\ell_n'-p-p'} \Bigg[\Bigg\{ \mathcal{H}^{\alpha'}_{n_n'\ell_n'}(1) \left(\frac{d^2}{d\sigma_2^2} - \frac{\ell_3(\ell_3+1)}{\sigma_2^2} \right.$$

$$\left. - \frac{8}{r_p} + k_\mu^2 \right) \mathcal{H}^{\alpha}_{n_n\ell_n}(2) + 8\mathcal{H}^{\alpha'}_{n_n'\ell_n'}(1)\,\mathcal{G}^{\alpha}_{n_n\ell_n}(2)$$

$$+ 4\mathcal{N}^{\alpha'}_{n_n'\ell_n'}(1)\,\mathcal{H}^{\alpha}_{n_n\ell_n}(2) \Bigg\}\, C(\alpha p \ell_3;000)\, C(\alpha' p' \ell_3';000)$$

$$\times \begin{Bmatrix} \ell_3 & \ell_n & L \\ \ell_n-p & \alpha & p \end{Bmatrix} \begin{Bmatrix} \ell_3' & \ell_n' & L \\ \ell_n'-p' & \alpha' & p' \end{Bmatrix} \delta_{\mathcal{L}''L}$$

$$- 2(2L+1)(2\mathcal{L}''+1)(2\ell_3+1)^{\frac{1}{2}}(2\ell_3'+1)^{\frac{1}{2}} \sum_{\lambda\mathcal{L}\mathcal{L}'} \frac{\gamma_\lambda}{2\lambda+1}$$

$$\times \frac{\mathcal{H}^{\alpha'}_{n_n'\ell_n'}(1)\,\mathcal{H}^{\alpha}_{n_n\ell_n}(2)}{(2\mathcal{L}+1)(2\mathcal{L}'+1)}\, C(\alpha p \mathcal{L};000)\, C(\ell_3 \lambda \mathcal{L};000) \times$$

$$\times C(\alpha'_\rho \ell'; 000)\, C(\ell_3' \lambda \ell'; 000) \begin{Bmatrix} \ell_n & \ell & \ell'' \\ \alpha & \ell_n - \rho & \rho \end{Bmatrix}$$

$$\times \begin{Bmatrix} \ell_n' & \ell' & \ell'' \\ \alpha' & \ell_n' - \rho' & \rho' \end{Bmatrix} \begin{Bmatrix} \lambda & \ell'' & L \\ \ell_n & \ell_3 & \ell \end{Bmatrix} \begin{Bmatrix} \lambda & \ell'' & L \\ \ell_n' & \ell_3' & \ell' \end{Bmatrix} \Big] dr_\rho \qquad 6.67$$

where $\mathcal{H}^\alpha_{(2)} = \mathcal{H}^\alpha(r_\rho, \sigma_2)$ etcetera.

$$\gamma_\lambda = \frac{\sigma_<^\lambda}{\sigma_>^{\lambda+1}}$$

$$\begin{cases} \sigma_< = \sigma_1 \text{ and } \sigma_> = \sigma_2 & \text{if } \sigma_1 < \sigma_2 \\ \sigma_< = \sigma_2 \text{ and } \sigma_> = \sigma_1 & \text{if } \sigma_2 < \sigma_1 \end{cases}$$

and $$\frac{\varphi_\alpha(r_1)\, \omega_{n\ell}(\rho_1)}{\rho_1^{\ell+1}} = \frac{1}{r_\rho \sigma_1} \sum_\alpha \mathcal{N}^\alpha_{n\ell}(r_\rho, \sigma_1) P_\alpha(\hat{r}_\rho \cdot \hat{\sigma}_1) \qquad 6.68$$

The appropriate values of ν, ν', μ and μ' can now be substituted into equations (6.55), (6.61), (6.65) and (6.67) to obtain the particular sets of equations for the 2P states of Helium and Positronium.

APPENDIX A

Simplification of $A_L^{(1)}(r_p)$ and $A_L^{(2)}(\sigma)$

Substituting equations (2.3), (2.28), (2.24) and (2.26) into (2.28a) we obtain the following

$$A_L^{(1)}(r_p) = \int \left\{ \psi_0(\bar{12}) \right\}^2 Y_{LM}(\hat{r}_p) \left[-\nabla_p^2 + \frac{4}{r_p} - \frac{2}{\rho_1} - \frac{2}{\rho_2} + k_1^2 \right] F_{(p)}^{(L)} d\hat{r}_p \, d\underline{r}_1 \, d\underline{r}_2$$

$$+ 2 \int \psi_0(\bar{12}) \phi_0(2) w(\rho_1) Y_{LM}(\hat{r}_p) \left[-\frac{1}{2}\nabla_{\sigma_1}^2 + \frac{4}{r_p} - \frac{4}{r_1} - \frac{2}{\rho_2} + \frac{2}{r_{12}} - \frac{1}{2}k_2^2 \right] G_{(\underline{\sigma}_1)}^{(L)} d\hat{r}_p \, d\underline{r}_1 \, d\underline{r}_2$$

where the factor of 2 in the second integral occurs because of the symmetry of the Hamiltonian and of the wave functions of the integrand in the coordinates 1 and 2. We change the independent variables from $(\underline{r}_1, \underline{r}_2, \underline{r}_p)$ to $(\underline{\sigma}_1, \underline{r}_2, \underline{r}_p)$, the Jacobian of the transformation being 2^3. Applying Green's Theorem to the second integral we obtain:

$$A_L^{(1)}(r_p) \quad \int \left\{ \psi_0(\bar{12}) \right\}^2 Y_{LM}(\hat{r}_p) \left[-\nabla_p^2 + \frac{4}{r_p} - \frac{2}{\rho_1} - \frac{2}{\rho_2} - k_1^2 \right] F_{(p)}^{(L)} d\hat{r}_p \, d\underline{r}_1 \, d\underline{r}_2$$

$$+ 2^3 \int u(2) \phi_0(2) Y_{LM}(\hat{r}_p) G_{(\underline{\sigma}_1)}^{(L)} \left[-\nabla_{\sigma_1}^2 + \frac{8}{r_p} - \frac{8}{r_1} - \frac{4}{\rho_2} + \frac{4}{r_{12}} - k_2^2 \right] u(1) w(\rho_1) d\hat{r}_p \, d\underline{\sigma}_1 \, d\underline{r}_2$$

The surface integral term $\int_{S_{\sigma_1}} \left[G_{(\underline{\sigma}_1)}^{(L)} \underset{\sim}{\nabla}_{\sigma_1} \left\{ u(1) w(\rho_1) \right\} - u(1) w(\rho_1) \underset{\sim}{\nabla}_{\sigma_1} \left\{ G_{(\underline{\sigma}_1)}^{(L)} \right\} \right] \cdot d\underline{S}_{\sigma_1}$ of Green's Theorem is zero since $u(1)$ and $w(\rho_1)$ are bound state

functions. We define

$$S = \int d\underline{r}\, \varphi(r)\, u(r) \qquad \text{A.1a}$$

$$P(r) = \int \frac{d\underline{r}'\, \varphi_0(r')\, u(r')}{|\underline{r}-\underline{r}'|} \qquad \text{A.1b}$$

$$U(\underline{r}_p) \quad \iint d\underline{r}_1 d\underline{r}_2 \left\{\psi_0(\overline{12})\right\}^2 \left[\frac{2}{\rho_1} + \frac{2}{\rho_2} - \frac{4}{r_p}\right] \qquad \text{A.1c}$$

Therefore $A_L^{(1)}(r_p)$ may be written as follows:

$$A_L^{(1)}(r_p) = -\int Y_{LM}(\hat{r}_p)\left[\nabla_p^2 + U(\underline{r}_p) + k_1^2\right] F_{(p)}^{(L)} d\hat{r}_p$$

$$- \int Y_{LM}(\hat{r}_p)\, G_{(\underline{r}_1)}^{(L)} K_1(\underline{r}_p, \underline{r}_1)\, d\hat{r}_p\, d\underline{r}_1 \qquad \text{A.2}$$

where $K_1(\underline{r}_p, \underline{r}_1) = 8\left[S\left(\nabla_{r_1}^2 - \frac{8}{r_p} + \frac{8}{r_1} + k_2^2\right) + 4P(r_p) - 4P(r_1)\right] u(1)\, w(\rho_1)$ A.3

A similar procedure is followed for $A_L^{(2)}(r_1)$. The independent variables are changed from $(\underline{r}_1, \rho_1, \underline{r}_2)$ to $(\underline{r}_1, \underline{r}_2, \underline{r}_p)$, the Jacobian being 2^3 also. Applying Green's Theorem to the first integral of $A_L^{(2)}$ and using equations (2.3), (2.23), (2.24) and (2.26) in equation (2.28b) we obtain:

$$\int \varphi_0(2)\, w(\rho_1)\, Y_{LM}(\hat{\sigma}_1) \left[H-E\right] \psi_0(\bar{2})\, F^{(L)}(\rho)\, d\hat{\sigma}_1\, d\rho_1\, d\underline{r}_2$$

$$= 2^3 \int \psi_0(\bar{2})\, F^{(L)}(\rho)\, Y_{LM}(\hat{\sigma}_1) \left[H-E\right] \varphi_0(2)\, w(\rho_1)\, d\hat{\sigma}_1\, d\underline{r}_p\, d\underline{r}_2$$

$$= -\frac{1}{2} \int Y_{LM}(\hat{\sigma}_1)\, F^{(L)}(\rho)\, K_1(\underline{r}_p, \underline{\sigma}_1)\, d\hat{\sigma}_1\, d\underline{r}_p \qquad \text{A.4}$$

The second integral of $A_L^{(2)}(\sigma_1)$ can be written as follows:

$$\int \left\{ \varphi_0(2)\, w(\rho_1) \right\}^2 Y_{LM}(\hat{\sigma}_1) \left[-\frac{1}{2}\nabla_{\sigma_1}^2 + \frac{4}{r_p} - \frac{4}{r_1} - \frac{2}{\rho_2} + \frac{2}{r_{12}} - \frac{1}{2}k_2^2 \right] G^{(L)}(\underline{\sigma}_1)\, d\hat{\sigma}_1\, d\rho_1\, d\underline{r}_2 + J \qquad \text{A.5}$$

where $J = \int \varphi_0(2)\, w(\rho_1)\, Y_{LM}(\hat{\sigma}_1) \left[H-E\right] \varphi_0(1)\, w(\rho_2)\, G^{(L)}(\underline{\sigma}_2)\, d\hat{\sigma}_1\, d\rho_1\, d\underline{r}_2$

Applying Green's Theorem to J we obtain:

$$J = \int G^{(L)}(\underline{\sigma}_2)\, Y_{LM}(\hat{\sigma}_1) \left[H-E\right] \varphi_0(1)\, \varphi_0(2)\, w(\rho_1)\, w(\rho_2)\, d\hat{\sigma}_1\, d\rho_1\, d\underline{r}_2$$

Changing the independent variables from $(\underline{\sigma}_1, \rho_1, \underline{r}_2)$ to $(\underline{\sigma}_1, \underline{\sigma}_2, \underline{r}_p)$, the Jacobian of the transformation being 4^3 we obtain:

$$J = -\int G^{(L)}(\underline{\sigma}_2)\, Y_{LM}(\hat{\sigma}_1)\, K_2(\underline{\sigma}_1, \underline{\sigma}_2)\, d\hat{\sigma}_1\, d\underline{\sigma}_2 \qquad \text{A.6}$$

where $K_2(\underline{\sigma}_1, \underline{\sigma}_2) = 4^3 \int d\underline{r}_p \left[\frac{1}{2}\nabla_{\sigma_2}^2 - \frac{4}{r_p} + \frac{4}{r_1} + \frac{2}{\rho_2} - \frac{2}{r_{12}} + \frac{1}{2}k_2^2 \right] \varphi_0(1)\, \varphi_0(2)\, w(\rho_1)\, w(\rho_2)$

It can be seen that $K_2(\underline{\sigma}_1, \underline{\sigma}_2)$ is symmetric with respect to

interchange of 1 and 2. Therefore to preserve this symmetry explicitly in the form of K_2 we take the average of $K_2(\underline{\sigma}_1, \underline{\sigma}_2)$ and $K_2(\underline{\sigma}_2, \underline{\sigma}_1)$ as follows:

$$K_2(\underline{\sigma}_1, \underline{\sigma}_2) = \frac{4^3}{2}(1+P_{12}) \int d\underline{r}_p \left[\frac{1}{2}\nabla_2^2 - \frac{4}{r_p} + \frac{4}{r_1} + \frac{2}{\rho_2} - \frac{2}{r_{12}} + \frac{1}{2}k_2^2 \right] \varphi_0(1)\varphi_0(2) w(\rho_1) w(\rho_2) \qquad A.7$$

where P_{12} is the operator interchanging all coordinates 1 and 2. Referring back to equation (A.5), it is shown in Appendix B that if only s - states of Positronium are included then:

$$\int \left\{ \varphi_0(2) w(\rho_1) \right\}^2 Y_{LM}(\hat{\sigma}_1) \left[\frac{4}{r_p} - \frac{4}{r_1} - \frac{2}{\rho_2} + \frac{2}{r_{12}} \right] G^{(L)}(\underline{\sigma}_1)\, d\hat{\sigma}_1\, d\rho_1\, d\underline{r}_2 = 0$$

Combining equations (A.4), (A.5), (A.6) and (A.7) we obtain:

$$F_L^{(2)}(\sigma_1) = -\frac{1}{2} \int Y_{LM}(\hat{\sigma}_1) \left[\nabla_{\sigma_1}^2 + k_2^2 \right] G^{(L)}(\underline{\sigma}_1)\, d\hat{\sigma}_1$$

$$-\frac{1}{2}\int Y_{LM}(\hat{\sigma}_1) F^{(L)}(\rho) K_1(\underline{r}_p, \underline{\sigma}_1)\, d\hat{\sigma}_1 d\underline{r}_p - \int Y_{LM}(\hat{\sigma}_1) G^{(L)}(\underline{\sigma}_2) K_2(\underline{\sigma}_1, \underline{\sigma}_2)\, d\hat{\sigma}_1 d\underline{\sigma}_2 \qquad A.8$$

APPENDIX B

Consider the expression $X_{LM}(\sigma_1)$:

$$X_{LM}(\sigma_1) = \int \left\{ \varphi_0(2)\omega(\rho_1) \right\}^2 Y_{LM}(\hat{\sigma}_1) \left[\frac{4}{r_p} - \frac{4}{r_1} - \frac{2}{\rho_2} + \frac{2}{r_{12}} \right] G^{(L)}(\underline{\sigma}_1)\, d\hat{\sigma}_1\, d\rho_1 d\underline{r}_2$$

$$= \int \left\{ \varphi_0(2)\omega(\rho_1) \right\}^2 \frac{g^{(L)}(\sigma_1)}{\sigma_1} \rho_1^2 r_2^2 d\rho_1 dr_2 \int |Y_{LM}(\hat{\sigma}_1)|^2 \left[\frac{4}{r_p} - \frac{4}{r_1} - \frac{2}{\rho_2} + \frac{2}{r_{12}} \right] d\hat{\sigma}_1 d\hat{\rho}_1 d\hat{r}_2 \qquad \text{B.1}$$

Using the expansion:

$$\frac{1}{|\underline{a}-\underline{b}|} - \frac{1}{|\underline{a}+\underline{b}|} = \sum_\lambda \gamma_\lambda \left\{ 1-(-1)^\lambda \right\} P_\lambda(\hat{a}\cdot\hat{b}) \qquad \text{B.2a}$$

where $\gamma_\lambda = \dfrac{r_<^\lambda}{r_>^{\lambda+1}}$ and $r_< = a$, $r_> = b$ if $a < b$ B.2b

$r_< = b$, $r_> = a$ if $b < a$

With reference to the expressions B.1 and B.2 it can be seen that:

$$\frac{4}{r_p} - \frac{4}{r_1} - \frac{2}{\rho_2} + \frac{2}{r_{12}} = 2\left\{ \frac{1}{|\underline{\sigma}_1 - \frac{\underline{\rho}_1}{2}|} - \frac{1}{|\underline{\sigma}_1 + \frac{\underline{\rho}_1}{2}|} \right\} + \left\{ \frac{1}{|\underline{r}_2 - \underline{\sigma}_1 - \frac{\underline{\rho}_1}{2}|} - \frac{1}{|\underline{r}_2 - \underline{\sigma}_1 + \frac{\underline{\rho}_1}{2}|} \right\}$$

$$= \sum_\lambda \left\{ 1-(-1)^\lambda \right\} \left[2\gamma_\lambda P_\lambda(\hat{\sigma}_1\cdot\hat{\rho}_1) + \gamma_\lambda' P_\lambda(\widehat{r_2 - \sigma_1}\cdot\hat{\rho}_1) \right]$$

$= 0$ when $\lambda = 0$ or an even integer.

Where γ_λ denotes that $a = \sigma_1$, $b = \frac{\rho_1}{2}$ and γ_λ' denotes that $a = |\underline{r}_2 - \underline{\sigma}_1|$ and $b = \frac{\rho_1}{2}$ in equations (B.2).

Considering the angular integrations of equation (B.1) we have the following factor:

$$\int |Y_{LM}(\hat{\sigma}_1)|^2 \sum_\lambda \left\{1-(-1)^\lambda\right\}\left[2\gamma_\lambda P_\lambda(\hat{\sigma}_1\cdot\hat{\rho}_1)+\gamma_\lambda' P_\lambda(\widehat{r_2-\sigma_1}\cdot\hat{\rho}_1)\right] d\hat{\sigma}_1\, d\hat{\rho}_1\, d\hat{r}_2$$

Using the addition formula given by equation (2.43) this reduces to:

$$\sum_\lambda \frac{(4\pi)^2}{2\lambda+1}\,\delta_{\lambda 0}\left\{1-(-1)^\lambda\right\}\left[2\gamma_0+\gamma_0'\right]$$

Thus $X_{LM}(\sigma_1)=0$.

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