On the formation and properties of positronium and its interactions with gaseous atoms

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ON THE FORMATION AND PROPERTIES OF POSITRONIUM AND ITS INTERACTIONS WITH GASEOUS ATOMS

ON THE FORMATION AND PROPERTIES OF POSITRONIUM AND ITS INTERACTIONS WITH GASEOUS ATOMS

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BY

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TO

MY FATHER AND MOTHER

ABSTRACT

A presentation of the formation and properties of the positronium atom are given in the early part of the thesis from a more or less historical viewpoint.

This is followed by the major part of the thesis dealing with the scattering of orthopositronium by helium atoms in two approximations.

The first is the static approximation including exchange and the elastic scattering cross sections and the corresponding phase shifts are calculated. The second calculation allows for the long range van der Waal's forces acting between the neutral atoms. The evaluation of the long range potential in the adiabatic approximation using a Rayleigh-Ritz method is presented and the elastic cross sections and phase shifts are recomputed with the potential included in the analysis. Little difference is found in the values from the two approximations except at very low energies.

A survey is presented of the quenching phenomena exhibited by positronium in gases and the quenching of orthopositronium in helium is studied in detail.

Measurements of the quenching rate of orthopositronium in helium determine the parameter Z_{eff} , the effective number of electrons per atom in a singlet state relative to the

positron. This number may be calculated from the wave function for the orthopositronium-helium atom system. Since we have computed this wave-function in two approximations for the scattering problem we have utilised the results to calculate Z_{eff}. At thermal energies we find $Z_{eff} = 0.037$ and $Z_{eff} = 0.048$ in the static exchange case and long range polarisation case respectively. These results are considerably smaller than the most recent, measured values of $Z_{eff} \sim 0.1 - 0.25$, and the possible reasons for the discrepancy are discussed.

The presence of a resonance in positron-atom scattering can be viewed as the attachment of a positron to the atom or as the binding of a positronium atom to the positive ion. The process is likely to be important in various scattering problems and the simplest case, that of positron attachment to a hydrogen atom, is considered here.

The method used is that of the projection operator in conjunction with a Rayleigh-Ritz variational technique.

The evidence for a positron-hydrogen atom bound state is presented as a result of the calculation and comparison made with the results of other workers.

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CONTENTS

CHAPTER 1 Positronium Page

Introduction 1

Annihilation 2

Positrons in Gases 4

Detection of Positronium 9

The Structure of Positronium 10

CHAPTER 2 Positronium Collisions in Gases

Introduction 17

Orthopositronium Collisions with Hydrogen 18

Positronium Collisions with Helium Ions 19

Orthopositronium Collisions with Helium Atoms 20

- (i) Statement of the Problem 21
- (ii) The Variational Proceedure 25
- (iii) The Integro-differential Equation 29
- (iv) Inclusion of the Long Range Potential 34

CHAPTER-3 The Van der-Waal's Interaction

Introduction 36

The Long Range Orthopositronium-helium Atom Interaction 39

- (i) Statement of the Problem 39
- (ii) Evaluation of the Integrals 43
- (iii) The Form of the Potential 49

CHAPTER 4 The Quenching of Orthopositronium in Gases

Introduction 54

The Quenching of Orthopositronium in Helium 57

CHAPTER 5 Numerical and Computational Techniques

Introduction 70

The Scattering Analysis 70

(i) Kernals 70

(ii) The Integro-differential Equation 74

The Analysis for Z_{eff} 78

CHAPTER 6 The Numerical Results

Introduction 81

The Scattering Results 81

(i) The Static Approximation 81

(ii) The Long Range Potential Approximation 83

(iii) Comparison of the Two Approximations 84

The Results for Z_{eff} 85

Conclusions 87

CHAPTER 7 The Attachment of Positrons to Gaseous Atoms

Introduction 90

The Projection Operator Method 94

The Variational Calculation 99

CHAPTER 8 The Numerical Solution of the Positron-hydrogen Atom Problem

Introduction 104

Numerical and Computational Techniques 104

Results and Discussion 106

APPENDICES

A The Variational Calculation and the Kernel 111

B The Functional I_t 118

C Evaluation of the Integrals in the Positron-hydrogen Atom Problem 121

REFERENCES 129

CHAPTER 1

POSITRONIUM

Introduction

The Schrodinger wave equation is applicable to studies of systems of particles in cases where the velocities involved are negligible compared with the velocity of light. Using the special theory of Relativity and a modification of the wave equation, (Dirac, 1930) predicted both positive and negative energy solutions for the case of a free electron. The negative energy case corresponds to a positive energy solution in which the electron has a positive charge instead of a negative one. The positively charged electron was called a positron. It was postulated that all the negative energy states were normally occupied by electrons, and a positron appeared as a 'hole' in the negative region when an electron made a transition to a positive energy level. Two years later (Anderson, 1932) detected the positron in a cloud chamber experiment. The charge to mass ratio was measured and found to have the same absolute value as that of the electron,(Thibaud, 1933). Later more accurate estimations confirmed this fact. The possible existence of a bound state of the electron and positron was postulated by (Mohorovicic, 1934), and (Ruark, 1945) gave the name Positronium to this system. The atom of positronium was calculated to have an ionization potential of 6.77 ev. Certain other polyelectron structures were also found to be stable, the system of two positrons and an electron, two electrons and a positron, and the positronium molecule (Hylleraas, 1947), (Hylleraas and Ore, 1947) and (Wheeler, 1946). The lifetimes of these latter, however, were negligibly small compared to that of positronium itself.

Annihilation

Since electromagnetic radiation can excite an electron from a negative energy state to one of positive energy in the phenomenon of pair creation, we must also consider the reverse effect, i.e. the electron colliding with a positron and making a radiative transition to the unoccupied negative energy level. If E_+ and E_- are the total energies of each particle and m their masses, then the energy of the emitted radiation will be,

$$E\gamma = E_- + E_+ + 2mc^2$$

In the absence of external fields at least two quanta of radiation must be emitted to conserve momentum. If the magnitude of E_- and E_+ are small the two quanta emitted in opposite directions in the centre of mass system will each have an energy of about $mc^2 = 0.51$ Mev. This characteristic radiation was observed soon after the discovery of the positron by (Thibaud, 1933) and (Curie and Joliot, 1933). The two quanta emission in predominantly opposite directions was demonstrated by (Klemperer, 1934).

The two quantum annihilation is allowed only for a pair state of complete spherical symmetry. This means that the two particles meet with zero orbital angular momentum, i.e. head on and with their spins antiparallel. Quantum mechanically the pair can be in close proximity only in two states; with their spins antiparallel in a singlet state, or parallel in a triplet state. In the case of a head on collision in the triplet state the selection rules, (Deutsch, 1953), show that three quanta are produced, coplaner in the centre of mass coordinates with an energy sum of 1.022 Mev and a statistically distributed individual energy shown in figure 1, (Ore and Powell, 1949). The line spectrum at 0.51 Mev for the singlet, two quantum annihilation is shown also for comparison.

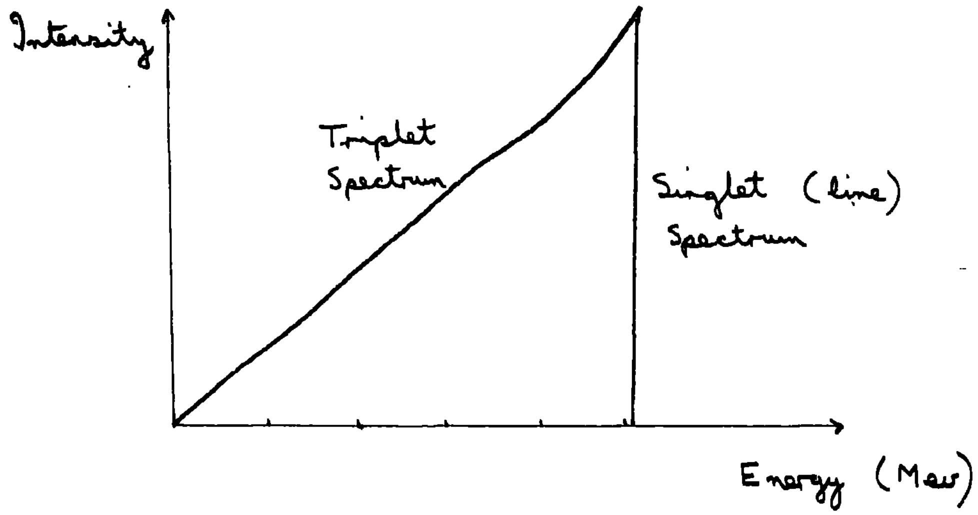


FIGURE 1.

The two cases of annihilation described are the only ones of importance. The probability of a triplet event is only 1/1120 that of a singlet event. The smallness of the triplet annihilation probability and the corresponding longer lifetime of the triplet state, is an important feature in the study of positronium as we will show. Suppose now that a positron in a gas prises loose an atomic electron and forms positronium. The positronium atom is held in dynamic equilibrium by a balance of electrostatic attraction of the two particles and the opposing force due to their rotary motion. The atom is formed in either the triplet or singlet state, statistical arguments showing that the triplet is three times as likely as the singlet state.

The two particles eventually suffer mutual annihilation and exhibit a predictable mean life. The mode of decay depends on the state they are in as discussed already. The lifetime of the singlet state is 1.25×10^{-10} seconds and the triplet lifetime is 1.4×10^{-7} seconds. Because of the long lifetime of triplet or orthopositronium, most of the work to date has been directed to its particular study.

The evaluation of the various lifetimes is discussed by (De Benedetti, 1956), and (De Benedetti and Corben, 1954).

Positrons in Gases

At the present time it is still impossible to obtain a clear picture in theory or experiment as to the history of a positron in passing through a gas, and only a broad outline can be given.

The usual source is ^{22}Na , emitting positrons of maximum energy 0.54 MeV which enter the gas and eventually fall to thermal energies of about 0.025 ev.

As the ^{22}Na emits a positron it decays to ^{22}Ne in an excited state which then decays to the ground state in 10^{-11}sec, emitting a photon of 1.28 MeV. This gives the indication to the experimentalist of the birth of the positron; the resulting annihilation radiation gives the subsequent death.

The important process of thermalization has been considered by (Massey and Mohr, 1954) and (Tao et al., 1963). As an indication of the processes involved we will consider the fate of positrons in argon gas.

The positrons undergo many reactions and the result is a composite lifetime for the annihilation depending on various components each indicating a particular process. The times have been estimated and we give a table in figure 2, indicating the processes for positrons in argon at a pressure of one atmosphere.

We can see that the positron first loses energy very quickly by inelastic collisions that cause ionization and excitation of argon atoms. On reaching the first ionization energy of argon, E_{ion} , the positron can form positronium by extracting an electron from the atom. An estimated 30% of all the positrons will form positronium. Alternatively the

Energy (ev)	Slowing Mechanism	Time(nsec.)	Process
500	Inelastic collision dominates	7	1. Slowing down 2. Other loss negligible
E_{ion} = 15.8	Inelastic and elastic		1. Slowing down 2. Small annihilation loss
E_{exc} = 11.6	Collisions comparable	90	1. Ps formation 2. Free annihilation 3. Slowing down
E_{thr} = 3.0	Elastic collisions only	12	1. Ps formation 2. Small free annihilation 3. Slowing down
0.9	Elastic collisions only	276	1. Slowing down 2. Compound formation 3. Eventual free annihilation
	Elastic collisions only	Long	1. Slowing down 2. Compound formation 3. Eventual free annihilation

FIGURE 2

positron can slow down by excitation of the argon or by elastic collisions. E_{thr} is the threshold below which positronium cannot be formed and is equal to the E_{ion} minus the positronium binding energy, 6.8 ev.

Above E_{ion} inelastic collisions predominate since they put less restriction on the subsequent electron velocity than does positronium formation. Even if positronium is formed from a fast moving positron it will soon break up in subsequent collisions due to its excess energy. Excitation levels such as $E_{exc} = 11 \cdot 6$ ev, the first excitation level of argon, will compete in the region between E_{exc} and E_{ion} . Most of the positronium formation then, occurs with positrons that have been reduced by a final inelastic collision to the energy region between E_{thr} and E_{exc} the so-called, 'Ore gap'.

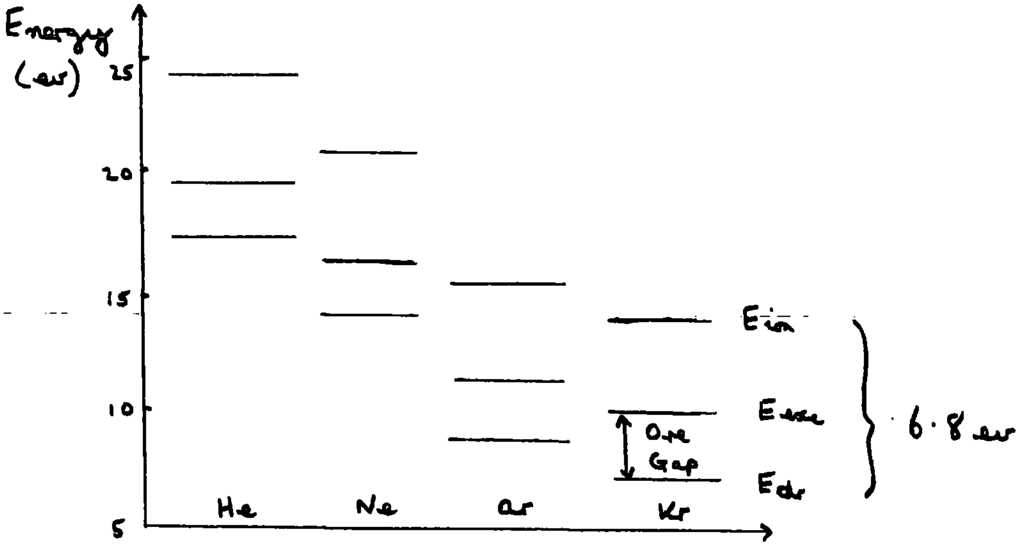
For some gases reasonable confirmation of the above theory has been found, (Deutsch 1953), (Pond, 1952), (Gittelman and Deutsch, 1956). Detailed calculations have been attempted on atomic and molecular hydrogen, (Massey and Mohr, 1954) and (Mohr, 1955), and helium (Lee Chang, 1957, 1958).

In figure 3, we show the position of the Ore gap for various rare gases. If the formation probability of positronium is β then we can define it as lying between the limits, (Green, 1966),

$$\frac{E_{ion} - (E_{ion} - 6 \cdot 8)}{E_{exc}} > \beta > \frac{E_{exc} - (E_{ion} - 6 \cdot 8)}{E_{ion}}$$

Experimental estimates of f for some gases are within or near the limits predicted, (Pond, 1952). The formation fraction f is influenced by magnetic and electric fields. A static electric field produces an increase in positronium formation, (Deutsch, 1953), and (Deutsch and Brown, 1952). The theory is that positrons which fall below the formation threshold for positronium are accelerated by the field back into the Ore gap and are then capable of forming positronium again.

FIGURE 3



The electric field effect has been studied in detail, (Deutsch and Hughes, 1956), (Marder et al, 1956), for many gases and the acceleration effect is supported except in those gases where competition from low lying excitation levels of the gaseous atoms occur.

Recent work of a theoretical nature on positronium formation in gases has concentrated on hydrogen and hydrogenlike atoms. An advance on earlier calculations was made by (Cheshire, 1964) using a version of the impulse approximation, the results being within a factor of 2 of the Born approximation results. (Bransden and Jundi, 1967) using the two-state approximation took into account the long range interactions between the hydrogen and positronium atoms in each channel and found that polarization forces dominate the cross section near the formation threshold for positronium. Using a coupled equations technique (Fels and Mittleman, 1967) calculated the formation cross section and found it 40 times smaller than the Born approximation. Finally, (Roy and Das, 1968), used a method employing field theory for bound states in quantum-electrodynamics and obtained results similar to (Massey and Mohr, 1954) but with the cross section maximum moved to a higher positron energy.

The phenomenon of positronium formation during the passage of positrons through gases has caused interesting modifications theoretically, in calculations of positron scattering cross sections and phase shifts in collisions with gaseous atoms. Even when the positron energy is too small to ionize the atom one can still allow for the virtual positronium formation where the positron in the scattering region moves as a bound system with an atomic electron without completely freeing that electron, and on leaving the scattering region it is energetically unable to detach the said electron and so leaves it behind. This would indicate virtual positronium formation as a short range correlation mainly in the form of a polarization arising from Coulombian forces. The importance of the process has been shown in the hydrogen case by (Spruch and Rosenberg, 1960), (Cody et al, 1964) and (Bransden, 1962). The case of positrons in helium is dealt with by (Kraidy, 1967) where virtual positronium is again shown to be an important effect.

Detection of positronium

Experimental evidence of positronium was first found by (Shearer and Deutsch, 1949). It was calculated that the ratio of two-photon to three photon annihilations for free positrons in a gas should be in the ratio of 372 to 1, (Ore and Powell, 1949). Now positronium formation will enhance the three-photon effect since the triplet state is three times as well populated as the singlet state.

Indication of positronium formation then, will be given by three factors.

(i) a decrease in the ratio mentioned above

(ii) a pressure independent orthopositronium lifetime of order 10^{-7} secs.

(iii) a change in the annihilation spectrum due to a decrease in the intensity of the singlet annihilation 0.5 MeV line.

(Shearer and Deutsch, 1949) confirmed positronium formation in nitrogen and argon by method (ii) and verified the fact by measurement of the triplet decay rate, (Deutsch, 1951). Method (i) and (iii) were used by (Rich, 1951), (Pond 1952), (Siegal, 1952), (Benedetti and Siegal, 1954) and (Dulit, 1956) for various gases. The direct observation of positron lifetime in gases also indicated formation of positronium, (Gittleman, 1958), (Celitans and Green, 1964), (Green and Tao, 1963), (Tao et al,1963). The annihilation spectrum of figure 1 was found to be in agreement with the experimental observation by (Lewis and Ferguson, 1953).

Two other possibilities are open for positronium detection but as they are dependent on the fine structure of positronium atom we will deal with them in the next section.

The Structure of Positronium

The gross structure of positronium states is exactly like that of hydrogen except for the effect of the different reduced mass of the electron. This leads to a reduction in energies by a factor of 2 as compared with a hydrogen atom with an infinitely massive nucleus. Consequently the ionization potential is 6.8 ev, the energy of the first excited state 5.1 ev, and the Lyman α-line of positronium lies at 2400 Å . To this degree of approximation the wave functions for positronium are the same as those for hydrogen but the relevant coordinate, i.e. the electron-positron seperation is twice as large as the electron-proton seperation in hydrogen. Since the two particles in the positronium atom are distinguishable there are no difficulties connected with the Pauli exclusion principle. The transition probability for optical dipole transitions is half that for corresponding hydrogen lines, the transition dipole moment is twice as large and the emitted frequency half that of hydrogen.

The possibility of observing positronium by detection of its Lyman α-line has been investigated. (Deutsch, 1953) showed that if formed in any excited state the positronium would radiate optically to the ground state rather than annihilate. Attempts to detect this radiation have not succeeded, (Brock and Streib, 1958), (Hughes, 1957) and (Duff and Heymann, 1963). However the concentrations of positronium obtained in practice, and especially in excited states, are extremely small in comparison with gas-concentrations typicallly used in spectroscopic work, thus no completely unambiguous result has yet been obtained.

The fine structure of positronium has been theoretically investigated by (Pirenne, 1947), (Berestetzki, 1949) and (Ferrell, 1951). Radiative corrections to the fine structure are discussed by (Karplus and Klein, 1952). A suitable review of the investigations is given in (DeBenedetti and Corben, 1954).

The main differences between the positronium and hydrogen fine structures are as follows.

(i) There is a relativistic orbit-orbit interaction between the particles which is negligible in the case of the slow moving proton of hydrogen.

(ii) The magnetic spin-spin interaction between the particles is of the same order as the fine structure, while in hydrogen this hyperfine structure is smaller in the ratio of the magnetic moments of proton and electron.

(iii) There is an additional spin dependent interaction arising from the possibility of virtual annihilation and recreation of the pair. This is a short range force important only in s-states. This annihilation force has also been considered by (Bhabha, 1936) in connection with positron-electron scattering. Of particular interest in the fine structure of positronium is the splitting between the triplet and singlet components of the 1s ground state. Basically this is due to two terms.

(i) The magnetic spin-spin interaction

(ii) The annihilation force.

If the splitting is ΔW then calculation gives,

$$\Delta W = 2.044 \times 10^5 \text{ Mc/sec.}$$

correct to order α^4 with respect to the gross structure where $\alpha = e^2/\bar{h}c$ as usual.

(Karplus and Klein, 1952), corrected this value to order α^5 by using advanced quantum electrodynamics and a number of refined theoretical arguments. Their corrected value was,

$$\Delta W = 2.0337 \times 10^5 \text{ Mc/sec.}$$

Let us now consider the ground state 1s in a magnetic field. Positronium does not show a first order Zeeman effect in any of its states. Since the masses of its two particles are equal and their charges opposite there is no magnetic moment due to the orbital motion. Similarly there is no net spin magnetic moment in triplet states. In singlet states there is no preferred spin direction so the expectation value of the moment is again zero.

There is however a second order Zeeman effect i.e. there can be an induced magnetic moment.

In figure 4, we show the ground state splitting of singlet and triplet positronium and the influence of the magnetic field on them.

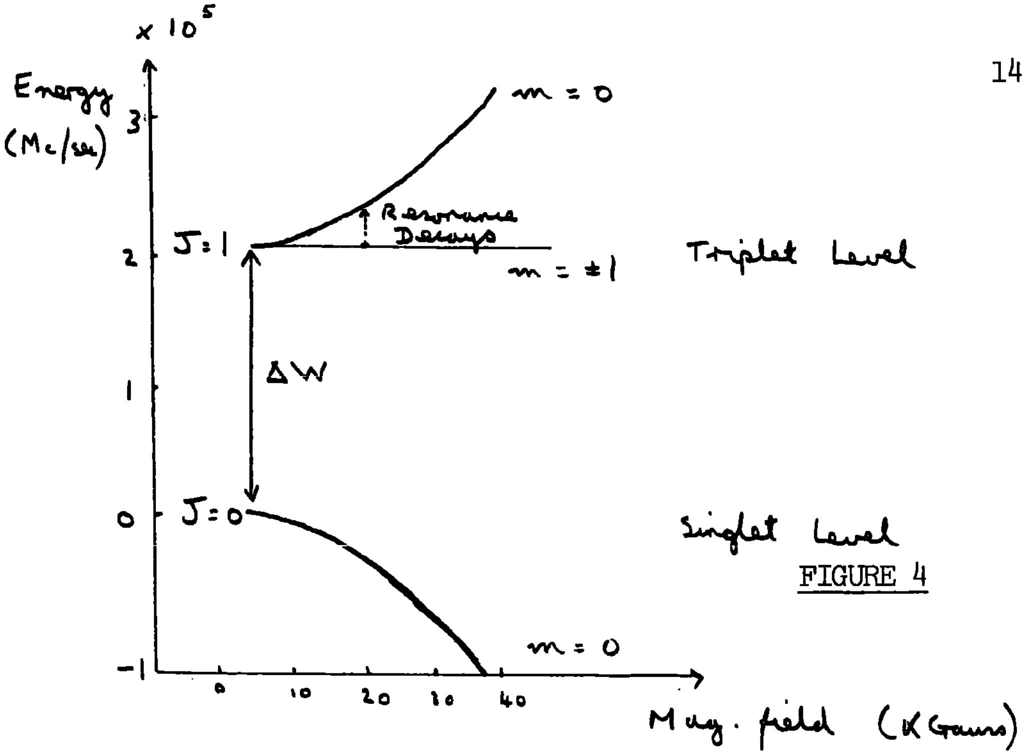


FIGURE 4

J is the total spin quantum number and m the magnetic quantum number. The important point is that the magnetic field introduces an admixture of singlet state in the triplet term with $m = 0$. As a result of this the number of triplet annihilations due to positronium decreases when a magnetic field is applied. This is because $1/3$ of what was a pure triplet state in absence of the field has now a finite probability of decaying as a singlet. This effect can be observed on applying a magnetic field and consequently related to ΔW. (Deutsch and Dulit, 1951) estimated ΔW by noting this so-called magnetic 'quenching' and found,

$$\Delta W = 2.26 \times 10^5 \text{ Mc/sec} \pm 15\%$$

Although the experiment could not measure to the α^r accuracy of the refined calculations if did indicate the presence of the annihilation force which is a correction to α^4

If a radiofrequency field is applied to the positronium already in a static magnetic field in a cavity then we expect resonance quenching to occur, i.e. the signal induces transitions from the $m = \pm 1$ levels of the triplet state to the $m = 0$ singlet state produced by the magnetic field. These decays are indicated in figure 4 by a dotted arrow. The resonance is sharp and the frequency and magnetic field values can be related to the value ΔW. In their brilliant experiments (Deutsch and Brown, 1952) and (Weinstein, Deutsch and Brown, 1954), the resonance was found and ΔW estimated. The value was,

$$\Delta W = 203380 \pm 40 \text{ Mc/sec.}$$

This remarkable agreement with the theoretical value was a triumph of modern day physics. It not only proved beyond all doubt the presence of positronium but confirmed the validity of the quantum electrodynamics used in the theoretical calculations.

It is ironical that the fine structure of positronium tells so much but the gross structure cannot yet be observed at all.

That so much can be gained by a study of this, the most fundamental of atoms, is an incentive to proceed with further elaboration to the problems presented by its interactions with the simpler gaseous atoms.

CHAPTER 2

POSITRONIUM COLLISIONS IN GASES

Introduction

In considering the collisions of positronium with gaseous atoms we concentrate on the ortho-positronium state because of its longer lifetime against annihilation and its consequently greater probability of colliding.

In atomic hydrogen the ortho-positronium can be converted to the para state by exchange of its own electron with a suitably orientated atomic electron.

The other possibility is for direct annihilation of the positron with the atomic electron.

In helium gas the latter process is the only source of quenching for the ortho-positronium because of the spin alignment restrictions on the ground state helium electrons. Now the rate of these collisions depends on the overlap of the wave functions describing the system so experimental observations of the quenching cross section can lead to correlation with theoretical calculation and an indication of the accuracy of the postulated form of the wave functions involved.

(Fraser, 1961) has calculated the total elastic and conversion cross sections for ortho-positronium with atomic hydrogen and the elastic cross section for ortho-positronium in helium. As a consequence of our work Fraser has recalculated his helium results and our results now agree for the static approximation.

(Kraidy, 1967) has considered the collision of positronium with helium ions, He^+, as part of his work on positron collisions in helium, considering only the case that is symmetric with respect to the space coordinates of the two electrons.

Of course, only the results for collisions in helium offer any hope of experimental verification.

We will give a brief outline of the results of Fraser and Kraidy for the hydrogen and helium ion case and the proceed to a detailed study of the atomic helium problem.

Ortho-positronium collisions with hydrogen

The total elastic and conversion cross sections were calculated for positronium kinetic energies 0 to 9.8 ev for the $\ell = 0$ partial wave only. A variational argument led to integro-differential equations which were solved numerically.

The cross sections were very strongly energy dependent. The ratio of conversion/total cross sections ranged from 0.176 to 0.070 over the range 0 to 6.8 ev. This is to be compared with the value 1/4 given by (Massey and Mohr, 1954). However Massey and Mohr used the Born approximation which can only be expected to give an indication of the higher energy results. The results of (Fraser, 1961) are outlined on next page.

Wave no. of O-Ps (atomic units)	Elastic (a_0^2)	Conversion (a_0^2)
0	603	106
0.2	109.3	16.1
0.4	43.4	4.48
0.6	25.4	2.00
0.8	15.5	1.08
1.0	9.2	0.64

The cross sections are seen to be very large at low energies.

Positronium collisions with helium ions

This collision is of no practical interest but is useful in that is was used to investigate the effect of allowing for positronium polarisation. The elastic cross section was calculated corresponding to,

$$Ps + He^+ \longrightarrow Ps + He^+$$

and also the effect on this cross section of the reaction

$$Ps + He^+ \rightarrow e^+ + He$$

due to coupling with the elastic case.

The cross sections were taken from the $\ell = 0 - 4$ cases. It was found that the second channel decreased the cross-sections considerably at the lower energies. The atomic polarizability was found to have almost no effect. The positronium polarization however considerably increased the elastic cross section, mainly in the $\ell = 0$ and $\ell = 1$ contributions, by a factor of ten at low positronium energies. This was thought to be due to the large polarizability of the positronium.

With all the corrections the range of cross section was $> 1200\ a_0^2$ at zero energy to $> 80\ a_0^2$ at 0.8 a.u. positronium kinetic energy, somewhat larger than the hydrogen atom cross sections.

Ortho-positronium collision with Helium atoms

We are calculating here the elastic cross sections in the static field approximation first and then extending the work to include the long range van der Waals interaction between the positronium and helium atoms.

We will consider the cases of $\ell = 0$, 1 and 2 although the extension to higher ℓ values will be quite apparent.

We neglect any excitation of the positronium and helium. Because of the coincidence of mass and electrical centres in normal positronium the direct interaction with the helium vanishes. The long range interaction was expected to have greatest effect at the lower energies, the effect at thermal energies being the pertinant one in view of the subsequent work on the quenching calculation in helium and the available experimental results.

(i) Statement of the Problem

As the helium nucleus has a much greater mass than the electrons and positron we assume it at rest and at the coordinate origin.

For a Hamiltonian H, total energy of the system E and wave function Ψ describing the system, Schrodinger's equation gives us,

$$(H - E)\Psi = 0$$

choosing units,

$$\left.\begin{aligned} \hbar &= 1 \\ m_e &= 1/2 \\ e^2 &= 2 \end{aligned}\right\}$$

results in the unit of length as a_0 and the unit of energy as the Rydberg, 13.6 ev.

In these units,

$$H = -\nabla_p^2 - \nabla_1^2 - \nabla_2^2 - \nabla_3^2 - \frac{2}{r_{1p}} - \frac{2}{r_{2p}} - \frac{2}{r_{3p}} + \frac{4}{r_p}$$

$$- \frac{4}{r_1} + \frac{4}{r_2} - \frac{4}{r_3} + \frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{23}}$$

Here r_{ij} is the distance between the i'th and j'th particles, either electrons or positron.

$\underset{\sim}{r}_1$ denotes the positronium electron and $\underset{\sim}{r}_2$ and $\underset{\sim}{r}_3$ the atomic electron coordinates.

$\underset{\sim}{r_p}$ is the positron coordinate.

It is convenient to define two new coordinates,

$$\underset{\sim}{\sigma_1} = \frac{1}{2}\left(\underset{\sim}{r_1} + \underset{\sim}{r_p}\right) \quad , \quad \underset{\sim}{\rho_1} = \underset{\sim}{r_1} - \underset{\sim}{r_p}$$

Here $\underset{\sim}{\sigma_1}$ is the distance of the positronium centre of mass from the helium nucleus and $\underset{\sim}{\rho_1}$ is the internal coordinate of the positronium atom. Coordinates are shown in figure 5.

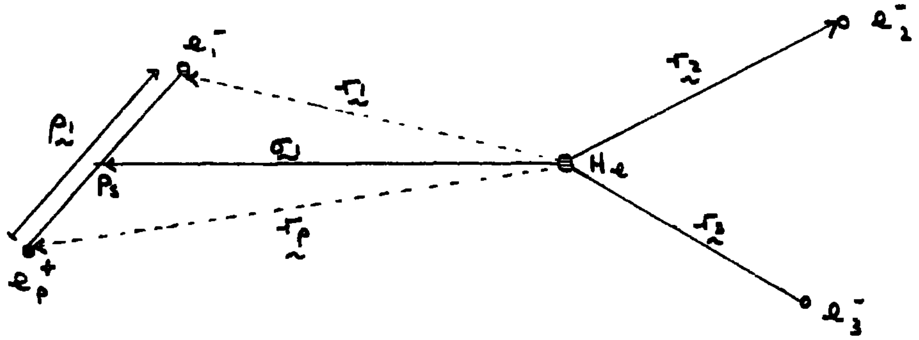


FIGURE 5

We can decompose the Hamiltonian as follows.

Transform,

$$-\nabla_p^2 - \nabla_1^2 - \frac{2}{r_{1p}}$$

into

$$-\frac{1}{2}\nabla_{\sigma_1}^2 - 2\nabla_{\rho_1}^2 - \frac{2}{\rho_1}$$

Now the normalized positronium ground state wave function can be written

$$\phi(\rho_1) = \left(\frac{1}{8\pi}\right)^{1/2} e^{-\frac{\rho_1}{2}}$$

because of the similarity of the atom to hydrogen. Its ground state energy will be, $E_0^{Ps} = -\frac{1}{2}$ and the wave function will satisfy,

$$\left(-2\nabla_{\rho_1}^2 - \frac{2}{\rho_1}\right)\phi(\rho_1) = E_0^{Ps}\,\phi(\rho_1)$$

The helium ground state wave function is symmetric in the coordinates of its electrons and satisfies,

$$\left(-\nabla_2^2 - \nabla_3^2 - \frac{4}{r_2} - \frac{4}{r_3} + \frac{2}{r_{23}}\right)\psi(\underset{\sim}{r_2},\underset{\sim}{r_3}) = E_0^{He}\,\psi(\underset{\sim}{r_2},\underset{\sim}{r_3})$$

with $\psi(\underset{\sim}{r_2},\underset{\sim}{r_3})$ the wave function and E_0^{He} the ground state. Now the eigenfunction of the above equation is not known in closed form.

As a first approximation we assume,

$$\psi_t(\underset{\sim}{r_2},\underset{\sim}{r_3}) = \left(\frac{\mu^3}{\pi}\right)e^{-\mu(r_2+r_3)}$$

where $\mu = \frac{27}{16}$ and gives an energy value of $-2\mu^2$ which is 2% from the experimental value. It is open to question whether this is a good or bad approximation in the present case, probably the only definite indication will be by trying a better one, a problem to be attempted in the near future. However at low energies, it has given some success in electron-helium collisions, (Moisewitch, 1953),(Massey and Moisewitch, 1954) so we assume its applicability here.

If we take E as the total energy of the system and k as the magnitude of the positronium momentum then,

$$E = \frac{1}{2}k^2 - E_0^{Ps} - E_0^{He}$$

The exact solution of the Schrodinger equation in the limit of $\sigma_1 \to \infty$ will be a product function of the positronium and helium ground states with a function describing the centre of mass motion of the positronium.

Since the system of the two atoms form triplet states we require an asymptotic form, for a particular value of ℓ ,

$$\Psi_\ell \underset{\sigma_1\to\infty}{\sim} v_\ell(\sigma_1)\,\phi(\rho_1)\,\psi(\underset{\sim}{r_2},\underset{\sim}{r_3})\,\chi_1^1(p,1)\,\chi_0^0(2,3)$$

where $v_\ell(\sigma_1)$ is the function describing the positronium centre of mass motion and the χ_1^1 is a triplet spin function and χ_0^0 a singlet spin function.

We write

$$v_\ell(\sigma) = \frac{f_\ell(\sigma)}{\sigma}\,Y_\ell^0(\Omega_\sigma)$$

where Y_ℓ^0 is the spherical harmonic and Ω_σ the angular coordinate of $\underset{\sim}{\sigma}$ and we require the following boundary conditions on $f(\sigma)$,

$$f_\ell(0) = 0$$

and

$$f_\ell(\sigma) \underset{\sigma\to\infty}{\sim} \sin\left(k\sigma - \frac{\ell\pi}{2}\right) + a_\ell \cos\left(k\sigma - \frac{\ell\pi}{2}\right)$$

The parameter a_ℓ is the tangent of the phase shift η_ℓ i.e.

$$a_\ell = \tan\eta_\ell$$

The partial cross section for elastic scattering is given by,

$$\sigma_\ell = \frac{4\pi}{k^2}(2\ell+1)\sin^2\eta_\ell$$

and the total elastic cross section σ_T is,

$$\sigma_T = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\eta_\ell$$

We also define the diffusion or momentum transfer cross-section as,

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

The asymptotic form consequently suggests the trial wave function, Ψ_ℓ^t , which must be antisymmetric for interchange of any two electrons,

$$\begin{aligned} \Psi_\ell^t (\underline{r}_p, \underline{r}_1, \underline{r}_2, \underline{r}_3) = {} & v_\ell(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underline{r}_2, \underline{r}_3)\, \chi_1^1(p,1)\, \chi_0^0(2,3) \\ & + v_\ell(\sigma_2)\, \phi(\rho_2)\, \psi_t(\underline{r}_3, \underline{r}_1)\, \chi_1^1(p,2)\, \chi_0^0(3,1) \\ & + v_\ell(\sigma_3)\, \phi(\rho_3)\, \psi_t(\underline{r}_1, \underline{r}_2)\, \chi_1^1(p,3)\, \chi_0^0(1,2) \end{aligned}$$

The basic problem then is to find the $v_\ell(\sigma)$ with the correct boundary conditions and with asymptotic form giving the necessary phase shifts, η_ℓ .

(ii) <u>The Variational Proceedure</u>

We will follow the Kohn variational method, (Kohn, 1948), and so form

$$I_t = \sum_{\text{SPINS}} \int d\underline{r}_p\, d\underline{r}_1\, d\underline{r}_2\, d\underline{r}_3\; \Psi_\ell^t (H - E_t)\, \Psi_\ell^t \qquad (1)$$

Note that we use E_t as the approximation to the true energy where,

$$E_t = \frac{1}{2} k^2 - \frac{1}{2} - 2\mu^2$$

i.e. we have assumed the helium binding energy to be given by the simple variational result. The use of E_t preserves the consistency of the proceedure but it is difficult to see how to justify the neglect of the difference between E and E_t in a rigorous manner.

We express the spin functions in the usual notation,

$$\chi_1^1(i,j) = \alpha(i)\,\beta(j)$$

$$\chi_0^0(i,j) = \frac{1}{\sqrt{2}}\left\{\alpha(i)\,\beta(j) - \beta(i)\,\alpha(j)\right\}$$

and we know,

$$\left.\begin{aligned} \sum \alpha^2(i) &= 1 \\ \sum \beta^2(i) &= 1 \\ \sum \alpha(i)\,\beta(i) &= 0 \end{aligned}\right\}$$

Considering the spin summation in (1) we see there are three products of the type,

$$\sum_{\text{SPINS}} \chi_1^1(p,1)\,\chi_0^0(2,3)\,\chi_1^1(p,1)\,\chi_0^0(2,3) = 1$$

and six cross products of the type,

$$\sum_{\text{SPINS}} \chi_1^1(p,1)\,\chi_0^0(2,3)\,\chi_1^1(p,2)\,\chi_0^0(3,1) = -\frac{1}{2}$$

Allowing for the symmetry of the positional coordinate parts of Ψ_ℓ^t we find, changing $d\mathbf{r}_p\,d\mathbf{r}_1$ to $d\boldsymbol{\sigma}_1\,d\boldsymbol{\rho}_1$ that,

$$I_t = 3\int d\boldsymbol{\sigma}_1\,d\boldsymbol{\rho}_1\,d\mathbf{r}_2\,d\mathbf{r}_3\,v_\ell(\sigma_1)\,\phi(\rho_1)\,\psi_t(\mathbf{r}_2,\mathbf{r}_3)$$

$$[H - E_t]\left[v_\ell(\sigma_1)\,\phi(\rho_1)\,\psi_t(\mathbf{r}_2,\mathbf{r}_3) - v_\ell(\sigma_2)\,\phi(\rho_2)\,\psi_t(\mathbf{r}_3,\mathbf{r}_1)\right]$$

we now compute δI_* for variations $\delta v_\ell(\sigma)$ i.e. for variations $\delta f_\ell(\sigma)$ where,

$$\delta f_\ell(\sigma) \underset{\sigma\to\infty}{\sim} \delta a_\ell^* \cos\left(k\sigma - \frac{\ell\pi}{2}\right)$$

The calculation of δI_* is given in Appendix A as it is somewhat lengthy and complicated. We arrive at,

$$\frac{1}{3}\left[\delta I_* - 6\pi k\,\delta a_*\right] = \int d\underset{\sim}{\sigma_1}\;\delta v_\ell(\sigma_1)\Big[\left\{-\nabla_{\sigma_1}^2 - k^2\right\} v_\ell(\sigma_1) + \int d\underset{\sim}{\sigma_2}\; L(\underset{\sim}{\sigma_1},\underset{\sim}{\sigma_2})\, v_\ell(\sigma_2)\Big]$$

and

$$L(\underset{\sim}{\sigma_1},\underset{\sim}{\sigma_2}) = \frac{8\mu^3}{\pi^2}\int d\underset{\sim}{r}\Big\{k^2 + 1 + 8\mu + \frac{2\mu(\underset{\sim}{\sigma_1}-\underset{\sim}{r}).(2\underset{\sim}{\sigma_1}-\underset{\sim}{r})}{|\underset{\sim}{\sigma_1}-\underset{\sim}{r}|\;|2\underset{\sim}{\sigma_1}-\underset{\sim}{r}|}$$
$$+ \frac{2\mu(\underset{\sim}{\sigma_2}-\underset{\sim}{r}).(2\underset{\sim}{\sigma_2}-\underset{\sim}{r})}{|\underset{\sim}{\sigma_2}-\underset{\sim}{r}|\;|2\underset{\sim}{\sigma_2}-\underset{\sim}{r}|} - (6\mu-4)\left[\frac{1}{|2\underset{\sim}{\sigma_1}-\underset{\sim}{r}|} + \frac{1}{|2\underset{\sim}{\sigma_2}-\underset{\sim}{r}|}\right] - \frac{8}{r}$$
$$- \frac{2}{|\underset{\sim}{\sigma_1}-\underset{\sim}{\sigma_2}|} + 4\left[\frac{1}{r} - \left(\frac{1}{r}+\mu\right)e^{-2\mu r}\right] + \frac{4e^{-2\mu|2\underset{\sim}{\sigma_1}-\underset{\sim}{r}|}}{|2\underset{\sim}{\sigma_1}-\underset{\sim}{r}|}$$
$$+ \frac{4e^{-2\mu|2\underset{\sim}{\sigma_2}-\underset{\sim}{r}|}}{|2\underset{\sim}{\sigma_2}-\underset{\sim}{r}|} + 4\mu e^{-2\mu|2\underset{\sim}{\sigma_1}-\underset{\sim}{r}|} + 4\mu e^{-2\mu|2\underset{\sim}{\sigma_2}-\underset{\sim}{r}|}\Big\}$$
$$e^{-|\underset{\sim}{\sigma_1}-\underset{\sim}{r}|}\, e^{-|\underset{\sim}{\sigma_2}-\underset{\sim}{r}|}\, e^{-\mu|2\underset{\sim}{\sigma_1}-\underset{\sim}{r}|}\, e^{-\mu|2\underset{\sim}{\sigma_2}-\underset{\sim}{r}|} \tag{4}$$

and we have changed $\underset{\sim}{r_p}$ to $\underset{\sim}{r}$.

Requiring that,

$$\delta I_* - 6\pi k\,\delta a_* = 0$$

we find,

$$(\nabla_{\sigma_1}^2 + k^2)\,v_\ell(\sigma_1) = \int d\underset{\sim}{\sigma_2}\; L(\underset{\sim}{\sigma_1},\underset{\sim}{\sigma_2})\; v_\ell(\sigma_2) \tag{3}$$

If the $v_\ell(\sigma)$ satisfy the equation then $I_t = 0$ as is shown in appendix B.

If Ψ_ℓ was the exact wave function and E the exact energy then we could form,

$$I = \sum_{\text{SPINS}} \int d r_{\underset{\sim}{\ell}}\, d r_{\underset{\sim}{1}}\, d r_{\underset{\sim}{2}}\, d r_{\underset{\sim}{3}}\; \Psi_\ell (H - E)\, \Psi_\ell = 0 \qquad (2)$$

Then varying Ψ_ℓ as $\delta \Psi_\ell$ with asymptotic form,

$$\delta \Psi_\ell \sim \delta v_\ell(\sigma_1)\, \phi(\rho_1)\, \psi(r_{\underset{\sim}{2}}, r_{\underset{\sim}{3}})\, \chi_1^1(\rho, 1)\, \chi_0^0(2,3)$$

we would get,

$$\delta I - 6\pi k\, \delta a = 0$$

Suppose $\Delta \Psi_\ell$ is the error in Ψ_ℓ^* i.e.,

$$\Psi_\ell^* = \Psi_\ell + \Delta \Psi_\ell$$

Substitution in (1) and using (2) would give,

$$I_t = I + \Delta I$$

$$\therefore \quad I_t = 6\pi k\, \Delta a$$

where,

$$a_t = a + \Delta a$$

A better approximation to the real a would be then,

$$a = a_* - \frac{I_t}{6\pi k}$$

Since I_* is zero for the satisfaction of the equation (3) we see that a_* is a good approximation to a to second order in the difference between Ψ_ℓ^* and Ψ_ℓ . This assumes that we may neglect the difference between E_* and E of course.

(iii) The Integro-differential equation

The equation to be solved is,

$$(\nabla_{\sigma_1}^2 + k^2)\, v_\ell(\sigma_1) = \int d\underset{\sim}{\sigma_2}\; L(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2})\; v_\ell(\sigma_2)$$

$$\therefore\; (\nabla_{\sigma_1}^2 + k^2)\, \frac{f_\ell(\sigma_1)}{\sigma_1}\, Y_\ell^0(\Omega_{\sigma_1}) = \int d\underset{\sim}{\sigma_2}\, L(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2})\, \frac{f_\ell(\sigma_2)}{\sigma_2} Y_\ell^0(\Omega_{\sigma_2})$$

Multiply by $Y_\ell^0(\Omega_{\sigma_2})$ and integrate over Ω_{σ_1} whence,

$$\left\{\frac{d^2}{d\sigma_1^2} + k^2 - \frac{\ell(\ell+1)}{\sigma_1^2}\right\} f_\ell(\sigma_1) = \sigma_1 \int d\Omega_{\sigma_1} Y_\ell^0(\Omega_{\sigma_1}) \int d\underset{\sim}{\sigma_2}\; L(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2})\, \frac{f_\ell(\sigma_2)}{\sigma_2}\, Y_\ell^0(\Omega_{\sigma_2})$$

Consider first the term resulting on the R.H.S. from the energy dependent part of $L(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2})$

This is,

$$\sigma_1 \int d\Omega_{\sigma_1} Y_\ell^0(\Omega_{\sigma_1}) \int d\underset{\sim}{\sigma_2}\; \frac{8\mu^3}{\pi^2} \int d\underset{\sim}{r}\; k^2 e^{-|\underset{\sim}{\sigma_1} - \underset{\sim}{r}|} e^{-|\underset{\sim}{\sigma_2} - \underset{\sim}{r}|}$$

$$e^{-\mu|2\underset{\sim}{\sigma_1} - \underset{\sim}{r}|} e^{-\mu|2\underset{\sim}{\sigma_2} - \underset{\sim}{r}|}\; \frac{f_\ell(\sigma_2)}{\sigma_2}\; Y_\ell^0(\Omega_{\sigma_2})$$

$$= k^2 \int_0^\infty f(\sigma_2)\, d\sigma_2\; L_1^{(\ell)}(\sigma_1, \sigma_2)$$

where,

$$L_1^{(\ell)}(\sigma_1, \sigma_2) = \frac{8\mu^3 \sigma_1 \sigma_2}{\pi^2} \int d\Omega_{\sigma_1} Y_\ell^0(\Omega_{\sigma_1}) e^{-|\underset{\sim}{\sigma_1} - \underset{\sim}{r}|}$$

$$e^{-\mu|2\underset{\sim}{\sigma_1} - \underset{\sim}{r}|} \int d\Omega_{\sigma_2} Y_\ell^0(\Omega_{\sigma_2}) e^{-|\underset{\sim}{\sigma_2} - \underset{\sim}{r}|} e^{-\mu|2\underset{\sim}{\sigma_2} - \underset{\sim}{r}|} \int d\underset{\sim}{r}$$

we now expand,

$$e^{-|\underset{\sim}{\sigma_1} - \underset{\sim}{r}|} e^{-\mu|2\underset{\sim}{\sigma_1} - \underset{\sim}{r}|} = \frac{1}{\sigma_1 r} \sum_{\ell=0}^{\infty} (2\ell+1) G_\ell(\sigma_1, r) P_\ell(\eta_1) \qquad (5)$$

where $\eta_1 = \dfrac{\underset{\sim}{\sigma_1} \cdot \underset{\sim}{r}}{\sigma_1 r}$

and in fact

$$G_\ell(\sigma_1, r) = \frac{\sigma_1 r}{2} \int_{-1}^{1} d\eta_1 \, P_\ell(\eta_1) e^{-|\underset{\sim}{\sigma_1} - \underset{\sim}{r}|} e^{-\mu|2\underset{\sim}{\sigma_1} - \underset{\sim}{r}|}$$

This is seen to be true by back substitution in the expansion (5). Substituting (5) in the expression for $L_1^{(\ell)}(\sigma_1, \sigma_2)$ and using,

$$P_\ell(\eta_1) = \frac{4\pi}{(2\ell+1)} \sum_{m=-\ell}^{\ell} Y_\ell^{m*}(\Omega_{\sigma_1}) Y_\ell^m(\Omega_r)$$

we find, using the orthogonality properties of the Y_ℓ^m that

$$L_1^{(\ell)}(\sigma_1, \sigma_2) = 128\mu^3 \int_0^\infty dr \, G_\ell(\sigma_1, r) G_\ell(\sigma_2, r)$$

We now consider the energy independent part of the kernal. This is taken as $L_2^{(\ell)}(\sigma_1, \sigma_2)$ such that,

$$\left\{ \frac{d^2}{d\sigma_1^2} + k^2 - \frac{\ell(\ell+1)}{\sigma_1^2} \right\} f_\ell(\sigma_1) = \int_0^\infty \left[k^2 L_1^{(\ell)}(\sigma_1, \sigma_2) + L_2^{(\ell)}(\sigma_1, \sigma_2) \right]$$

$$f_\ell(\sigma_2) \, d\sigma_2$$

i.e.,

$$L_2^{(l)}(\sigma_1,\sigma_2) = \frac{8\mu^3\sigma_1\sigma_2}{\pi^2}\int d\Omega_{\sigma_1}\, Y_l^0(\Omega_{\sigma_1})\int d\Omega_{\sigma_2}\, Y_l^0(\Omega_{\sigma_2})$$

$$\int d\underline{r}\,\Big\{1 + 8\mu + \frac{2\mu(\underline{\sigma_1}-\underline{r}).(2\underline{\sigma_1}-\underline{r})}{|\underline{\sigma_1}-\underline{r}|\,|2\underline{\sigma_1}-\underline{r}|} + \frac{2\mu(\underline{\sigma_2}-\underline{r}).(2\underline{\sigma_2}-\underline{r})}{|\underline{\sigma_2}-\underline{r}|\,|2\underline{\sigma_2}-\underline{r}|}$$

$$-(6\mu-4)\left[\frac{1}{|2\underline{\sigma_1}-\underline{r}|} + \frac{1}{|2\underline{\sigma_2}-\underline{r}|}\right] - \frac{8}{r} - \frac{2}{|\underline{\sigma_1}-\underline{\sigma_2}|} + 4\Big[\frac{1}{r} - \Big(\frac{1}{r}+\mu\Big)$$

$$e^{-2\mu r}\Big] + \frac{4\,e^{-2\mu|2\underline{\sigma_1}-\underline{r}|}}{|2\underline{\sigma_1}-\underline{r}|} + \frac{4\,e^{-2\mu|2\underline{\sigma_2}-\underline{r}|}}{|2\underline{\sigma_2}-\underline{r}|} + 4\mu\, e^{-2\mu|2\underline{\sigma_1}-\underline{r}|}$$

$$+ 4\mu\, e^{-2\mu|2\underline{\sigma_2}-\underline{r}|}\Big\}\, e^{-|\underline{\sigma_1}-\underline{r}|}\, e^{-|\underline{\sigma_2}-\underline{r}|}\, e^{-\mu|2\underline{\sigma_1}-\underline{r}|}$$

$$e^{-\mu|2\underline{\sigma_2}-\underline{r}|}$$

We will split $L_2^{(l)}(\sigma_1,\sigma_2)$ into components for ease of manipulation. The terms in curly brackets,

$$1 + 8\mu - \frac{8}{r} + 4\Big[\frac{1}{r} - \Big(\frac{1}{r}+\mu\Big)e^{-2\mu r}\Big]$$

give by comparison with the evaluation of $L_1^{(l)}(\sigma_1,\sigma_2)$

$$L_{2a}^{(l)}(\sigma_1,\sigma_2) = 128\mu^3\int_0^\infty dr\,\Big[1 + 8\mu - \frac{4}{r} - 4\Big(\frac{1}{r}+\mu\Big)e^{-2\mu r}\Big]$$

$$G_l(\sigma_1,r)\,G_l(\sigma_2,r)$$

By a similar expansion proceedure as before we define,

$$G_l^{(3)}(\sigma,r) = \frac{\sigma r}{2}\int_{-1}^{1} d\eta\, P_l(\eta)\, e^{-|\underline{\sigma}-\underline{r}|}\, e^{-3\mu|2\underline{\sigma}-\underline{r}|}$$

$$J_l(\sigma,r) = \frac{\sigma r}{2}\int_{-1}^{1} d\eta\, P_l(\eta)\,\frac{e^{-|\underline{\sigma}-\underline{r}|}\, e^{-\mu|2\underline{\sigma}-\underline{r}|}}{|2\underline{\sigma}-\underline{r}|}$$

$$J_l^{(3)}(\sigma,r) = \frac{\sigma r}{2}\int_{-1}^{1} d\eta\, P_l(\eta)\,\frac{e^{-|\underline{\sigma}-\underline{r}|}\, e^{-3\mu|2\underline{\sigma}-\underline{r}|}}{|2\underline{\sigma}-\underline{r}|}$$

$$K_l(\sigma,r) = \frac{\sigma r}{2}\int_{-1}^{1} d\eta\, P_l(\eta)\,\frac{e^{-|\underline{\sigma}-\underline{r}|}\, e^{-\mu|2\underline{\sigma}-\underline{r}|}}{|\underline{\sigma}-\underline{r}|\,|2\underline{\sigma}-\underline{r}|}$$

Substituting the various corresponding expansions back in the expression for $L_2^{(l)}(\sigma_1,\sigma_2)$ the terms in curly brackets,

$$-\frac{(6\mu-4)}{|2\underset{\sim}{\sigma}_1-\underset{\sim}{r}|}+4\mu\, e^{-2\mu|2\underset{\sim}{\sigma}_1-\underset{\sim}{r}|}+\frac{4\,e^{-2\mu|2\underset{\sim}{\sigma}_1-\underset{\sim}{r}|}}{|2\underset{\sim}{\sigma}_1-\underset{\sim}{r}|}$$

$$+\frac{2\mu(\underset{\sim}{\sigma}_1-\underset{\sim}{r}).(2\underset{\sim}{\sigma}_1-\underset{\sim}{r})}{|\underset{\sim}{\sigma}_1-\underset{\sim}{r}|\;|2\underset{\sim}{\sigma}_1-\underset{\sim}{r}|}$$

give,

$$L_{2b}^{(l)}(\sigma_1,\sigma_2)=128\mu^3\int_0^\infty dr\Big\{-(6\mu-4)\,J_l(\sigma_1,r)$$

$$+4\mu\, G_l^{(3)}(\sigma_1,r)+4\,J_l^{(3)}(\sigma_1,r)+2\mu(2\sigma_1^2+r^2)\,K_l(\sigma_1,r)$$

$$-\frac{6\mu\sigma_1 r}{(2l+1)}\Big[l\,K_{l-1}(\sigma_1,r)+(l+1)\,K_{l+1}(\sigma_1,r)\Big]\Big\}\,G_l(\sigma_2,r)$$

The $K_{l-1}(\sigma_1,r)$ and $K_{l+1}(\sigma_1,r)$ terms arise from the $\underset{\sim}{\sigma}_1 . \underset{\sim}{r}$ terms which contain $P_1(\eta_1)=\eta_1$ explicitly and result in products of three spherical harmonics.

To write $L_{2b}^{(l)}(\sigma_1,\sigma_2)$ more concisely we define $H_l(\sigma_1,r)$ such that

$$L_{2b}^{(l)}(\sigma_1,\sigma_2)=128\mu^3\int_0^\infty dr\; H_l(\sigma_1,r)\;G_l(\sigma_2,r)$$

The corresponding terms in σ_2 lead to,

$$L_{2c}^{(l)}(\sigma_1,\sigma_2)=128\mu^3\int_0^\infty dr\; H_l(\sigma_2,r)\;G_l(\sigma_1,r)$$

The remaining term in curly brackets in $L_2^{(l)}(\sigma_1,\sigma_2)$ is,

$$-\frac{2}{|\underset{\sim}{\sigma}_1-\underset{\sim}{\sigma}_2|}$$

We expand,

$$\frac{1}{|\underset{\sim}{\sigma_1}-\underset{\sim}{\sigma_2}|} = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\frac{4\pi}{2\ell+1}\,\gamma_\ell(\sigma_1,\sigma_2)\,Y_\ell^{m*}(\Omega_{\sigma_1})\,Y_\ell^{m}(\Omega_{\sigma_2})$$

where

$$\gamma_\ell(\sigma_1,\sigma_2) = \frac{\sigma_<^{\ell}}{\sigma_>^{\ell+1}}$$

We also make use of the expansion,

$$\int d\Omega\, Y_{\ell_1}^{m_1}(\Omega)\, Y_{\ell_2}^{m_2}(\Omega)\, Y_{\ell_3}^{m_3 *}(\Omega)$$

$$= \left[\frac{(2\ell_1+1)(2\ell_2+2)}{4\pi\,(2\ell_3+1)}\right]^{1/2} C(\ell_1\ell_2\ell_3;\, m_1 m_2)$$

$$C(\ell_1\ell_2\ell_3;\, 0\,0)$$

where the C are Clebsch-Gordon coefficients.

Substituting the various expansions back we arrive at,

$$L_{2d}^{(\ell)}(\sigma_1,\sigma_2) = 128\,\mu^3 \int_0^\infty dr\,(-2) \sum_{\ell'=0}^{\infty} D_{\ell'}(\sigma_1\,\sigma_2,\,\ell)\, G_{\ell'}(\sigma_1,r)$$

$$G_{\ell'}(\sigma_2,r)$$

and

$$D_{\ell'}(\sigma_1,\sigma_2,\ell) = \sum_{\ell''=0}^{\infty}\frac{(2\ell'+1)}{(2\ell+1)}\, C^2(\ell'\,\ell\,\ell'';\,0\,0)\,\gamma_{\ell''}(\sigma_1,\sigma_2)$$

We have calculated for ℓ = 0, 1 and 2. For these low values of ℓ the expression for $D_{\ell'}(\sigma_1\sigma_2,\ell)$ can be shown to reduce to simple expressions by the rules of Clebsch-Gordon coefficients.

ℓ	$D_{\ell'}(\sigma_1\sigma_2,\ell)$
0	$\gamma_{\ell'}$
1	$\frac{\ell'}{(2\ell'-1)}\gamma_{\ell'-1} + \frac{(\ell'+1)}{(2\ell'+3)}\gamma_{\ell'+1}$
2	$\frac{3(\ell'-1)\ell'}{2(2\ell'-1)(2\ell'+3)}\gamma_{\ell'-2} + \frac{\ell'(\ell'+1)}{(2\ell'-1)(2\ell'+3)}\gamma_{\ell'} + \frac{3(\ell'+1)(\ell'+2)}{2(2\ell'+3)(2\ell'+5)}\gamma_{\ell'+2}$

Finally then the complete term for $L_2^{(\ell)}(\sigma_1,\sigma_2)$ is,

$$L_2^{(\ell)}(\sigma_1,\sigma_2) = 128\mu^3\int_0^\infty dr\left\{\left[1+8\mu-\frac{4}{r}-4\left(\frac{1}{r}+\mu\right)e^{-2\mu r}\right]\right.$$

$$G_\ell(\sigma_1,r)\,G_\ell(\sigma_2,r) + H_\ell(\sigma_1,r)\,G_\ell(\sigma_2,r) + H_\ell(\sigma_2,r)$$

$$\left.G_\ell(\sigma_1,r) - 2\sum_{\ell'=0}^{\infty} D_{\ell'}(\sigma_1\sigma_2,\ell)\,G_{\ell'}(\sigma_1,r)\,G_{\ell'}(\sigma_2,r)\right\}$$

We define,

$$L^{(\ell)}(\sigma_1,\sigma_2) = k^2 L_1^{(\ell)}(\sigma_1,\sigma_2) + L_2^{(\ell)}(\sigma_1,\sigma_2)$$

and the integro-differential equation is finally,

$$\left\{\frac{d^2}{d\sigma_1^2} + k^2 - \frac{\ell(\ell+1)}{\sigma_1^2}\right\}f_\ell(\sigma_1) = \int_0^\infty d\sigma_2\, L^{(\ell)}(\sigma_1,\sigma_2)\, f_\ell(\sigma_2)$$

(iv) Inclusion of the long range potential

The Van der Waals potential V_{vdw} is derived from V by considering V at large constant σ_1 . In appendix A then we must include this as the direct interaction between the positronium and helium atoms, i.e., we replace,

$$\int d\underset{\sim}{\rho_1}\, d\underset{\sim}{r_2}\, d\underset{\sim}{r_3}\;\; \phi(\rho_1)\; \Psi_*(\underset{\sim}{r_2}, \underset{\sim}{r_3})\; V\; \phi(\rho_1)\; \Psi_*(\underset{\sim}{r_2}, \underset{\sim}{r_3})$$

by,

$$V_{VDW}$$

Following the analysis through we arrive at the modified integro-differential equation,

$$\left\{ \frac{d^2}{d\sigma_1^2} + k^2 - \frac{\ell(\ell+1)}{\sigma_1^2} - 2V_{VDW} \right\} f_\ell(\sigma_1) = \int_0^\infty d\sigma_2\; L^{(\ell)}(\sigma_1, \sigma_2)\, f_\ell(\sigma_2)$$

The equation has to be solved for the $f_\ell(\sigma)$ which can then be used to compute the various phase shifts and cross sections.

CHAPTER 3

THE VAN DER WAAL'S INTERACTION

Introduction

The existence of the van der Waal's forces was known as long ago as the middle of the eighteenth century and speculation as to their nature and effect continued throughout the nineteenth century in connection with work on capillary action and surface tension. Eventually it was realised that the forces were due to electrical interactions and various theoretical postulates of the form taken by the forces had success in explaining physical effects dependent on the forces. The present century started with the work of (Reinganum, 1903, 1912) who pointed out that neutral molecules carrying localized charges repel or attract each other with forces varying more rapidly with distance then $1/R$, where R is the distance between the molecules. On the average the force is attractive due to torques tending to rotate the molecules into attractive positions. (Keesom, 1921) considered molecules bearing dipoles. He showed that if the molecules could feel each others presence, rather than rotate randomly, then a net attraction between the molecules would result. For dipoles of moment P_1 and P_2 a mean interaction energy is generated proportional to $P_1^2 P_2^2 / R^6$. He postulated also an effect of alignment which enabled molecules caught in attractive positions to be restricted to oscillation rather than rotation.

Objections to the theory were that many molecules exhibiting attractive forces were known to have no dipole moments and also, due to higher kinetic energies of the molecules at higher temperatures, the alignment effect should disappear at high temperatures; but in fact the van der Waals forces persisted. Even the extension to quadrupole interaction could not explain this temperature dependent problem.

(Debye, 1920) showed that molecules should not be regarded as rigid structures but as deformable distributions of charge. If placed in an external field they would become polarized and for a non-uniform field attractive forces would be called into play, This explained the high temperature persistence of the forces since their magnitude is independent of the state of motion of the molecules. Again quadrupole effects were assumed to produce the polarizing field.

Now molecules with closed shells, in particular the rare gas atoms, posses a high degree of spherical symmetry in their charge distribution and so should not display much van der Waal's attraction. The fact that they do possessstrong van der Waal's attraction was a major difficulty in the existing theory.

It was left to (Wang, 1927) using quantum mechanics to first lead the way to the true explanation of the major van der Waals effect. He calculated the interactions between two hydrogen atoms for large separation and showed them to be attractive. Then (London, 1930) recognized the fuller meaning of these forces and derived formulae for their calculation, calling the phenomenon the dispersion effect. The explanation of the effect is that due to the movement of the electrons in the atom, say hydrogen, each atom is momentarily a dipole capable of inducing in a neighbouring atom a dipole moment parallel to itself. This causes rotation in phase, alignment, and corresponding attraction. The method of (London, 1930) and also (Eisenschitz and London, 1930) was a perturbation calculation dependent on an expansion of the wave function of the system in terms of a selected set of the unperturbed wave functions of the two molecules or atoms.

A variational theory of the forces was launched,due chiefly to (Hasse, 1930) and extended by (Slater and Kirkwood, 1931) (Hasse, 1930) calculated the interatomic force at large distances for hydrogen and helium while (Slater and Kirkwood, 1931) made the method applicable to most non-polar molecules in the normal state. (Buckingham, 1936) calculated the value of the mutual van der Waal's interaction energy between the two atoms and related the dipole-dipole constant to the atomic polarizabilities of the atoms. He evaluated dipole-dipole constants for the rare-gases and also showed the importance of the dipole-quadrupole terms.

A fine review of the early work is given in (Margenau, 1939) and of further progress by (Dalgarno and Kingston, 1959).

It might be mentioned that since our calculation presented in this chapter, a new formula has been derived for the dipole-dipole term in the van der Waal's interaction between two spherically symmetrical atoms by (Öpik, 1967). The approximation takes the distortion of each atom in the instantaneous dipole field of the other atom to be proportional to the corresponding adiabatic distortion. A variational technique gives good agreement for atomic hydrogen and the rare gases.

The long-range Orthopositronium-helium Interaction

The calculation presented here is a variational one based on the methods of (Slater and Kirkwood, 1931), (Hasse, 1931), and (Pauling and Beach, 1935). The trial function used was also mentioned in (Schiff, 1949) together with a brief indication of the calculation of the van der Waal's energy for two atoms. The principle of minimum energy which is used is seen in a similar calculation on the polarisation of hydrogen by positron impact (Stone, 1966).

(i) Statement of the Problem

In our problem we are dealing with two dissimilar atoms, one of which, the positronium atom, has a very high polarisability, in fact eight times that of a hydrogen atom. This led us to expect a considerable change in the cross sections and phase shifts of the collision problem and an improvement in the final values of the Z_{eff} mentioned in the next chapter, expecially at the very low energies. Even if the changes were found not to be large, the trend of the interaction is important since, because of the coincidence of the mass and electrical centres in the positronium, the mean interaction energy with the helium nucleus vanishes and the only effects arise from polarization of the positronium.

It is known (Bransden and Jundi, 1967) that the polarisation potential for distortion of a positronium atom moving in the field of a proton only contains contributions from odd multipoles, the even multipoles vanishing identically because of the coincidence of the centres of mass and charge in the positronium atom. It is clear, therefore, that the dipole component alone will be an accurate approximation to the complete adiabatic potential in this case. Similarly in this problem we take the dipole component only as a sufficiently accurate approximation.

Since we are chiefly concerned with scattering at very low velocities it is appropriate to introduce the adiabatic approximation in which the kinetic energy of the positronium atom is at first neglected, i.e. in the coordinates of the previous chapter we regard the atoms initially as being fixed in space at a distance σ_1 apart.

The total Hamiltonian for the system is,

$$H = -\nabla_p^2 - \nabla_1^2 - \nabla_2^2 - \nabla_3^2 - \frac{2}{r_{1p}} - \frac{2}{r_{2p}} - \frac{2}{r_{3p}} + \frac{4}{r_p}$$

$$-\frac{4}{r_1}+\frac{4}{r_2}-\frac{4}{r_3}+\frac{2}{r_{12}}+\frac{2}{r_{13}}+\frac{2}{r_{23}}$$

We regard the potential V as a perturbation on an unperturbed Hamiltonian H_0 so that,

$$H = H_0 + V$$

where

$$H_0 = -\nabla_p^2-\nabla_1^2-\nabla_2^2-\nabla_3^2-\frac{2}{r_{1p}}-\frac{4}{r_2}-\frac{4}{r_3}+\frac{2}{r_{23}}$$

and,

$$V = -\frac{2}{r_{2p}}-\frac{2}{r_{3p}}+\frac{4}{r_p}-\frac{4}{r_1}+\frac{2}{r_{12}}+\frac{2}{r_{13}}$$

We now approximate V by considering σ_1 as large and fixed and expanding V in terms of $1/\sigma_1$, retaining the term in $1/\sigma_1^3$ only. In the modified coordinates,

$$V = \frac{4}{|\underset{\sim}{\sigma_1}-\frac{1}{2}\underset{\sim}{\rho_1}|}-\frac{4}{|\underset{\sim}{\sigma_1}+\frac{1}{2}\underset{\sim}{\rho_1}|}+\frac{2}{|\underset{\sim}{\sigma_1}+\frac{1}{2}\underset{\sim}{\rho_1}-\underset{\sim}{r_2}|}$$

$$+\frac{2}{|\underset{\sim}{\sigma_1}+\frac{1}{2}\underset{\sim}{\rho_1}-\underset{\sim}{r_3}|}-\frac{2}{|\underset{\sim}{\sigma_1}-\frac{1}{2}\underset{\sim}{\rho_1}-\underset{\sim}{r_2}|}-\frac{2}{|\underset{\sim}{\sigma_1}-\frac{1}{2}\underset{\sim}{\rho_1}-\underset{\sim}{r_3}|}$$

Expanding the denominators and keeping the term in $1/\sigma_1^3$ we have the approximation to the above perturbing potential,

$$V_p = \frac{2}{\sigma_1^3}\left\{\underset{\sim}{\rho_1}\cdot(\underset{\sim}{r_2}+\underset{\sim}{r_3}) - 3(\underset{\sim}{n}\cdot\underset{\sim}{\rho_1})\left[\underset{\sim}{n}\cdot(\underset{\sim}{r_2}+\underset{\sim}{r_3})\right]\right\}$$

where $\underset{\sim}{n}$ is a unit vector in the direction of $\underset{\sim}{\sigma_1}$. If the z axis is taken along the line of centres of the two atoms,

$$V_p = \frac{2}{\sigma_1^3}\left\{\rho_{1x}(r_{2x}+r_{3x})+\rho_{1y}(r_{2y}+r_{3y})-2\rho_{1z}(r_{2z}+r_{3z})\right\}$$

This interaction is treated in second order perturbation theory, the effective interaction between the atoms, being quadratic in V_p, varies like $1/\sigma_1^6$ and is the van der Waals interaction. In the adiabatic approximation we define the wave function of the system as Ψ_{POL} which satisfies the Schroedinger equation,

$$\left\{ H - (E + E_0) \right\} \Psi_{POL} = 0$$

where $E = E(\sigma_1)$ is the van der Waal's energy and E_0 the sum of the ground state energies of the helium and positronium atoms. We define the total energy in the adiabatic approximation as,

$$E_T = E(\sigma_1) + E_0$$

For each fixed value of σ_1 the eigenvalue of the Hamiltonian is E_T then. We now wish to determine $E(\sigma_1)$. This was done by the Raeleigh-Ritz variational method. The trial form of Ψ_{POL} was taken as,

$$\Psi^t_{POL} = \phi(\rho_1)\, \psi_t(\underline{r}_2, \underline{r}_3) \left\{ 1 + A(\sigma_1) V_p \right\}$$

Adiabatically for a fixed σ_1, $A(\sigma_1)$ is effectively a constant. $\psi_t(\underline{r}_2, \underline{r}_3)$ was the same as that used in the collision calculation giving a helium ground state energy of

$E_0^{He} = -5.695$ and hence,

$$E_0 = -6.195$$

The trial wave function was not antisymmetrised because exchange effects are of short range and not important in determining the long range part of $E(\sigma_1)$.

We now define the total energy of the system as,

$$E_T = \frac{\langle \Psi_{POL}^* | H | \Psi_{POL}^* \rangle}{\langle \Psi_{POL}^* | \Psi_{POL}^* \rangle} \qquad (1)$$

With the condition that,

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

These last two equations lead to a determination of $A(\sigma_1)$, which is the variational parameter in the van der Waal's potential,

$$V_{VDW} = \langle \Psi_{POL}^* | V | \Psi_{POL}^* \rangle$$

(ii) <u>Evaluation of the Integrals</u>

The integrals in (1) are taken in three sets .

(a) $IA = \langle \Psi_{POL}^* | \Psi_{POL}^* \rangle$

(b) $IB = \langle \Psi_{POL}^* | H_0 | \Psi_{POL}^* \rangle$

(c) $IC = \langle \Psi_{POL}^* | V | \Psi_{POL}^* \rangle$

The term V_p arises in Ψ^{*}_{POL} and it is convenient to express V_p in terms of spherical harmonic functions in polar coordinates.

We note,

$$Y_0^0(\Omega) = \sqrt{\frac{1}{4\pi}}$$

$$Y_1^{\pm 1}(\Omega) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$$

$$Y_1^0(\Omega) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

where Ω is the solid angle and θ and ϕ the angular polar coordinates. If in V_p we express the coordinates as spherical polars, inspection shows that,

$$V_p = -\frac{8\pi}{3}\frac{\rho_1 r_2}{\sigma_1^3}\left\{Y_1^1(\Omega_{\rho_1})Y_1^{-1}(\Omega_{r_2}) + Y_1^1(\Omega_{r_2})Y_1^{-1}(\Omega_{\rho_1}) + 2Y_1^0(\Omega_{\rho_1})Y_1^0(\Omega_{r_2})\right\} - \frac{8\pi}{3}\frac{\rho_1 r_3}{\sigma_1^3}\left\{Y_1^1(\Omega_{\rho_1})Y_1^{-1}(\Omega_{r_3}) + Y_1^1(\Omega_{r_3})Y_1^{-1}(\Omega_{\rho_1}) + 2Y_1^0(\Omega_{\rho_1})Y_1^0(\Omega_{r_3})\right\} \tag{2}$$

(a) $IA = \langle \Psi^{*}_{POL} \mid \Psi^{*}_{POL} \rangle$

$$= \langle \phi\psi^{*}(1 + AV_p) \mid \phi\psi^{*}(1 + AV_p) \rangle$$

$$\therefore\ IA = \langle \phi\psi^{*} \mid \phi\psi^{*} \rangle + 2A\langle \phi\psi^{*} \mid \phi\psi^{*}V_p \rangle + A^2\langle \phi\psi^{*}V_p \mid \phi\psi^{*}V_p \rangle$$

Because of the normalisation of $\phi(\rho_1)$ and $\Psi_t(r_2, r_3)$ the first term is unity. From the form of V_p we see that the second term vanishes. The third term is evaluated by substituting (2) and integrating over the angular variables. The remaining non-zero terms are then integrated over the radial coordinates. This leads to,

$$I_A = 1 + \frac{192\, A^2}{\mu^2 \sigma_1^6}$$

(b) $$I_B = \langle \bar{\Psi}^t_{POL} \,|\, H_0 \,|\, \bar{\Psi}^t_{POL} \rangle$$

$$\therefore I_B = \langle \phi \Psi_t | H_0 | \phi \Psi_t \rangle + A \langle \phi \Psi_t | H_0 | \phi \Psi_t V_p \rangle$$

$$+ A \langle \phi \Psi_t V_p | H_0 | \phi \Psi_t \rangle + A^2 \langle \phi \Psi_t V_p | H_0 | \phi \Psi_t V_p \rangle$$

The first term is the expression for the unperturbed ground state energy E_0, and the second and third terms are again evidently zero. The fourth term is non-zero and rather complicated, though straight forward, to evaluate.

First we express H_0 in terms of σ_1 and ρ_1 as in the previous chapter, i.e. we put,

$$H_0 = -\frac{1}{2} \nabla_{\sigma_1}^2 - 2 \nabla_{\rho_1}^2 - \frac{2}{\rho_1} - \nabla_2^2 - \nabla_3^2 - \frac{4}{r_2} - \frac{4}{r_3} + \frac{2}{r_{23}}$$

Since $\nabla_{\sigma_1}^2$ is here a null operator we ignore it. We have to consider now the result of operating on $| \phi \, \psi_* \, V_\rho \rangle$ with $\nabla_{\rho_1}^2$ and ∇_2^2 and ∇_3^2.

Substitution of V_ρ and the expresions for the wave functions leads to,

$$\nabla_{\rho_1}^2 \, | \phi \, \psi_* \, V_\rho \rangle = \left[\frac{1}{4} - \frac{2}{\rho_1} \right] | \phi \, \psi_* \, V_\rho \rangle$$

If we write V_ρ as the sum of two terms $V_\rho(2)$ and $V_\rho(3)$ as those containing terms in r_2 and r_3 then we find,

$$(\nabla_2^2 + \nabla_3^2) \, | \phi \, \psi_* \, V_\rho \rangle = \left[2\mu^2 V_\rho - \frac{8\mu}{r_2} V_\rho(2) - \frac{4\mu}{r_2} V_\rho(3) \right] | \phi \, \psi_* \rangle$$

The term in $1/r_{23}$ is evaluated by expanding,

$$\frac{1}{r_{23}} = \sum_{l=0}^{\infty} \frac{r_<^{\,l}}{r_>^{\,l+1}} \, \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}(\Omega_{r_2}) \, Y_l^{m}(\Omega_{r_3})$$

In all integrations over angular variables we use of course the orthonormality property of the spherical harmonics, namely,

$$\int d\Omega \; Y_l^{m*}(\Omega) \, Y_{l'}^{m'}(\Omega) = \delta_{ll'} \, \delta_{mm'}$$

and also the equality,

$$Y_l^{-m}(\Omega) = (-1)^m \, Y_l^{m*}(\Omega)$$

In the radial integrations over r_2 and r_3 in the integral containing $1/r_{23}$ we remember to allow for the two ranges, i.e. for $r_2 > r_3$ and $r_2 < r_3$.

The evaluation is straight-forward but lengthy and we will simply tabulate the results.

We let, $\langle p | = \langle \phi \, \Psi_t \, V_p |$

then,

$$IB_1 = \langle p | -2 \nabla_{\rho_1}^2 | p \rangle = \frac{96}{\mu^2 \sigma_1^6}$$

$$IB_2 = \langle p | -\nabla_2^2 - \nabla_3^2 | p \rangle = \frac{384}{\sigma_1^6}$$

$$IB_3 = \langle p | -2/\rho_1 - 4/r_2 - 4/r_3 | p \rangle = -\frac{1152}{\mu \sigma_1^6} - \frac{96}{\mu^2 \sigma_1^6}$$

$$IB_4 = \langle p | 2/r_{23} | p \rangle = \frac{196}{\mu \sigma_1^6}$$

whence,

$$IB = E_0 + \frac{4A^2}{\sigma_1^6} \left(96 - \frac{239}{\mu} \right)$$

(c) $$IC = \langle \Psi_{pol}^t | V | \Psi_{pol}^t \rangle$$

$$\therefore \; IC = \langle \phi \, \Psi_t | V | \phi \, \Psi_t \rangle + 2A \langle \phi \, \Psi_t | V | \phi \, \Psi_t \, V_p \rangle$$

$$+ A^2 \langle \phi \, \Psi_t \, V_p | V | \phi \, \Psi_t \, V_p \rangle$$

The symmetric nature of the first and third terms, and the fact that the centres of charge of the electron and positron in the unperturbed positronium atom are coincident, makes them zero. The second term is non-zero and leads to rather complicated integrals which are dealt with by (Roothaan, 1951) in his papers on molecular integrals.

We have,

$$IC = 2A \left\langle \phi\,\psi_t \right| -\frac{2}{|\underset{\sim}{\sigma_1} - \underset{\sim}{r_2} - \frac{1}{2}\underset{\sim}{\rho_1}|} + \frac{2}{|\underset{\sim}{\sigma_1} - \underset{\sim}{r_2} + \frac{1}{2}\underset{\sim}{\rho_1}|}$$

$$-\frac{2}{|\underset{\sim}{\sigma_1} - \underset{\sim}{r_2} - \frac{1}{2}\underset{\sim}{\rho_1}|} + \frac{2}{|\underset{\sim}{\sigma_1} - \underset{\sim}{r_2} + \frac{1}{2}\underset{\sim}{\rho_1}|} - \frac{4}{|\underset{\sim}{\sigma_1} + \frac{1}{2}\underset{\sim}{\rho_1}|} + \frac{4}{|\underset{\sim}{\sigma_1} - \frac{1}{2}\underset{\sim}{\rho_1}|} \left| \phi\,\psi_t V_p \right\rangle$$

From symmetry considerations, this reduces to,

$$IC = 2A \left\langle \phi\,\psi_t \right| \frac{4}{|\underset{\sim}{\sigma_1} - \underset{\sim}{r_2} + \frac{1}{2}\underset{\sim}{\rho_1}|} + \frac{4}{|\underset{\sim}{\sigma_1} - \underset{\sim}{r_2} + \frac{1}{2}\underset{\sim}{\rho_1}|} \left| \phi\,\psi_t V_p \right\rangle$$

By splitting V_p as before we finally get,

$$IC = 2A \left\langle \phi\,\psi_t \right| \frac{8}{|\underset{\sim}{\sigma_1} - \underset{\sim}{r_2} + \frac{1}{2}\underset{\sim}{\rho_1}|} \left| \phi\,\psi_t V_p(2) \right\rangle$$

Of course $|\underset{\sim}{\sigma_1} - \underset{\sim}{r_2} + \frac{1}{2}\underset{\sim}{\rho_1}|$ is r_{12} and we can imagine the positronium atom with a centre of coordinates such that the electron is situated at $\frac{1}{2}\underset{\sim}{\rho_1}$ and the positron at $-\frac{1}{2}\underset{\sim}{\rho_1}$. This enables a comparison to be made with the above mentioned paper and in the notation of that paper,

$$IC = \frac{128A}{\mu\sigma_1^3}\left\{ [2P\Pi_a | 2P\Pi_b] + [2P\Sigma_a | 2P\Sigma_b] \right\}$$

where we define,

$$\xi = \frac{1}{2}(\mu+1) \quad , \quad K = \frac{\mu^2+1}{\mu^2-1}$$

$$\tau = \frac{\mu-1}{\mu+1} \quad , \quad \rho_a = \mu\,\sigma_1$$

$$\rho = \frac{\sigma_1}{2}(\mu+1) \quad , \quad \rho_b = \sigma_1$$

and, a refers to the helium and b to the positronium atoms. The molecular integrals are,

$$[2p\pi_a|2p\pi_b] = [\xi / (1+\tau)(1-\tau)\rho^3][1 - (1-\kappa)^3$$

$$\{\tfrac{1}{16}(8+9\kappa+3\kappa^2)(1+2\rho_a) + \tfrac{1}{8}(5+3\kappa)\rho_a^2 + \tfrac{1}{8}\rho_a^3\}e^{-2\rho_a}$$

$$-(1+\kappa)^3\{\tfrac{1}{16}(8-9\kappa+3\kappa^2)(1+2\rho_b) + \tfrac{1}{8}(5-3\kappa)\rho_b^2 + \tfrac{1}{8}\rho_b^3\}e^{-2\rho_b}]$$

$$[2p\Sigma_a|2p\Sigma_b] : [2\xi / (1+\tau)(1-\tau)\rho^3][1 - (1-\kappa)^3$$

$$\{\tfrac{1}{16}(8+9\kappa+3\kappa^2)(1+2\rho_a+2\rho_a^2) + \tfrac{3}{16}(3+2\kappa)\rho_a^3 + \tfrac{1}{8}\rho_a^4\}$$

$$e^{-2\rho_a} - (1+\kappa)^3\{\tfrac{1}{16}(8-9\kappa+3\kappa^2)(1+2\rho_b+2\rho_b^2)$$

$$+ \tfrac{3}{16}(3-2\kappa)\rho_b^3 + \tfrac{1}{8}\rho_b^4\}e^{-2\rho_b}]$$

Define,

$$F(\sigma_1) = [2p\pi_a|2p\pi_b] + [2p\Sigma_a|2p\Sigma_b]$$

then,

$$IC = \frac{128\ A\ F(\sigma_1)}{\mu\ \sigma_1^3} \qquad (3)$$

(iii) <u>The form of the potential</u>

Equation (1) can now be expressed in terms of the integrals

i.e., $$E_T = \frac{IB + IC}{IA}$$

$$\therefore E_T = \frac{E_0 + \frac{4A^2}{\sigma_1^6}\left(96 - \frac{239}{\mu}\right) + \frac{128\ A\ F(\sigma_1)}{\mu\ \sigma_1^3}}{1 + \frac{192\ A^2}{\mu^2\sigma_1^6}}$$

Let

$$\left.\begin{aligned} \alpha &= \frac{4}{\sigma_1^{\,6}}\left(96 - \frac{239}{\mu}\right) \\ \beta &= \frac{128\ F(\sigma_1)}{\mu\ \sigma_1^{\,3}} \\ \gamma &= \frac{192}{\mu^2\ \sigma_1^{\,6}} \end{aligned}\right\}$$

Then,

$$E_T = \frac{E_0 + \alpha A^2 + \beta A}{1 + \gamma A^2}$$

Differentiating E_T with respect to A and putting the result equal to zero we find, on taking the negative square root in the quadratic solution for A, that,

$$A = \frac{1}{\beta\gamma}\left\{(\alpha - \gamma E_0) - \left[(\alpha - \gamma E_0)^2 + \beta^2\gamma\right]^{1/2}\right\}$$

The negative square root is taken in order that the long range interaction vanishes at $\sigma_1 = 0$. This is substituted back in the expression (3), for $IC = V_{vdw}$ giving,

$$V_{vdw} = \frac{1}{\gamma}\left\{(\alpha - \gamma E_0) - \left[(\alpha - \gamma E_0)^2 + \beta^2\gamma\right]^{1/2}\right\} \qquad (4)$$

We use a computer to evaluate this expression for various values of σ_1 . The results are in Table I and the potential is displayed graphically in figure 6.

We note that as $\sigma_1 \to \infty$ the expression for $F(\sigma_1)$ becomes zero since $[2p\pi_a|2p\pi_b] = -[2p\Sigma_a|2p\Sigma_b]$ in the limit. Hence, from (4) with $\beta = 0$,

$$V_{vDW}\Big]_{\sigma_1=0} = 0$$

Consider now the expansion of A for large σ_1 .

$$A \underset{\sigma_1\to\infty}{\sim} \frac{1}{\beta\gamma}\left\{(\alpha-\gamma E_0)-(\alpha-\gamma E_0)\left(1+\frac{\beta^2\gamma}{2(\alpha-\gamma E_0)^2}\right)\right\}$$

$$\therefore \quad A \underset{\sigma_1\to\infty}{\sim} -\frac{\beta}{2(\alpha-\gamma E_0)} \tag{5}$$

Now for large σ_1 also,

$$E_T \underset{\sigma_1\to\infty}{\sim} (E_0+\alpha A^2+\beta A)(1-\gamma A^2)$$

which becomes on keeping terms in $1/\sigma_1^6$ only,

$$E_T \underset{\sigma_1\to\infty}{\sim} E_0 + \frac{\beta A}{2} \;----$$

Using (5),

$$E_T - E_0 \underset{\sigma_1\to\infty}{\sim} \frac{\beta^2}{4(\gamma E_0-\alpha)}$$

$$\therefore \quad E_T - E_0 \underset{\sigma_1\to\infty}{\sim} -\frac{19.33}{\sigma_1^6}$$

But $E_T - E_0$ is equivalent to the van der Waal's energy corresponding to V_{VDW} , so,

$$V_{vdw} \underset{\sigma_1 \to \infty}{\sim} - \frac{19.33}{\sigma_1^6}$$

TABLE I

The van der Waal's potential variation. V_{vdw} in atomic units and σ_1 in units of a_0 .

σ_1	V_{vdw}
0	0
0.25	-0.0001
0.5	-0.0013
0.75	-0.0050
1.0	-0.0113
1.5	-0.0245
2.0	-0.0288
2.5	-0.0244
3.0	-0.0170
3.5	-0.0107
4.0	-0.0064
4.5	-0.0037
5.0	-0.0022
5.5	-0.0013
6.0	-0.0008
6.5	-0.0005
7.0	-0.0003
7.5	-0.0002
8.0	-0.0002
8.5	-0.0001
9.0	-0.0001
9.5	-0.0001

A method giving a rough estimate of the van der Waal's forces from molecular polarizabilities was given by (London, 1930). The interaction energy is given as,

$$E(\sigma_1) = -\frac{3}{2} \cdot \frac{P_A P_B}{\sigma_1^6} \cdot \frac{I_A I_B}{I_A + I_B}$$

where P_A and P_B are the molecular or atomic polarizabilities, and I_A and I_B the first ionization energies approximately. For helium, $I_{He} = 1.809$, $P_{He} = 1.376$. $I_{Ps} = \frac{1}{4}$, $P_{Ps} = 36$. We take $P_{Ps} = 36$ i.e. eight times the calculated value of $9/2$ for hydrogen, because the P_{Ps} value is a volume dependent number and the diameter of positronium is twice that of hydrogen. The P_{He} is the experimental value. Substituting these values gives,

$$E(\sigma_1) = -\frac{29.11}{\sigma_1^{6}}$$

If we use the value of $P_{He} = 1.11$ calculated by (Kraidy, 1967) we get,

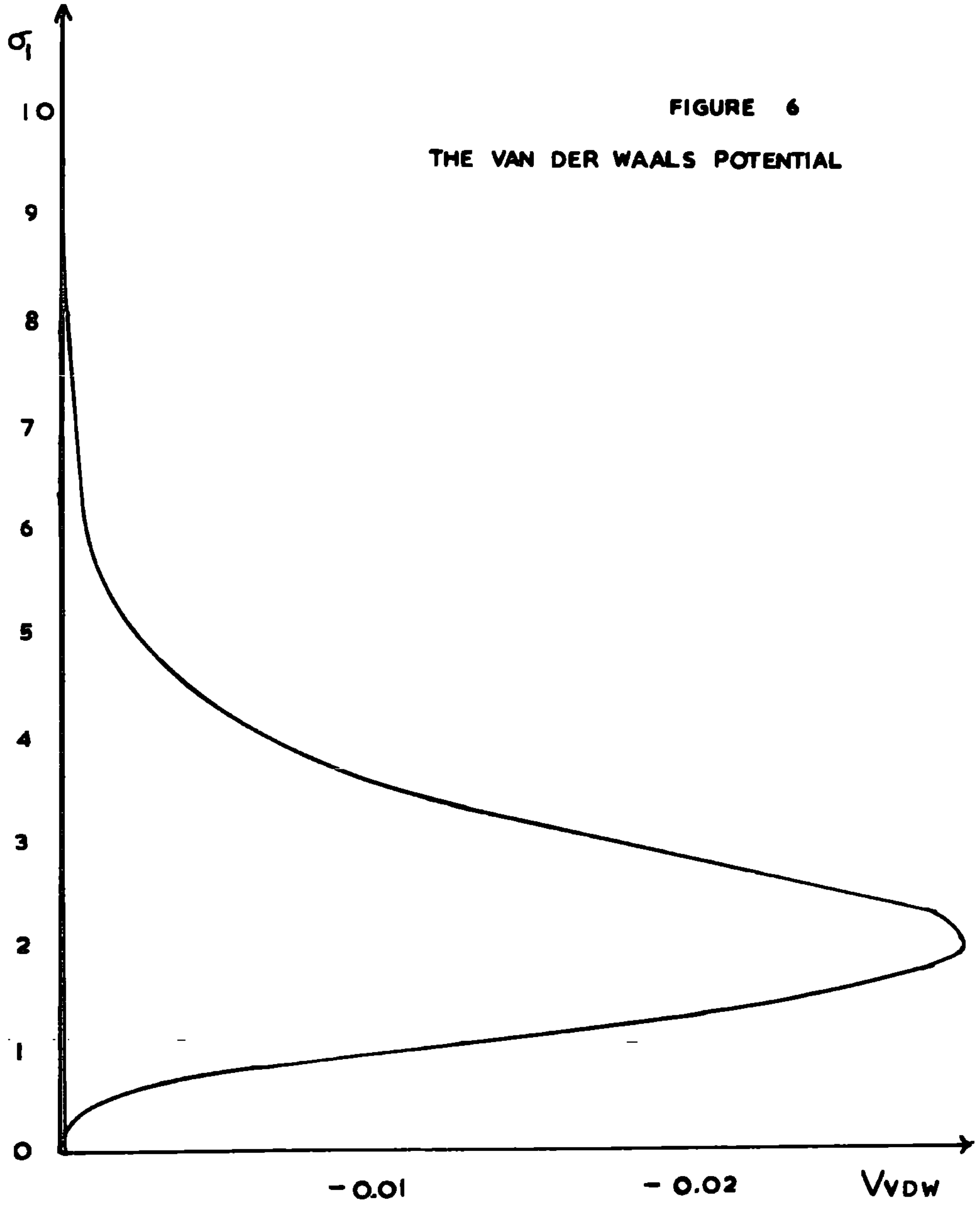
$$E(\sigma_1) = -\frac{23.48}{\sigma_1^{6}}$$

These equations show the rough approximation to our more accurate form of the asymptotic van der Waal's potential. The comparison is favourable and the above method gives the expected overestimation of the constant term shown by results in (Pauling and Wilson, 1935).

Figure 6 shows the usual form of a long range interatomic potential with a minimum energy value of about -0.029 atomic units at an atomic separation of about $2a_0$. The half width of the well in the potential is also about $2a_0$.

FIGURE 6

THE VAN DER WAALS POTENTIAL



CHAPTER 4

THE QUENCHING OF ORTHOPOSITRONIUM BY GASES

Introduction

We can define the quenching of positronium as the conversion in collision of triplet orthopositronium to singlet parapositronium, which experimentally means a reduction in the observed number of three γ-ray annihilation events.

Quenching can also take place in the presence of an external magnetic field and under application of a further radio frequency electromagnetic field but we are concerned here with quenching due to collisions with other gaseous atoms. We can list the various effects causing quenching in these cases.

(a) Electron exchange quenching. Here the orthopositronium atom exchanges its electron in triplet spin orientation with the positron, for an electron in a gas atom or molecule in a singlet spin orientation with the positron. The ground states of most stable gas molecules are singlet states so the proposed exchange would require an excitation of the molecule to a higher, triplet state which generally is too high to be reached at thermal energies.

Now a small number of gases such as the oxides of nitrogen NO and NO_2 contain an odd number of electrons. The exchange occurs with the odd electron and the accompanying spin reversal . involves only spin-orbit coupling energies which are of the order of thermal kinetic energies. So the presence of an unpaired electron in the molecule and consequent low energy transfer during exchange allows the quenching to proceed.

The other common oxide of nitrogen N_2O has an even number of electrons and does not produce triplet to singlet conversion.

The probability of direct electron exchange will depend on the amount of overlap of the electrons during collision and therefore will be energy dependent. We expect the quenching cross section to be about $1/4$ of that for elastic collisions, since after collision there are three ortho states to go to, and one para with a negligible energy difference between them. If there is more than one free electron spin the quenching probability is increased and so the quenching cross section should be dependent on the magnetic moment of the colliding molecule.

The direct exchange, or 'spin-flip' process obeys the spin selection rule in that total spin momentum is conserved. The quenching can also occur without energy exchange or change in multiplicity of the colliding molecule, all that is required is an unpaired electron on the molecule and the presence of a third body to remove the excess energy generated. This case is discussed by (Ferrell, 1958) and (Porter and Wright, 1959) and is thought to explain the quenching in oxygen in particular.

(b) Pickoff annihilation. Here the positron in the positronium annihilates directly with an electron in the target atom or molecule. The process is similar to the annihilation of a free positron with a gas atom electron but the presence of the positron-

-ium electron modifies the motion of the positron and its chance of annihilation on collision. The process will depend on the time spent by the positronium in sufficient overlap with the molecular electronic orbital for annihilation to be probable. This is dependent on the positronium energy and other factors such as the polarizability of the molecule. In practice, in most gases at atmospheric pressure measurement shows that pick-off is not a very probable process although it is probably the most frequently occuring quenching mechanism. The quenching rate is found experimentally to be about a factor to ten down on that for free positron annihilations, due to the screening of the positronium positron by its electron.

(c) Chemical Reactions. Suppose we have a gaseous molecule AB On collision the positronium atom e^+e^- causes the reaction,

$$AB + e^+e^- \rightarrow Ae^+e^- + B$$

The positronium is now bound to an atom of the molecule and is so bringing the positron in constant close proximity to the electrons of that atom. This will give an enhancement of the positron-electron annihilation effect observed as orthopositronium quenching. The halogens are strong quenching agents and are thought to form halides with the positronium atom, the strong attraction being due to van der Waal's forces or exchange forces. The system Positronium chloride has been studied theoretically and has a binding energy indicative of dynamic stability, (Simons 1948, 1949). Other work on positronium compounds in the gaseous state has been discussed by (Gittelman and Deutsch, 1956, 1958), (Gittelman, 1957, 1958) and (Heymann, 1961).

(d) Radiative or three body capture. If the energy of the complex is less than that of the ground state of **A** then **A** may capture a positronium atom with emission of radiation. The capture cross section will be greater than or comparable with pickoff annihilation cross sections. The process will become more important at higher pressure.

(e) Other quenching mechanisms. Quenching by direct spin reversal was considered by (Massey and Mohr, 1954) and found to be negligible under experimental conditions even for exchange between the colliding systems of two electrons having initally the same spin. The magnetic interaction of positronium in collision with a paramagnetic molecule may be strong enough to cause transitions. The most paramagnetic gas is oxygen but calculation indicates a conversion rate, much less than the orthopositronium self-annihilation rate. The paramagnetic quenching cannot alone explain the rate observed in oxygen, the exchange effect without spin-flip is the more likely cause. (Ore, 1949) showed that spontaneous change in direction of the positronium parallel spins was a negligible effect and this is also the case for collisions with non-paramagnetic molecules on considering the conversion possible by the electromagnetic field.

The Quenching of Orthopositronium in Helium

The nature of the helium atom ground state makes exchange quenching impossible and the only important quenching process is due to the pickoff quenching, for the low energies we are interested in. The quenching rate is given by (Ore, 1949), (Ferrell, 1956), as

$$\Lambda = 4\pi r_0^2 c N Z_{eff} P \quad sec^{-1}$$

Here r_0 = 2.82 10^{-13}cm. the classical electron radius

c is the velocity of light

N is Loschmidt's number (N = 2.69x10^{19} atoms/cm^3)

P is the pressure in atmospheres

Z_{eff} is the effective number of electrons/atom in a single state relative to the positron i.e. the number contributing to the annihilation.

This number Z_{eff} can be inferred from experiment and we are also about to show its calculation using the results on the elastic scattering of orthopositronium by helium atoms. The experimental values will correspond to thermalised positronium i.e $k^2 \sim 0.0036$, but we expect Z_{eff} to be energy dependent. The comparison between theory and experiment can then be made in terms of the Z_{eff} values.

We will now illustrate the theoretical calculation of Z_{eff} following (Fraser and Kraidy, 1966).

The trial wave function used is the same as that used in the elastic collision problem but is normalised to give one orthopositronium atom per unit volume asymptotically. We will now write the trial wave function as,

$$\begin{aligned}\Psi_k(\underset{\sim}{r}_p, \underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{r}_3) = \; & v(\sigma_1)\, \phi(\rho_1)\, \psi_k(\underset{\sim}{r}_2, \underset{\sim}{r}_3)\, \chi^1_1(p,1)\, \chi^0_0(2,3) \\ & + v(\sigma_2)\, \phi(\rho_2)\, \psi_k(\underset{\sim}{r}_3, \underset{\sim}{r}_1)\, \chi^1_1(p,2)\, \chi^0_0(3,1) \\ & + v(\sigma_3)\, \phi(\rho_3)\, \psi_k(\underset{\sim}{r}_1, \underset{\sim}{r}_2)\, \chi^1_1(p,3)\, \chi^0_0(1,2)\end{aligned}$$

Again $v(\sigma)$ describes the motion of the orthopositronium centre of mass but here $v(\sigma)$ takes account of all the ℓ values in that its value in terms of partial waves $g_\ell(\sigma)$ is,

$$v(\sigma) = \frac{1}{\sqrt{3}} \cdot \frac{1}{k\sigma} \cdot \sum_{\ell=0}^{\infty} i^{\ell} (2\ell+1)\, e^{i\eta_\ell}\, P_\ell(\cos\theta_\sigma)\, g_\ell(\sigma)$$

and asymptotically,

$$v(\sigma) \underset{\sigma\to\infty}{\sim} \frac{1}{\sqrt{3}} \left\{ e^{ik\sigma_z} + f(\theta_\sigma) \frac{e^{ik\sigma}}{\sigma} \right\}$$

where $f(\theta_\sigma)$ is the amplitude of the scattering wave and the $1/\sqrt{3}$ term arises from the new normalisation, (Ore, 1949), (Ferrell, 1956). The asymptotic form of $g_\ell(\sigma)$ is,

$$g_\ell(\sigma) \underset{\sigma\to\infty}{\sim} \sin\left(k\sigma - \tfrac{1}{2}\ell\pi + \eta_\ell\right)$$

and by comparison with the asymptotic form of the $f_\ell(\sigma)$ in the collision problem we see,

$$g_\ell(\sigma) = \cos\eta_\ell \cdot f_\ell(\sigma)$$

For high ℓ values we expect small η_ℓ and for the $g_\ell(\sigma)$ to reduce to the partial plane waves $u_\ell(\sigma)$ where,

$$u_\ell(\sigma) \underset{\sigma \to \infty}{\sim} \sin\left(k\sigma - \tfrac{1}{2}\ell\pi\right)$$

and only the plane wave part of $v(\sigma)$ is involved; i.e. for very small η_ℓ values, the term in $e^{ik\sigma_z}$ which can be expanded in the usual way as,

$$e^{ik\sigma_z} = \frac{1}{k\sigma} \sum_{\ell=0}^{\infty} i^\ell (2\ell+1) P_\ell(\cos\theta_\sigma)\, u_\ell(\sigma)$$

is the term containing the $u_\ell(\sigma)$.

The pick off quenching process requires the positron of the ortho positronium atom to annihilate with an electron in the helium atom. This occurs when the two particles are in a relative singlet state and consequently we project the trial wave function Ψ_t onto a spin singlet state $\chi_0^0(p,1)$ of the positron and, say, electron 1 of the helium atom. This leads to a function $\Phi(\underset{\sim}{r}_p, \underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{r}_3, 2, 3)$ where,

$$\Phi = \left(\chi_0^0(p,1),\ \Psi_t\right) \tag{1}$$

Now Z_{eff} is the effective number of electrons/atom in a singlet state relative to the positron. For electron 1 say this effective number is

$$\sum_{2,3} \int d\underset{\sim}{r}_1\, d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 \left| \Phi(\underset{\sim}{r}_1, \underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{r}_3, 2, 3)\right|^2$$

where we note that the $\underset{\sim}{r_p}$ in Φ has gone to $\underset{\sim}{r_1}$ which indicates the fact that the positron and electron 1 must be at the same position in space for annihilation to occur. A similar expression to the one above is discussed for positron free annihilation by (Ferrell, 1956), (Wallace 1960), (Drachman, 1966) and (Lee, 1958).

Noting the symmetry in the three electrons present we define

$$Z_{eff} = 3 \sum_{2,3} \int d\underline{r_1}\, d\underline{r_2}\, d\underline{r_3}\, \left| \Phi \right|^2 \qquad (2)$$

and the sum is over spins.

Defining as before,

$$\chi_1^1(i,j) = \alpha(i)\beta(j)$$

$$\chi_0^0(i,j) = \frac{1}{\sqrt{2}}\left\{ \alpha(i)\beta(j) - \beta(i)\alpha(j) \right\}$$

and using,

$$\left.\begin{array}{l} \sum \alpha^2(i) = 1 \\ \sum \beta^2(i) = 1 \\ \sum \alpha(i)\beta(i) = 0 \end{array}\right\}$$

we can find an expression for Φ without involving spin terms. Evidently, on substitution and summation of Ψ_x in (1),

$$\Phi = \frac{1}{2}\alpha(2)\alpha(3)\left\{ v(\sigma_2)\,\phi(\rho_2)\,\psi_\kappa(\underset{\sim}{r_3},\underset{\sim}{r_1}) - v(\sigma_3)\,\phi(\rho_3)\,\psi_\kappa(\underset{\sim}{r_1},\underset{\sim}{r_2}) \right\}$$

This can be substituted in (2) and due to the coordinate symmetry,

$$Z_{eff} = 3/2 \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \left\{ v^2(\sigma_2)\, \phi^2(\rho_2)\, \Psi_*^2(\mathbf{r}_3, \mathbf{r}_1) - v(\sigma_2)\, v(\sigma_3)\, \phi(\rho_2)\, \phi(\rho_3)\, \Psi_*(\mathbf{r}_3, \mathbf{r}_1)\, \Psi_*(\mathbf{r}_1, \mathbf{r}_2) \right\}$$

It is interesting to note that if instead of $v(\sigma)$ we just use the simple plane wave part then Z_{eff} is equal to $1/2$. Our scattering results show a totally repulsive field between the helium atom and the orthopositronium atom. This leads us to expect a value of Z_{eff} less than $1/2$ which is in fact the case as our results will show. We now define,

$$I_1 = \frac{3}{2} \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, v^2(\sigma_2)\, \phi^2(\rho_2)\, \Psi_*^2(\mathbf{r}_3, \mathbf{r}_1)$$

and

$$I_2 = -\frac{3}{2} \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, v(\sigma_2)\, v(\sigma_3)\, \phi(\rho_2)\, \phi(\rho_3)\, \Psi_*(\mathbf{r}_3, \mathbf{r}_1)\, \Psi_*(\mathbf{r}_1, \mathbf{r}_2)$$

changing coordinates and dropping subscripts,

$$I_1 = \frac{3}{2} \int d\boldsymbol{\sigma}\, d\boldsymbol{\rho}\, d\mathbf{r}_3\, v^2(\sigma)\, \phi^2(\rho)\, \Psi_*^2(\mathbf{r}_3, \mathbf{r})$$

substituting the expressions for the various functions

$$I_1 = \frac{3\mu^3}{16\pi^2} \int d\boldsymbol{\sigma}\, d\boldsymbol{\rho}\, e^{-\rho} e^{-\mu|2\boldsymbol{\sigma}-\boldsymbol{\rho}|}\, v^2(\sigma)$$

we now expand,

$$e^{-\rho} e^{-\mu|2\boldsymbol{\sigma}-\boldsymbol{\rho}|} = \frac{1}{\sigma\rho} \sum_{\ell=0}^{\infty} (2\ell+1)\, Q_\ell(\sigma, \rho)\, P_\ell(\eta)$$

where

$$Q_\ell(\sigma, \rho) = \frac{\sigma\rho}{2} \int_{-1}^{1} d\eta\, P_\ell(\eta)\, e^{-\rho} e^{-\mu|2\boldsymbol{\sigma}-\boldsymbol{\rho}|}$$

Then substitute back in the expression for I_1 together with the expansion of $v(\sigma)$. The $P_\ell(\gamma)$ are expanded in products of spherical harmonics of Ω_σ and Ω_ρ. Integrating over Ω_σ leads to,

$$I_1 = \frac{1}{2k^2} \sum_{\ell=0}^{\infty} (2\ell+1) \int_0^{\infty} d\sigma \; N(\sigma) \; g_\ell^2(\sigma)$$

where,

$$N(\sigma) = \frac{\mu^3}{2\pi} \int d\boldsymbol{\rho} \; e^{-\rho} e^{-\mu|2\boldsymbol{\sigma} - \boldsymbol{\rho}|} \tag{3}$$

The integration of $N(\sigma)$ is now performed analytically.

Let, $N(\sigma) = \mu^3 I_A$

and,

$$I_A = -\frac{\partial I_B}{\partial \mu}$$

where,

$$I_B = \frac{1}{2\pi} \int d\boldsymbol{\rho} \; \frac{e^{-\rho} e^{-\mu|2\boldsymbol{\sigma} - \boldsymbol{\rho}|}}{|2\boldsymbol{\sigma} - \boldsymbol{\rho}|}$$

then,

$$N(\sigma) = -\mu^3 \frac{\partial I_B}{\partial \mu}$$

We can employ a standard expansion here,

$$\frac{e^{-\mu|\boldsymbol{r} - \boldsymbol{\rho}|}}{|\boldsymbol{r} - \boldsymbol{\rho}|} = \frac{2\mu}{\pi} \sum_{n=0}^{\infty} (2n+1) \left[\sqrt{\frac{\pi}{2\mu r}} \; I_{n+\frac{1}{2}}(\mu r)\right] \left[\sqrt{\frac{\pi}{2\mu\rho}} \; K_{n+\frac{1}{2}}(\mu\rho)\right] P_n(\cos\theta)$$

where,

$$\cos\theta = \frac{\boldsymbol{r} \cdot \boldsymbol{\rho}}{r\rho} \quad , \quad r \leq \rho$$

Here,

$$K_{n+1/2}(\mu\rho) = \sqrt{\frac{\pi}{2\mu\rho}}\; e^{-\mu\rho} \sum_{m=0}^{n} \frac{(n+m)!}{m!\,(n-m)!\,(2\mu\rho)^m}$$

and

$$I_{n+1/2}(\mu r) = \frac{1}{\sqrt{2\mu\pi r}} \left\{ e^{\mu r} \sum_{m=0}^{n} \frac{(-1)^m (n+m)!}{m!\,(n-m)!\,(2\mu r)^m} \right.$$

$$\left. + (-1)^{n+1} e^{-\mu r} \sum_{m=0}^{n} \frac{(n+m)!}{m!\,(n-m)!\,(2\mu r)^m} \right\}$$

by a simple reduction,

$$I_B = \int \rho^2 e^{-\rho} d\rho \int_{-1}^{1} d(\cos\theta)\, \frac{e^{-\mu|2\underset{\sim}{\sigma} - \underset{\sim}{\rho}|}}{|2\underset{\sim}{\sigma} - \underset{\sim}{\rho}|}$$

We remember that the integration over ρ must be split into two regions corresponding to $\rho \leqslant 2\sigma$ and $\rho \geqslant 2\sigma$. Substitution leads to,

$$I_B = \int_0^{2\sigma} \rho^2 e^{-\rho} d\rho\; \frac{e^{-2\mu\sigma}}{2\mu\sigma\rho} \left\{ e^{\mu\rho} - e^{-\mu\rho} \right\} + \int_{2\sigma}^{\infty} \rho^2 e^{-\rho} d\rho$$

$$\frac{e^{-\mu\rho}}{2\mu\sigma\rho} \left\{ e^{2\mu\sigma} - e^{-2\mu\sigma} \right\}$$

whence,

$$I_B = \frac{e^{-2\mu\sigma}}{2\mu\sigma} \left[\frac{1}{(\mu-1)^2} - \frac{1}{(\mu+1)^2} \right] + \frac{e^{-2\sigma}}{2\mu\sigma} \left[\frac{2\sigma}{\mu-1} - \frac{1}{(\mu-1)^2} \right]$$

$$+ \frac{e^{-2\sigma}}{2\mu\sigma} \left[\frac{1}{(\mu+1)^2} + \frac{2\sigma}{\mu+1} \right]$$

We now differentiate with respect to μ multiply by $-\mu^3$ and arrive at,

$$N(\sigma) = \frac{\mu}{2\sigma} \left\{ e^{-2\mu\sigma} \left[\frac{1}{(\mu-1)^2} - \frac{1}{(\mu+1)^2} \right] + e^{-2\sigma} \left[\frac{2\sigma}{\mu-1} - \frac{1}{(\mu-1)^2} \right. \right.$$

$$\left. \left. + \frac{1}{(\mu+1)^2} + \frac{2\sigma}{\mu+1} \right] \right\} - \frac{\mu^2}{\sigma} \left\{ e^{-2\mu\sigma} \left[\frac{1}{(\mu+1)^3} - \frac{1}{(\mu-1)^3} + \frac{\sigma}{(\mu+1)^2} - \frac{\sigma}{(\mu-1)^2} \right] \right.$$

$$\left. + e^{-2\sigma} \left[\frac{1}{(\mu-1)^3} - \frac{1}{(\mu+1)^3} - \frac{\sigma}{(\mu-1)^2} - \frac{\sigma}{(\mu+1)^2} \right] \right\}$$

To check this equation we note in (3) that as $\sigma \to 0$ so $N(\sigma) \to \frac{4\mu^3}{(\mu+1)^3}$. If we expand the exponentials in (4) and approximate for small σ we find $N(\sigma)$ tending to the same value.

We now have to evaluate,

$$I_2 = -\frac{3}{2} \int d\underset{\sim}{r}_1 \, d\underset{\sim}{r}_2 \, d\underset{\sim}{r}_3 \; v(\sigma_2) \, v(\sigma_3) \; \phi(\rho_2) \, \phi(\rho_3)$$

$$\psi_{+}(\underset{\sim}{r}_3, \underset{\sim}{r}_1) \; \psi_{*}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$$

We again change coordinates to $\underset{\sim}{\sigma}$ and $\underset{\sim}{\sigma}'$ each corresponding to $\underset{\sim}{\sigma}_2$ and $\underset{\sim}{\sigma}_3$.

The Jacobian of the transformation is 4^3 so,

$$I_2 = -\frac{3}{2} \cdot 4^3 \cdot \int d\underset{\sim}{\sigma} \, d\underset{\sim}{\sigma}' \, d\underset{\sim}{r} \left\{ \frac{1}{8\pi} e^{-|\underset{\sim}{\sigma} - \underset{\sim}{r}|} e^{-|\underset{\sim}{\sigma}' - \underset{\sim}{r}|} \right.$$

$$\left. \frac{\mu^6}{\pi^2} e^{-\mu|2\underset{\sim}{\sigma} - \underset{\sim}{r}|} e^{-\mu|2\underset{\sim}{\sigma}' - \underset{\sim}{r}|} \right\} e^{-2\mu r} \, v(\sigma) \, v(\sigma')$$

We expand,

$$e^{-|\underset{\sim}{\sigma} - \underset{\sim}{r}|} e^{-\mu|2\underset{\sim}{\sigma} - \underset{\sim}{r}|} = \frac{1}{\sigma r} \sum_{l=0}^{\infty} (2l+1) \, G_l(\sigma, r) \, P_l(\eta)$$

where,

$$G_l(\sigma, r) = \frac{\sigma r}{2} \int_{-1}^{1} d\eta \; P_l(\eta) \, e^{-|\underset{\sim}{\sigma} - \underset{\sim}{r}|} e^{-\mu|2\underset{\sim}{\sigma} - \underset{\sim}{r}|}$$

and,

$$\eta = \frac{\underset{\sim}{\sigma} \cdot \underset{\sim}{r}}{\sigma r}$$

A similar expansion holds for the terms in $\underset{\sim}{\sigma}'$

We substitute back using the spherical harmonic expansion for $P_\ell(\gamma)$

and also substitute for the $v(\sigma)$, $v(\sigma')$

The subsequent reduction leads to

$$I_2 = -\frac{1}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\int_0^\infty d\sigma\int_0^\infty d\sigma'\; g_\ell(\sigma)\, M^{(\ell)}(\sigma,\sigma')\, g_\ell(\sigma')$$

where,

$$M^{(\ell)}(\sigma,\sigma') = 256\,\mu^6\int_0^\infty dr\; G_\ell(\sigma,r)\, G_\ell(\sigma',r)\, e^{-2\mu r}$$

This is evaluated numerically when required.

Finally, then we have,

$$Z_{eff} = \frac{1}{2k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\int_0^\infty d\sigma\; N(\sigma)\, g_\ell^2(\sigma) - \frac{1}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\int_0^\infty d\sigma\int_0^\infty d\sigma'\; g_\ell(\sigma)\; M^{(\ell)}(\sigma,\sigma')\; g_\ell(\sigma') \qquad (5)$$

We have shown that the $g_\ell(\sigma)$ are directly related to the $f_\ell(\sigma)$ of the elastic scattering problem and we consequently use these values in the numerical solution of the last equation.

We use the last equation in three approximations A, B and C, cutting the summations off at ℓ = 0, 1 and 2 respectively. For the static case the net of points is over σ = 0.1 to 5.4 in intervals of 0.1 and the range is extended to 10.8 for the long range potential case.

To allow for higher values of ℓ we adopt the following proceedure.

We assume a value L such that for $l > L$ the phase shifts are negligible and,

$$g_l(\sigma) = u_l(\sigma)$$

We assume also that for $l \geq L$ the contributions to the second term in the final equation for z_{eff} are negligible so we preserve the sum to infinity without introducing any error of importance.

We rewrite the first term of (5) as,

$$\frac{1}{2k^2} \sum_{l=0}^{L} (2l+1) \int_0^\infty d\sigma\, N(\sigma)\, g_l^2(\sigma) + \frac{1}{2k^2} \sum_{l=L+1}^{\infty} (2l+1)$$

$$\int_0^\infty d\sigma\, N(\sigma)\, g_l^2(\sigma)$$

$$= \frac{1}{2k^2} \sum_{l=0}^{L} (2l+1) \int_0^\infty d\sigma\, N(\sigma) \left\{ g_l^2(\sigma) - u_l^2(\sigma) \right\}$$

$$+ \frac{1}{2k^2} \sum_{l=0}^{\infty} (2l+1) \int_0^\infty d\sigma\, N(\sigma)\, u_l^2(\sigma)$$

The second term here is the aforementioned plane wave value of z_{eff} i.e. $1/2$. Hence the above expression is simply,

$$\frac{1}{2}\left[1 + \frac{1}{k^2} \sum_{l=0}^{L} (2l+1) \int_0^\infty d\sigma\, N(\sigma) \left\{ g_l^2(\sigma) - u_l^2(\sigma) \right\}\right]$$

and so,

$$z_{eff} = \frac{1}{2}\left[1 + \frac{1}{k^2} \sum_{l=0}^{L} (2l+1) \int_0^\infty d\sigma\, N(\sigma) \left\{ g_l^2(\sigma) - u_l^2(\sigma) \right\}\right]$$

$$- \frac{1}{k^2} \sum_{l=0}^{\infty} (2l+1) \int_0^\infty d\sigma \int_0^\infty d\sigma'\, g_l(\sigma)\, M^{(l)}(\sigma,\sigma')\, g_l(\sigma')$$

This equation was used for the approximation D where L was taken as 2 and for $l > 2$ we took $g_l(\sigma) = u_l(\sigma)$ and also ignored terms of $l > 2$ in the second term of the equation.

We note here an important point with regard to the long range potential case. The distortion due to this is not allowed for explicitely in the wave function used here as trial function. The distortion is inherent in the values $f_l(\sigma)$ from the elastic scattering problem and consequently in the $g_l(\sigma)$ here. We argue that to keep consistency in the two calculations it is necessary to preserve the form of the trial function Ψ_l^* through the elastic scattering calculation and the calculation for Z_{eff}. A further improvement to the calculations as a whole would be to include correlation terms in Ψ_l^* to allow for distortion, carrying these terms through into the Ψ_t used to calculate Z_{eff}.

In a similar calculation of positron collisions in helium, (Kraidy, 1967) a discussion is presented of the inclusion of polarisation effects in the trial Ψ_t. The Z_{eff} value in that case however is nearer the experimental value when such effects are not included in the form of Ψ_t.

Finally suppose we define a cross section per atom for the annihilation process by,

$$\sigma_a = \frac{\Lambda}{L p v}$$

where v is the relative velocity of the positronium and target atom.

Then,

$$\sigma_a = \frac{4\pi r_0^2 c Z_{eff}}{v}$$

We also have the competing process of elastic collisions

$\sigma_T \sim 10\pi a_0^2$ say in cm^2.

i.e.

$$\frac{\sigma_a}{\sigma_T} \sim \frac{1}{2}\left(\frac{r_0}{a_0}\right)^2 . \frac{c}{v} . Z_{eff}$$

At thermal energies we have $v \sim 7 \times 10^6$ cm/sec. Substituting for the other values shows that, σ_a/σ_T is always very small indeed so the probability of annihilation interfering with the elastic collision calculation is negligible which is a good argument for using the form of collision trial wave function in the annihilation problem.

Further work is however required on the influence of correlation terms in the trial functions in either calculation before one can be definite about any particular approximation.

CHAPTER 5

NUMERICAL AND COMPUTATIONAL TECHNIQUES

Introduction

In this chapter we present the numerical analysis and computational techniques used in evaluating the various phase shifts and cross sections and the use of the scattering results in evaluating Z_{eff} .

The Scattering analysis

(i) The Kernals

The full kernal in the integro-differential equation is,

$$L^{(\ell)}(\sigma_1,\sigma_2) = k^2 L_1^{(\ell)}(\sigma_1,\sigma_2) + L_2^{(\ell)}(\sigma_1,\sigma_2)$$

We require $L_1^{(\ell)}(\sigma_1,\sigma_2)$ and $L_2^{(\ell)}(\sigma_1,\sigma_2)$ over a suitable range of σ_1 and σ_2 . We have shown,

$$L_1^{(\ell)}(\sigma_1,\sigma_2) = 128\mu^3\int_0^\infty dr\ G_\ell(\sigma_1,r)\,G_\ell(\sigma_2,r)$$

and

$$L_2^{(\ell)}(\sigma_1,\sigma_2) = 128\mu^3\int_0^\infty dr\ \Big\{\Big[1+8\mu-\frac{4}{r}+4\Big(\frac{1}{r}+\mu\Big)e^{-2\mu r}\Big]G_\ell(\sigma_1,r)\,G_\ell(\sigma_2,r) + H_\ell(\sigma_1,r)\,G_\ell(\sigma_2,r) + H_\ell(\sigma_2,r)\,G_\ell(\sigma_1,r) - 2\sum_{\ell'=0}^{\infty} D_{\ell'}(\sigma_1\sigma_2,\ell)\,G_{\ell'}(\sigma_1,r)\,G_{\ell'}(\sigma_2,r)\Big\}$$

To evaluate $L_1^{(\ell)}(\sigma_1,\sigma_2)$ and $L_2^{(\ell)}(\sigma_1,\sigma_2)$ then we require the values of the $G_\ell(\sigma,r)$ and the $H_\ell(\sigma,r)$ over a suitable set of σ and r .

We have given expressions for the $G_\ell(\sigma,\tau)$, $G_\ell^{(3)}(\sigma,\tau)$ $J_\ell(\sigma,\tau)$, $J_\ell^{(3)}(\sigma,\tau)$ and $K_\ell(\sigma,\tau)$ upon which the $H_\ell(\sigma,\tau)$ depend. In these various expressions we have terms in the denominators of the integrands of the form $|\underset{\sim}{\sigma} - \underset{\sim}{\tau}|$ and $|2\underset{\sim}{\sigma} - \underset{\sim}{\tau}|$. In a numerical integration these may vanish and to avoid this difficulty we utilise a change in variable. It would of course be possible to expand the integrands in terms of sums of products of Bessel functions but these would be slowly convergent and the coordinate transformation method is easier and quicker.

Following (Fraser, 1961) we have p and q defined by,

$$\left.\begin{aligned} p &= \tau/\sigma \\ q &= \frac{2\sigma}{\tau} \end{aligned}\right\}$$

and the variable changes for $-1 \leqslant \xi \leqslant 1$ are,

$$0 < p \leqslant 1 \quad : \quad \eta = p/2 - \xi - \frac{p\xi^2}{2}$$

$$1 \leqslant p < \sqrt{2} \quad : \quad \eta = 1/2p - \xi - \xi^2/2p$$

$$0 < q \leqslant 1 \quad : \quad \eta = q/2 - \xi - \frac{q\xi^2}{2}$$

$$1 \leqslant q < \sqrt{2} \quad : \quad \eta = \frac{1}{2q} - \xi - \frac{\xi^2}{2q}$$

As an example of the transformation consider the region $0 < p \leqslant 1$

We have,

$$d\eta = -d\xi\,(1 + p\xi)$$

also,

$$|\underset{\sim}{\sigma} - \underset{\sim}{\tau}| = \left[\sigma^2 + \tau^2 - 2\sigma\tau\left(\frac{\rho}{2} - \xi - \frac{\rho\xi^2}{2}\right)\right]^{1/2}$$

$$\therefore \quad |\underset{\sim}{\sigma} - \underset{\sim}{\tau}| = \sigma(\rho\xi + 1)$$

and similarly,

$$|2\underset{\sim}{\sigma} - \underset{\sim}{\tau}| = \sigma\left[2(\rho\xi+1)^2 + (2-\rho^2)\right]^{1/2}$$

Substituting these values in the expansion for the terms of form $G_\ell(\sigma,\tau)$ we have,

$$G_\ell(\sigma,\tau) = \frac{\sigma\tau}{2}\int_{-1}^{1} d\xi\,(1+\rho\xi)\,P_\ell(\eta)\,\exp\left[-\sigma\left\{(\rho\xi+1) + \mu\left[2(\rho\xi+1)^2 + (2-\rho^2)\right]^{1/2}\right\}\right]$$

$$J_\ell(\sigma,\tau) = \frac{\tau}{2}\int_{-1}^{1} d\xi\,\frac{(1+\rho\xi)P_\ell(\eta)\exp\left[-\sigma\left\{(\rho\xi+1) + \mu\left[2(\rho\xi+1)^2 + (2-\rho^2)\right]^{1/2}\right\}\right]}{\left[2(\rho\xi+1)^2 + (2-\rho^2)\right]^{1/2}}$$

$$K_\ell(\sigma,\tau) = \frac{\tau}{2\sigma}\int_{-1}^{1} d\xi\,\frac{P_\ell(\eta)\exp\left[-\sigma\left\{(\rho\xi+1) + \mu\left[2(\rho\xi+1)^2 + (2-\rho^2)\right]^{1/2}\right\}\right]}{\left[2(\rho\xi+1)^2 + (2-\rho^2)\right]^{1/2}}$$

The expressions for $G_\ell^{(3)}(\sigma,\tau)$ and $J_\ell^{(3)}(\sigma,\tau)$ are as the above but with 3μ substituted instead of μ .

An exactly similar process is carried out for the other three regions of the variable change and corresponding expressions arrived at for the $G_\ell(\sigma,\tau)$ and $J_\ell(\sigma,\tau)$, $K_\ell(\sigma,\tau)$ in these regions.

The problem then is to evaluate the terms above numerically over the variable ξ for a suitable net of σ and τ and then to integrate numerically over τ using these values, in the expressions for $L_1^{(l)}(\sigma_1,\sigma_2)$ and $L_2^{(l)}(\sigma_1,\sigma_2)$ giving a net of kernals over σ_1 and σ_2. Simpson's rule was used to evaluate terms like $G_l(\sigma,\tau)$ and the trapezoidal rule for the final kernals. The sum in $L_2^{(l)}(\sigma_1,\sigma_2)$ from $l' = 0$ to ∞ was cut off after $l' = 10$ which gave a realistic computational time limit for the evaluation of $L_2^{(l)}(\sigma_1,\sigma_2)$.

The Simpson's rule interval was varied from $1/8$ to $1/16$ to $1/32$ and was accurate to four figures for all these intervals. The range of σ and τ was taken as

σ : 0.1 to 5.4 in intervals of 0.1

τ : 0.1 to 9.6 in intervals of 0.1

The range was then extended to 10.8 for σ and 14.4 for τ. This gave no difference in five figures so the first range was considered sufficiently accurate.

Simpson's rule was then used instead of the trapezoidal rule for the τ integration and agreement to four figures resulted.

Consequently values of $L_1^{(l)}(\sigma_1,\sigma_2)$ and $L_2^{(l)}(\sigma_1,\sigma_2)$ were obtained for $l = 0, 1, 2$ over a net of

σ_1 : 0.1 to 5.4 in intervals of 0.1

σ_2 : 0.1 to 5.4 in intervals of 0.1

accurate to four significant figures. They were found to be symmetrical in σ_1 and σ_2, a good indication of accuracy in computation. The computing was done on the Newcastle University I.B.M. 360/67 machine and, for each value of ℓ, the time taken was 2 mins. for the $L_1^{(\ell)}(\sigma_1,\sigma_2)$ and 25 mins. for the $L_2^{(\ell)}(\sigma_1,\sigma_2)$. The kernals were then stored for later use.

(ii) The Integro-differential Equation

The equation to be solved is,

$$\left\{ \frac{d^2}{d\sigma_1^2} + k^2 - \frac{\ell(\ell+1)}{\sigma_1^2} - 2V_{vow} \right\} f_\ell(\sigma_1)$$

$$= \int_0^\infty d\sigma_2 \; L^{(\ell)}(\sigma_1,\sigma_2) \; f_\ell(\sigma_2)$$

and it is solved for the $f_\ell(\sigma)$.

The static approximation has $V_{vow} = 0$ and with this in mind we will present the long range approximation only here.

Define,

$$U(\sigma_1) = 2V_{vow}$$

then,

$$\left\{ \frac{d^2}{d\sigma_1^2} + k^2 - \frac{\ell(\ell+1)}{\sigma_1^2} \right\} f_\ell(\sigma_1) = U(\sigma_1) f_\ell(\sigma_1) + \int_0^\infty d\sigma_2 \, L^{(\ell)}(\sigma_1,\sigma_2) f_\ell(\sigma_2)$$

With the known boundary conditions on the $f_\ell(\sigma)$ we can transform this equation into an integral equation for $f_\ell(\sigma_1)$

We write now σ for σ_1 and σ' for σ_2 since we have the dummy variable σ'' to distinguish and,

$$f_\ell(\sigma) = u_\ell(k\sigma) + \int_0^\infty d\sigma' \, M_\ell(\sigma,\sigma') \, U(\sigma') \, f_\ell(\sigma')$$
$$+ \int_0^\infty d\sigma' \, M_\ell(\sigma,\sigma') \int_0^\infty d\sigma'' \, L^{(\ell)}(\sigma',\sigma'') \, f_\ell(\sigma'')$$

Here $M_\ell(\sigma,\sigma')$ is the Green's function for the transformation

and,

$$M_\ell(\sigma,\sigma') = -\frac{1}{k} u_\ell(k\sigma) \, v_\ell(k\sigma') \quad \text{for} \quad \sigma \leqslant \sigma'$$

and

$$M_\ell(\sigma,\sigma') = -\frac{1}{k} u_\ell(k\sigma') \, v_\ell(k\sigma) \quad \text{for} \quad \sigma \geqslant \sigma'$$

Here,

$$\left.\begin{aligned} u_\ell(k\sigma) &= \sqrt{\frac{\pi k\sigma}{2}} \; J_{\ell+1/2}(k\sigma) \\ v_\ell(k\sigma) &= \sqrt{\frac{\pi k\sigma}{2}} \; (-1)^\ell \, J_{-(\ell+1/2)}(k\sigma) \end{aligned}\right\}$$

and the J functions here are the half integer spherical Bessel functions. The asymptotic behaviour is,

$$u_\ell(k\sigma) \underset{\sigma\to\infty}{\sim} \sin\left(k\sigma - \frac{\ell\pi}{2}\right)$$

$$v_\ell(k\sigma) \underset{\sigma\to\infty}{\sim} \cos\left(k\sigma - \frac{\ell\pi}{2}\right)$$

From the tables of Bessel functions we can determine the values of

$u_\ell(k\sigma)$ and $v_\ell(k\sigma)$ for the various ℓ values,

	$u_\ell(k\sigma)$	$v_\ell(k\sigma)$
$\ell = 0$:	$\sin k\sigma$	$\cos k\sigma$
$\ell = 1$:	$\frac{\sin k\sigma}{k\sigma} - \cos k\sigma$	$\frac{\cos k\sigma}{k\sigma} + \sin k\sigma$
$\ell = 2$:	$\left(\frac{3}{k^2\sigma^2} - 1\right)\sin k\sigma - \frac{3\cos k\sigma}{k\sigma}$	$\left(\frac{3}{k^2\sigma^2} - 1\right)\cos k\sigma + \frac{3\sin k\sigma}{k\sigma}$

Using these we can determine the Green's function $M_\ell(\sigma, \sigma')$ over a net of σ and σ' equivalent to that for the kernal $L^{(\ell)}(\sigma_1, \sigma_2)$ We now use subscripts i, j, k for particular values of σ, σ' and σ'' and write the integral equation as,

$$f_i = u_i + \sum_j \beta_j M_{ij} U_j f_j + \sum_{j,k} \beta_j \alpha_k M_{ij} L_{jk} f_k$$

where the α_i and β_i are numerical weighting coefficients.

Rewrite as,

$$u_i = \sum_{j,k} \left\{ \frac{\delta_{ik}}{J} - \beta_j \delta_{jk} M_{ij} U_j - \beta_j \alpha_k M_{ij} L_{jk} \right\} f_k$$

and J is the number of values of j taken and δ_{ij} the delta function,

$$\left.\begin{array}{lll} \delta_{ij} = 0 & & i \neq j \\ \delta_{ij} = 1 & & i = j \end{array}\right\}$$

The set of simultaneous equations was solved for the f_k by a standard matrix inversion technique for various energy values. In the static case i, j and k ranged over 1 to 54 corresponding to σ varying from 0.1 to 5.4 in intervals of 0.1.

In the long range potential approximation the range of σ was extended to 10.8 since the potential was expected to have an effect at the larger distance. For this range of σ, L_{jk} was taken as zero for j or k greater than 54. In the static case extending the range over 5.4. had no effect on the resulting phase shifts and cross sections to five figures. In the long range potential approximation an extension of the range over 10.8 had no effect to four figures. The usual integral equation was used to calculate the phase shifts i.e.,

$$a_\ell = -\frac{1}{k}\int_0^\infty d\sigma' \, u_\ell(k\sigma') \int_0^\infty d\sigma'' \, L^{(\ell)}(\sigma',\sigma'') \, f_\ell(\sigma'')$$

We rewrite this as,

$$a_\ell = -\frac{1}{k}\sum_{j,k} \beta_j \, \alpha_k \, u_j \, L_{jk} \, f_k$$

and using the f_k we obtain values for a_ℓ for various energies.

The values of $k\cot\eta_\ell$ and σ_ℓ are derived directly from the values a_ℓ.

The trapezoidal rule was used in the various integrations which reduced the numerical integration weights to unity. The computing time was 10 mins. for all phase shifts calculated in the static exchange approximation and 45 mins. for those in the long range potential approximation.

The matrix inversion technique was tested for accuracy by using the seperable kernal, (Fraser, 1961),

$$L_t(\sigma,\sigma') = 36\cdot45\,\sigma\sigma'\,e^{-1\cdot25(\sigma+\sigma')}$$

for which the cross sections and phase shifts can be computed analytically. The exact results for the cross section were reproduced within 10% at the very lowest energies. The phase shift errors were correspondingly less. As energy increases the errors lessen and cross sections are expected accurate to two figures and phase shifts to three.

The analysis for Z_{eff}

We have Z_{eff} expressed in terms of the $f_l(\sigma)$ of the scattering problem, i.e.,

$$Z_{eff} = \frac{1}{2k^2}\sum_{l=0}^{\infty}\cos^2\eta_l\,(2l+1)\int_0^\infty d\sigma\,N(\sigma)\,f_l^2(\sigma)$$

$$-\frac{1}{k^2}\sum_{l=0}^{\infty}\cos^2\eta_l\,(2l+1)\int_0^\infty d\sigma\int_0^\infty d\sigma'\,f_l(\sigma)$$

$$M^{(l)}(\sigma,\sigma')\,f_l(\sigma')$$

where, $$N(\sigma) = \frac{\mu^3}{2\pi}\int d\boldsymbol{\rho}\,e^{-\rho}\,e^{-\mu|2\boldsymbol{\sigma}-\boldsymbol{\rho}|}$$

and

$$M^{(l)}(\sigma,\sigma') = 256\mu^6\int_0^\infty dr\,G_l(\sigma,r)\,G_l(\sigma',r)\,e^{-2\mu r}$$

We have shown the analytic evaluation of $N(\sigma)$. The values of $M^{(l)}(\sigma,\sigma')$ are found over a net of σ and σ' in precisely the same way as the kernal $L_1^{(l)}(\sigma_1,\sigma_2)$ in the scattering problem.

The values of Z_{eff} for various energies were then found by using the trapezoidal rule for the integrations involved. Z_{eff} values were found from the formula above for $l = 0$, approximation A; $l = 0$ and 1, approximation B, and $l = 0$, 1 and 2, approximation C.

We also showed the approximation for Z_{eff} using the free-particle radial partial waves $u_l(\sigma)$.

We assume for $l > L$ that the phase shifts are negligible and that,

$$g_l(\sigma) = u_l(\sigma)$$

then,

$$Z_{eff} = \frac{1}{2}\left[1 + \frac{1}{k^2}\sum_{l=0}^{L}(2l+1)\int_0^\infty d\sigma\, N(\sigma)\left\{g_l^2(\sigma) - u_l^2(\sigma)\right\}\right] - \frac{1}{k^2}\sum_{l=0}^{\infty}(2l+1)\int_0^\infty d\sigma\int_0^\infty d\sigma'\, g_l(\sigma)\, M^{(l)}(\sigma,\sigma')\, g_l(\sigma')$$

The contributions to the second part of terms with $l > 2$ are negligible for the energies we are considering. Consequently if ${}^{C}Z_{eff}$ is the value of Z_{eff} in approximation C and if ${}^{D}Z_{eff}$ is the approximation used here,

$${}^{D}Z_{eff} = {}^{C}Z_{eff} + \frac{1}{2} - \frac{1}{2k^2}\sum_{l=0}^{2}(2l+1)\int_0^\infty d\sigma\, N(\sigma)\, u_l^2(\sigma)$$

The values of $u_\ell(\sigma)$ have been given and the trapezoidal rule was used to give ${}^{D}z_{eff}$.

In obtaining the values ${}^{D}z_{eff}$ the partial waves for $\ell > 2$ were replaced by free particle waves whose use is judged to overestimate the contribution of $\ell > 2$ in the light of the solutions for $\ell \leqslant 2$.

In the numerical integration for the static exchange case the range of σ was 0.1 to 5.4 and an interval of 0.1. In the long range potential case the range was 0.1 to 10.8 with an interval of 0.1.

The computation took 5 mins.for all values of z_{eff} in all the various approximations.

CHAPTER 6

THE NUMERICAL RESULTS

Introduction

The results are presented for the static approximation and the long range potential approximation of the various cross sections, phase shifts and Z_{eff} value. Comparisons of the two cases are drawn and a comparison with the results of other workers is given. Finally the conclusions and suggestions for further investigation are presented.

The Scattering Results

(i) The Static Approximation

In Table II we show the phase shifts η_0, η_1, η_2, the partial cross sections $\sigma_0, \sigma_1, \sigma_2$, the total cross section σ_T and the diffusion cross section σ_D for different values of k, the positronium momentum.

Figure 7 is the graph of the various cross sections with k^2, Figure 8 is the graph of the various phase shifts with k and Figure 9 is the graph of the $k\cot\eta_\ell$ with k^2 and Figure 10 the low energy limit for $k\cot\eta_0$ with k^2. We define the s-wave scattering length, a, by,

$$a = \lim_{k \to 0} \left(- \frac{1}{k\cot\eta_0} \right)$$

The zero energy cross section is then,

$$\sigma_z = 4\pi a^2$$

Also as $k \to 0$ we have the effective range r_e given by,

$$k\cot\eta_0 \underset{k\to 0}{\longrightarrow} -\frac{1}{a} + \frac{k^2 r_e}{2}$$

Both a and r_e are calculated using the graph of figure 10.

We find

$$a = 1.806$$
$$r_e = 1.002$$

both in units of a_0 . a being positive is indication of the repulsive nature of the interaction.

From the graph of figure 8 we see that the phase shifts decrease reasonably rapidly with increasing l especially at the lower energy values. Since the phase shifts are negative, then the potential involved is wholly repulsive. We note that at thermal energies, i.e. $k \sim 0{\cdot}06$ the only important phase shift is for $l = 0$.

The $l = 0$ importance is emphasised even more in figure 7, for low energies contributing virtually all of the total elastic scattering cross section.

The results can be compared with those of (Fraser, 1961). The results in Fraser's paper are now known to be in error and his recalculated results are known to us through a private communication.

There are no important differences except in an assumption of Fraser that the $l = 0$ phase shift has an attractive interaction operating during the collision. His phase shifts, η_0 are equal to ours with a value of π added. However his results are up to energy, $k = 1{\cdot}0$ only, so he will not have observed the minimum obtained by our calculation, exhibited in all the phase shifts, which indicates a repulsive interaction even for the $\ell = 0$ case. The turning over of the $k \cot \eta_\ell$ curves is also mentioned as this is also an effect above the $k = 1.0$ limit. The values given by Fraser for a and r_e are

$$a = 1.882$$

$$r_e = 0.940$$

both in units of a_0. This is in good agreement with our results.

(ii) <u>The long range potential approximation</u>

Table III shows the corresponding values to Table II for this new approximation. Figures 11, 12, 13 are the equivalent of figures 7, 8 and 9 in this case. Figure 14 contains the low-energy limit of $k \cot \eta_0$ with k^2 for the long range potential case as did figure 10 for the static case.

From figure 14 we find,

$$a = 2.055$$

in units of a_0. r_e is also defined in the case of our long range potential, (O'Malley et al 1961).

No comparison of the results can be made with those of other workers as this is the first of its kind in this particular approximation.

(iii) Comparison of the two approximations

It is evident from the two sets of graphs that the inclusions of the long range potential has very little difference on the shape of the curves or the absolute magnitudes except at low energies. At thermal energies for instance the cross section is increased considerably due to a large increase in the $\ell = 0$ partial cross section and a slight increase in that for $\ell = 1$. At higher energies the various cross sections are slightly less than the static case.

At thermal energies the long range potential is seen to increase the absolute value of the phase shift η_0 and to decrease it at higher energies. This is seen in the minimum of η_0 particularly. The phase shifts η_1 and η_2 are affected very little by the new approximation.

A similar influence is observed in the graphs of $k\cot\eta_\ell$ with k^2 and a particularly interesting modification arises in the low energy limit of $k\cot\eta_0$ with k^2. The modification is enough to change the scattering length from 1.806 to 2.055, an increase of $\sim 14\%$.

These important differences at low thermal energies are expected from the form of the potential which is long range and likely to be more effective at large separations of the colliding centres, i.e. at low energies of impact. We note from the phase shift curves that the effective potential acting between the colliding centres is still repulsive for all ℓ values.

The inclusion of the long range potential does not apparently increase the importance of the higher ℓ value contributions to the various values displayed on the graphs.

The Results for Z_{eff}

The Table IV gives the results for the static approximation and the long range potential approximation in the approximations A, B, C and D mentioned in the previous chapter. The graphs of Z_{eff} with k^2 are in figures 15 and 16 for the static and long range cases respectively.

In both approximations Z_{eff} is seen to be energy dependent and increases with energy except in the $\ell = 0$ case for the long range potential approximation where a minimum occurs in the low energy region.

(Fraser and Kraidy, 1966) have comparable results but an error in their paper has resulted in a recalculation and their new results are very close to ours.

The experimental results for Z_{eff} in this collision have evaluated at thermal energies i.e. for $k^2 \sim 0{\cdot}0036$.The results for orthopositronium in helium are listed below.

(Heymann et al, 1961 $Z_{eff} = 0.135 \pm 0.068$

(Duff and Heyman, 1962) $Z_{eff} = 0.118 \pm 0.11$

(Roellig and Kelly, 1967) $Z_{eff} = 0.25 \pm 25\%$

At thermal energies our values give, in the D curves,

Static Approximation Z_{eff} = 0.037

Long Range Potential Approximation Z_{eff} = 0.048

These values are much lower than the experimental values but it should be noted that inclusion of the long range potential has had a very important effect in increasing Z_{eff}. (Duff and Heymann, 1962) used helium gas at low densities but their results are questionable since the helium was deliberately contaminated by freon in order to remove the free positron annihilation component. The experiments of (Roellig and Kelly, 1967) relate to the formation of 'bubbles' in helium at high densities which are due to the repulsive exchange forces between the orthopositronium and helium atoms and their derivation of Z_{eff} is quite indirect.

It is of interest to know whether the value of Z_{eff} can be brought in agreement with the experimental estimates by varying the strength of the long range potential.

We have recalculated, for $k = 0.06$ the values of σ_0 and $^{A}Z_{eff}, (l=0)$, corresponding to a value of the long range potential multiplied by a constant factor β. Table V shows the results of this.

It is evident that the values of σ_0 and $^{A}Z_{eff}\ (l = 0)$, are very sensitive indeed to variations in the potential strength and it is obvious that the experimental value is obtainable for certain ranges of β .

Conclusions

The serious discrepency between the calculated values of Z_{eff} and those inferred from experiment prompt further investigations of the problem.

The static exchange wave function could be improved in several ways. The simple variational wave-function here for the helium has proved to be quite effective in determining phase shifts and cross sections for scattering processes in helium, but in the calculation of Z_{eff} it is possible that a better form of helium wave function would lead to an improvement in result. More accurate helium wave functions have been proposed by (Green et al, 1954) and (Eckart, 1930). These are respectively,

$$\psi_+(\underset{\sim}{r_1}, \underset{\sim}{r_2}) = \left\{ e^{-\alpha r_1} + c\, e^{-\beta r_1} \right\} \left\{ e^{-\alpha r_2} + c\, e^{-\beta r_2} \right\}$$

where

$$\left.\begin{aligned} \alpha &= 1.455799 \\ \beta &= 2\alpha \\ c &= 0.6 \end{aligned}\right\}$$

and,

$$\psi_+(\underset{\sim}{r_1}, \underset{\sim}{r_2}) = e^{-\alpha r_1} e^{-\beta r_2} + e^{-\beta r_1} e^{-\alpha r_2}$$

where

$$\left.\begin{aligned} \alpha &= 2.1832 \\ \beta &= 1.1885 \end{aligned}\right\}$$

The parameters are determined variationally.

These lead respectively to ground state energies, $E_0^{He} = -5.723$

and -5.571. These are comparable to the experimental value of E_0^{He} = -5.808.

Inclusion of either of these functions into the analysis would be straightforward but extremely lengthy. The second open shell function would be more tractable than the first but even so the labour involved would be considerable.

We must consider the fact that in the annihilation of the orthopositronium a positron and an electron of the correct spin are at the same position in space. This would suggest that correlation terms in the trial wave-function that depend explicitely on the coordinate joining the positron to a target electron are important.

Because of the great sensitivity of the Z_{eff} value to the strength of the long range potential it is possible that a more accurate evaluation ofthe potential would lead to an improvement in the result. This is possible by using a better form of helium wave function in the variational treatment or by including more variational parameters. We suggest however that this will only have a small effect and that the major improvement lies in the kernal evaluation of the main problem.

Finally, the work of (Khare et al, 1964) indicates the possibility of a bound state of a positron with a helium atom with a binding energy of $\sim$ 0.55 ev. If this is in fact physically possible then an improvement in the calculation would be to allow for virtual formation of the bound state in the trial wave function. Inclusion of this effect would allow for more penetration of the atom by the positron and since Z_{eff} depends on the square of the wave function in the atomic region we would expect an improvement in the result.

The importance of the effect of a virtual bound state was shown in the scattering of positrons by helium atoms, (Bransden, 1962). The various cross sections and phase shifts were considerably changed by inclusion of virtual positronium formation in the trial wave function.

TABLE II

Ortho-positronium helium atom elastic scattering in the static exchange approximation The phase shifts are in radians, the cross sections in a_0^2 and k is in atomic units as defined in anearlier chapter.

k	η_0	σ_0	η_1	σ_1	η_2	σ_2	$\sigma_T=\sigma_0+\sigma_1+\sigma_2$	σ_D
0	-	40.98	-	-	-	-	40.98	40.98
0.01	-0.0176	40.98	-	-	-	-	40.98	40.98
0.05	-0.0906	40.82	-0.0003	0.0011	-	-	40.82	40.58
0.06	-0.1088	40.76	-0.0005	0.0022	-	-	40.76	40.42
0.07	-0.1264	40.68	-0.0007	0.0040	-	-	40.68	40.23
0.1	-0.1801	40.39	-0.0021	0.0164	-	-	40.41	39.48
0.15	-0.2690	39.67	-0.0068	0.0778	-0.0001	-	39.75	37.79
0.2	-0.3585	38.69	-0.0155	0.2263	-0.0003	0.0001	38.92	35.69
0.3	-0.5321	36.03	-0.0468	0.9176	-0.0020	0.0027	36.95	31.03
0.4	-0.7007	32.67	-0.0967	2.194	-0.0073	0.0210	34.89	26.62
0.5	-0.8605	28.91	-0.1615	3.898	-0.0191	0.0914	32.90	22.91
0.6	-1.011	25.05	-0.2359	5.718	-0.0343	0.2691	31.04	19.91
0.7	-1.149	21.34	-0.3141	7.344	-0.0684	0.5985	29.28	17.47
0.8	-1.274	17.95	-0.3912	8.562	-0.1050	1.079	27.59	15.63
0.9	-1.385	14.98	-0.4630	9.283	-0.1466	1.656	25.92	13.84
1.0	-1.482	12.47	-0.5268	9.530	-0.1900	2.241	24.24	12.46
1.1	-1.566	10.39	-0.5812	9.390	-0.2321	2.749	22.52	11.29
1.2	-1.637	8.688	-0.6255	8.976	-0.2708	3.122	20.79	10.25
1.3	-1.695	7.321	-0.6599	8.384	-0.3047	3.345	19.05	9.305

TABLE II (cont.)

k	η_0	σ_0	η_1	σ_1	η_2	σ_2	σ_T	σ_D
1.4	-1.739	6.232	-0.6842	7.684	-0.3332	3.430	17.35	8.424
1.5	-1.766	5.375	-0.6980	6.921	-0.3564	3.400	15.70	7.582
1.6	-1.773	4.712	-0.7008	6.122	-0.3742	3.280	14.11	6.762
1.7	-1.753	4.207	-0.6921	5.312	-0.3864	3.087	12.61	5.950
1.8	-1.697	3.818	-0.6725	4.515	-0.3925	2.837	11.17	5.124
1.9	-1.591	3.480	-0.6430	3.755	-0.3926	2.548	9.78	4.251
2.0	-1.418	3.069	-0.5991	3.097	-0.3870	2.238	8.40	3.296

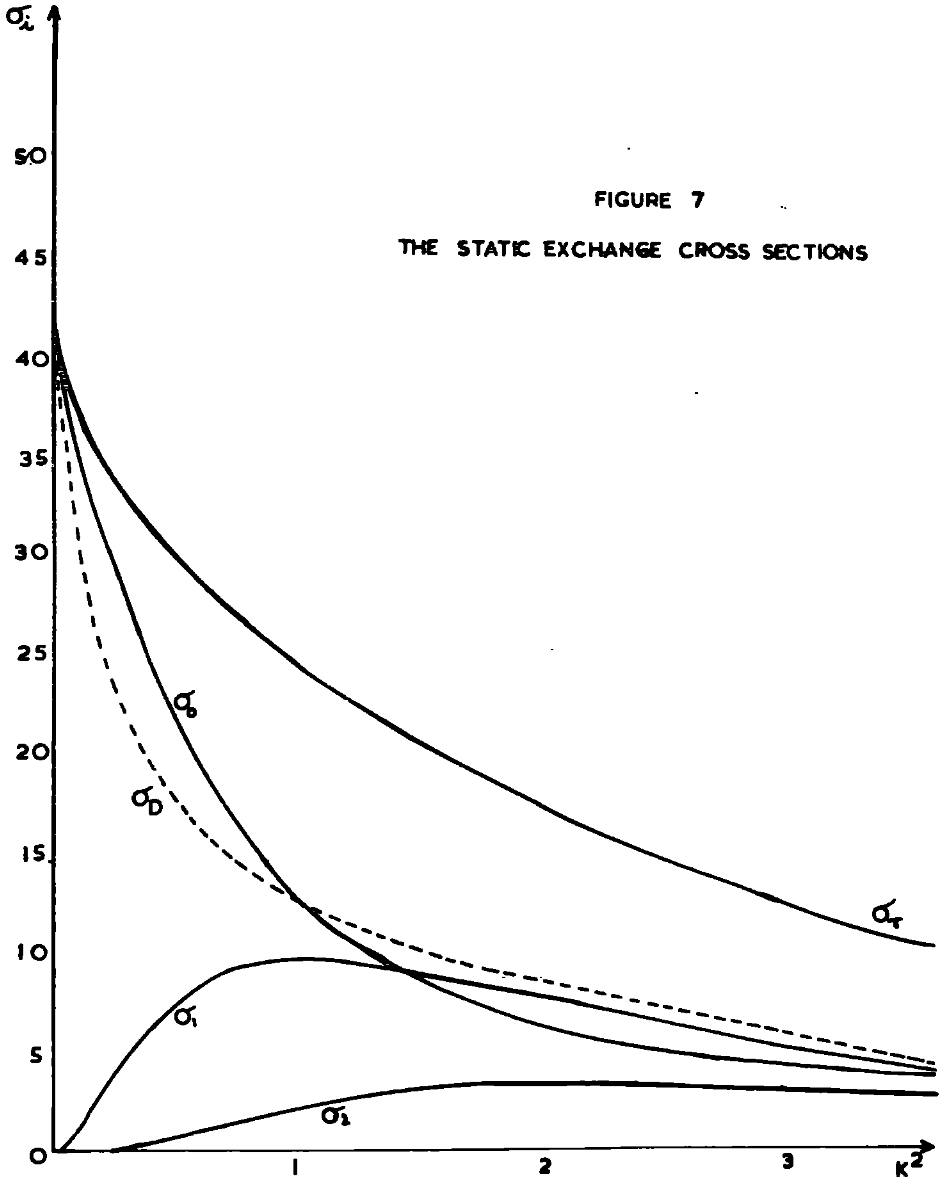


FIGURE 7

THE STATIC EXCHANGE CROSS SECTIONS

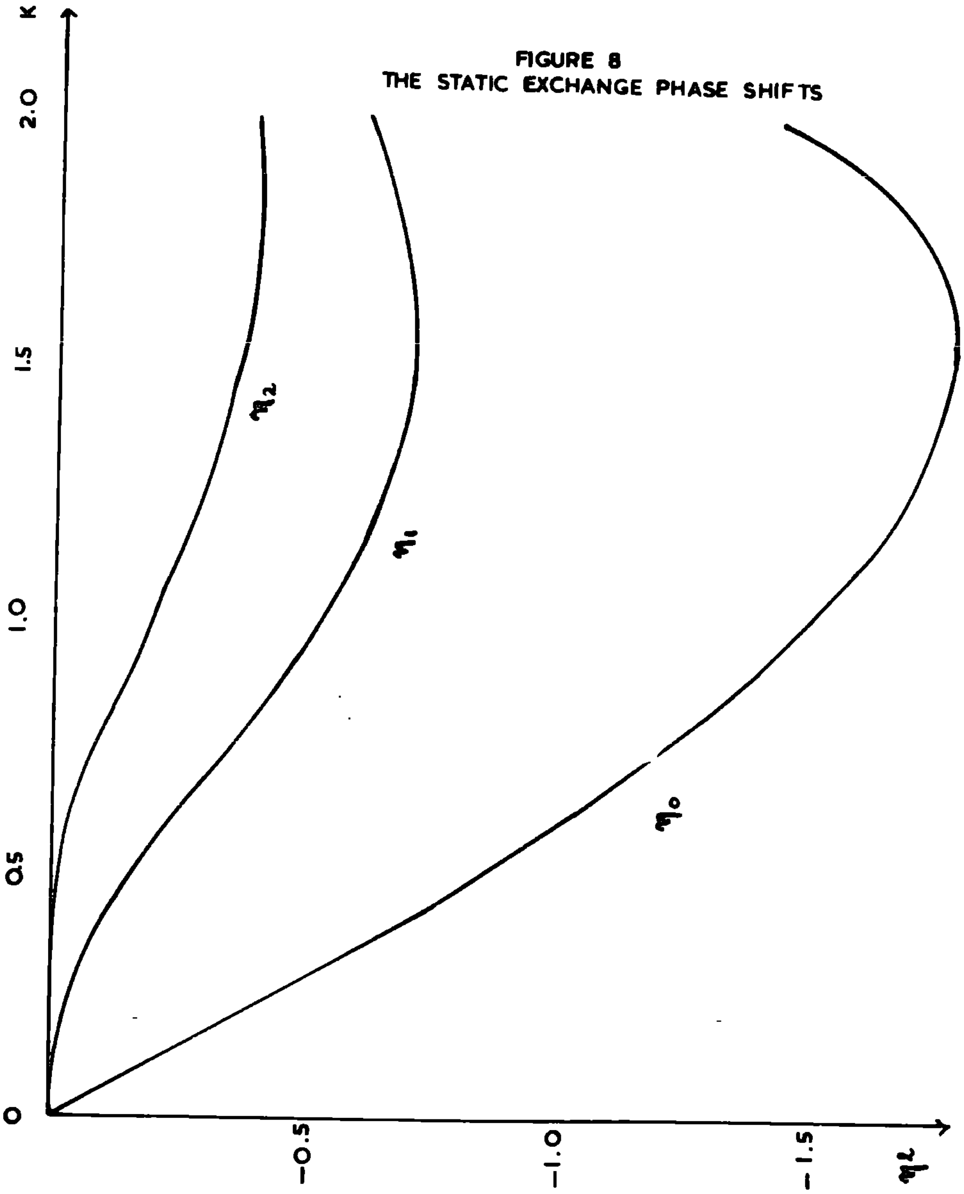


FIGURE 8
THE STATIC EXCHANGE PHASE SHIFTS

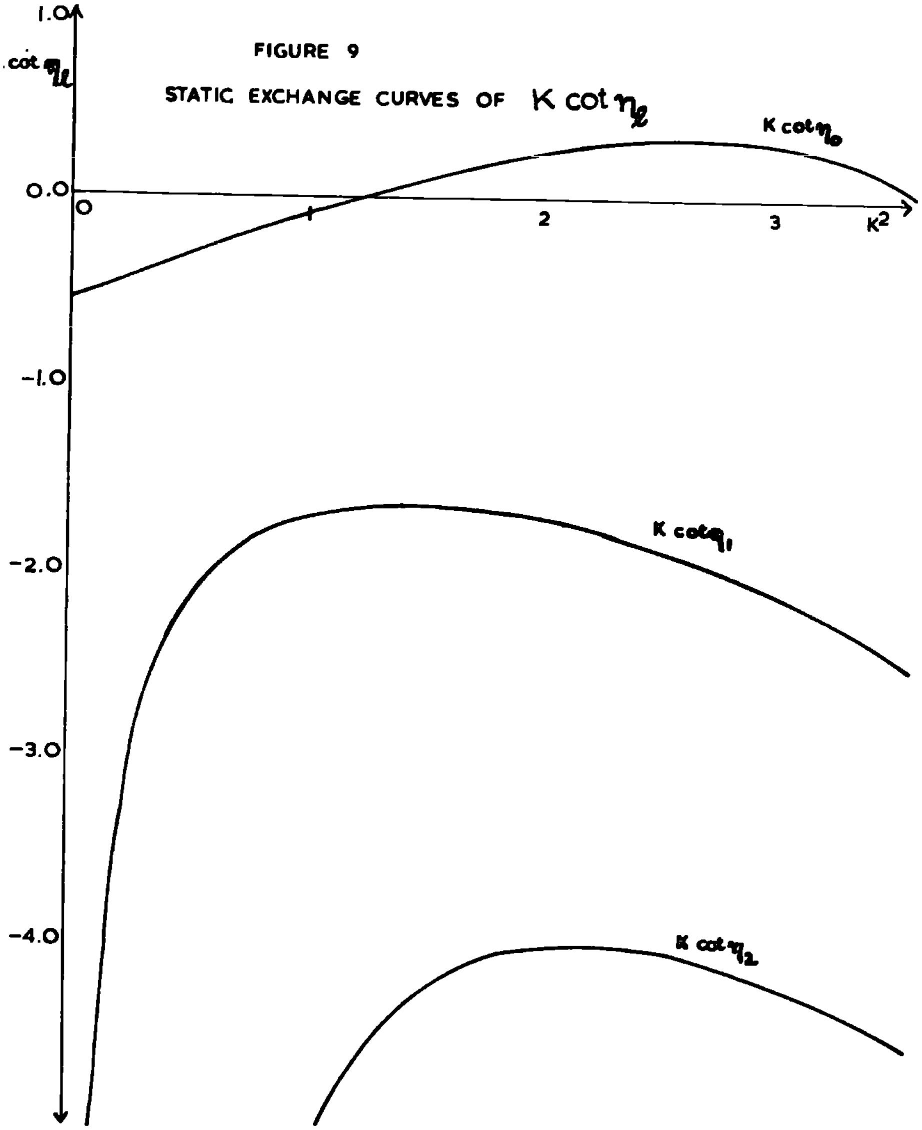


FIGURE 9

STATIC EXCHANGE CURVES OF $K \cot \eta_l$

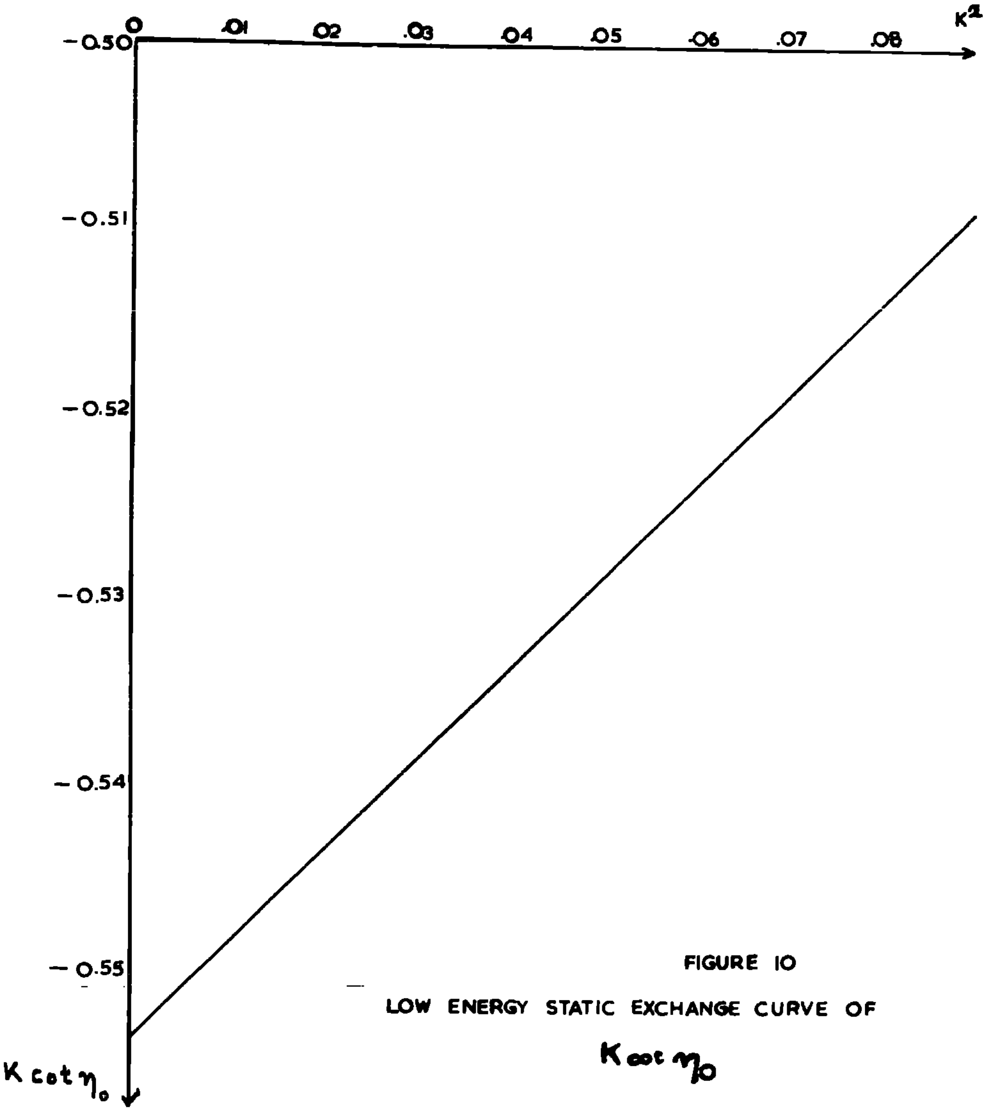


FIGURE 10

LOW ENERGY STATIC EXCHANGE CURVE OF

$K \cot \eta_0$

TABLE III

Orthopositronium-helium atom elastic scattering allowing for the long range interaction.
Units are as in Table II

k	η_0	σ_0	η_1	σ_1	η_2	σ_2	σ_T	σ_D
0	-	53.04	-	-	-	-	53.04	53.04
0.01	-0.0205	53.04	-	-	-	-	53.04	53.04
0.05	-0.1020	52.47	-0.0003	0.0012	-	-	52.47	52.19
0.06	-0.1226	52.23	-0.0005	0.0025	-	-	52.23	51.82
0.07	-0.1429	51.95	-0.0008	0.0046	-	-	51.95	51.40
0.1	-0.2027	50.88	-0.0022	0.0186	-	-	50.89	49.79
0.15	-0.2983	48.49	-0.0073	0.0891	-0.0001	-	48.58	46.28
0.2	-0.3900	45.64	-0.0166	0.2606	-0.0003	0.0001	45.90	42.19
0.3	-0.5607	39.54	-0.0503	1.060	-0.0020	0.0029	40.60	34.02
0.4	-0.7152	33.78	-0.1034	2.508	-0.0076	0.0227	36.31	27.37
0.5	-0.8567	28.69	-0.1709	4.360	-0.0199	0.0992	33.15	22.48
0.6	-0.9867	24.30	-0.2462	6.220	-0.0489	0.2917	30.81	18.97
0.7	-1.108	20.52	-0.3231	7.755	-0.0710	0.6451	28.92	16.37
0.8	-1.218	17.29	-0.3967	8.792	-0.1085	1.152	27.24	14.39
0.9	-1.319	14.55	-0.4635	9.304	-0.1506	1.746	25.60	12.82
1.0	-1.409	12.24	-0.5217	9.362	-0.1938	2.331	23.93	11.56
1.1	-1.489	10.32	-0.5704	9.083	-0.2351	2.818	22.22	10.49
1.2	-1.558	8.725	-0.6096	8.582	-0.2724	3.159	20.47	9.562

Table III Cont.

r	η_0	σ_0	η_1	σ_1	η_2	σ_2	σ_T	σ_D
1.3	-1.615	7.421	-0.6397	7.949	-0.3046	3.345	18.72	8.710
1.4	-1.659	6.362	-0.6607	7.243	-0.3314	3.394	17.00	7.905
1.5	-1.686	5.512	-0.6721	6.496	-0.3529	3.335	15.34	7.125
1.6	-1.692	4.838	-0.6736	5.730	-0.3691	3.194	13.76	6.355
1.7	-1.670	4.306	-0.6647	4.963	-0.3799	2.989	12.26	5.580
1.8	-1.612	3.872	-0.647	4.214	-0.3850	2.735	10.82	4.782
1.9	1.505	3.466	-0.6178	3.504	-0.3889	2.501	9.472	3.942
2.0	-1.334	2.968	-0.5824	2.851	-0.3837	2.199	8.018	3.021

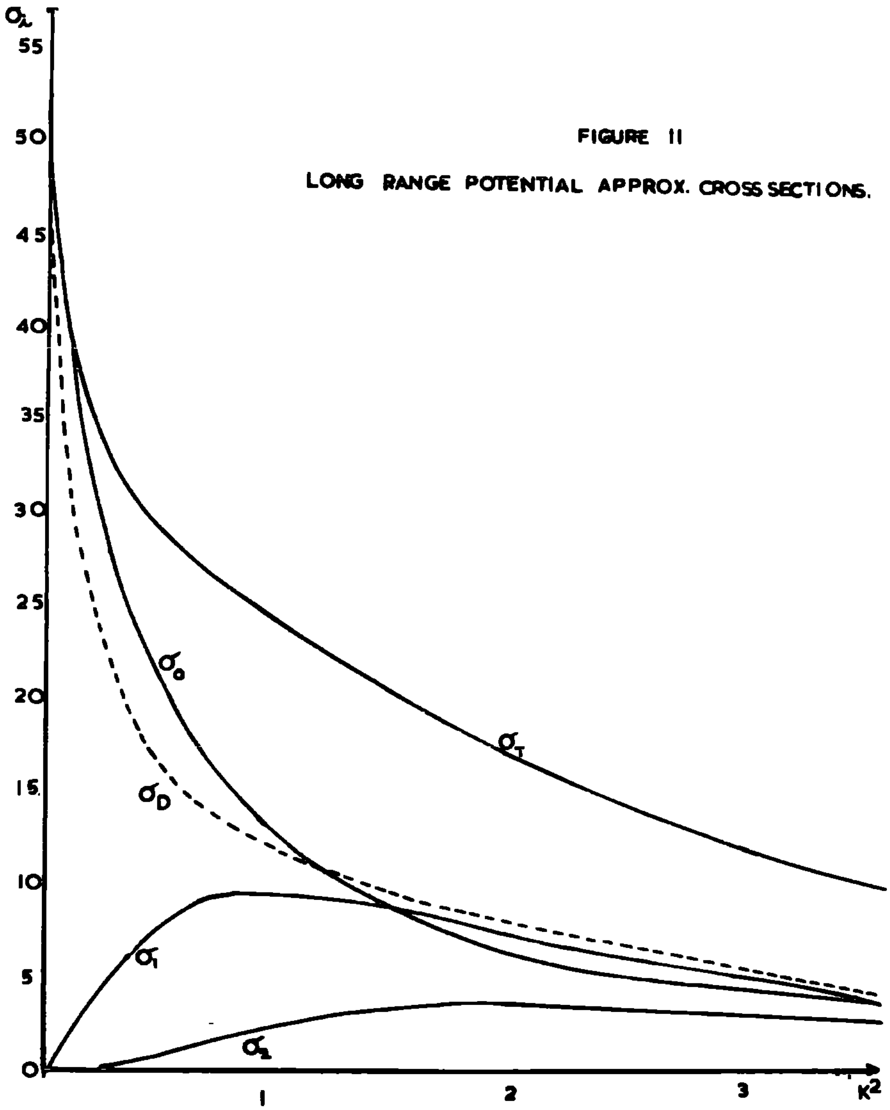


FIGURE II

LONG RANGE POTENTIAL APPROX. CROSS SECTIONS.

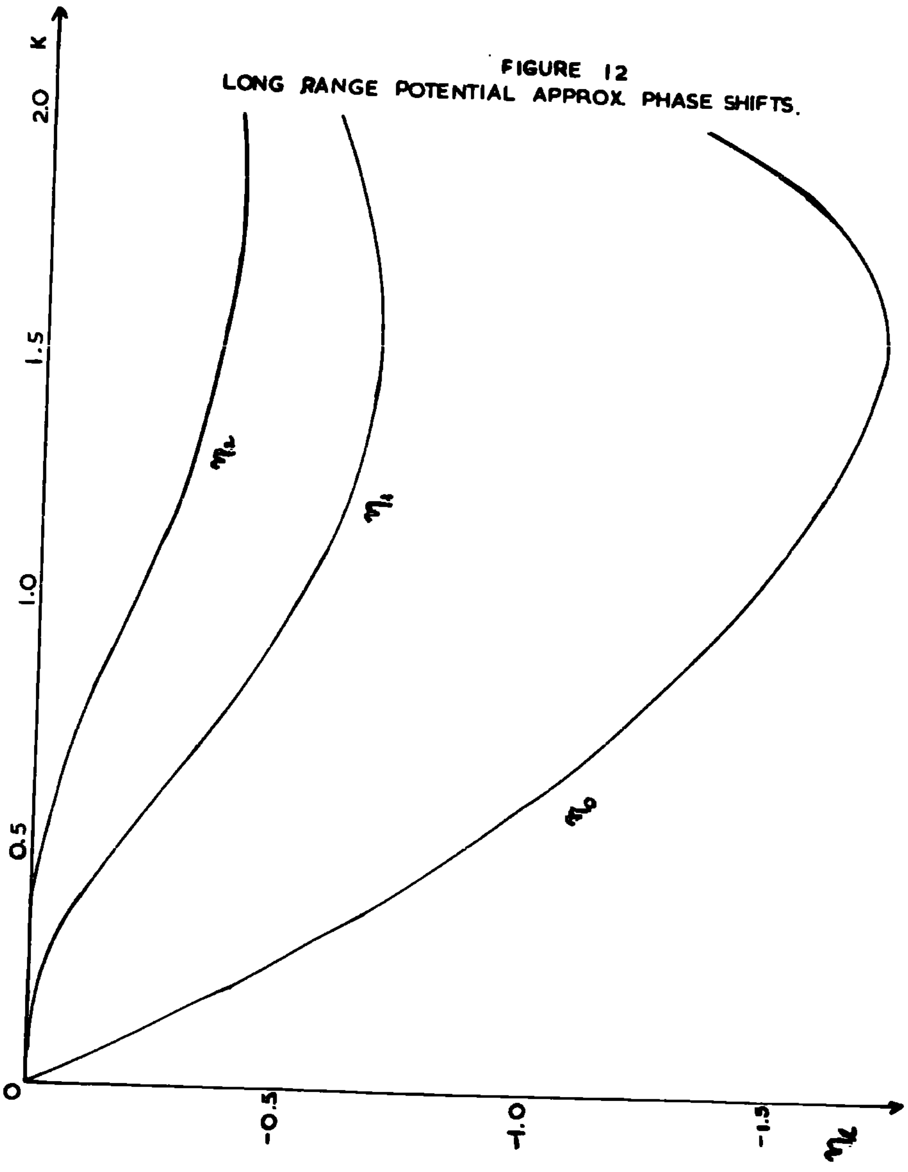


FIGURE 12
LONG RANGE POTENTIAL APPROX. PHASE SHIFTS.

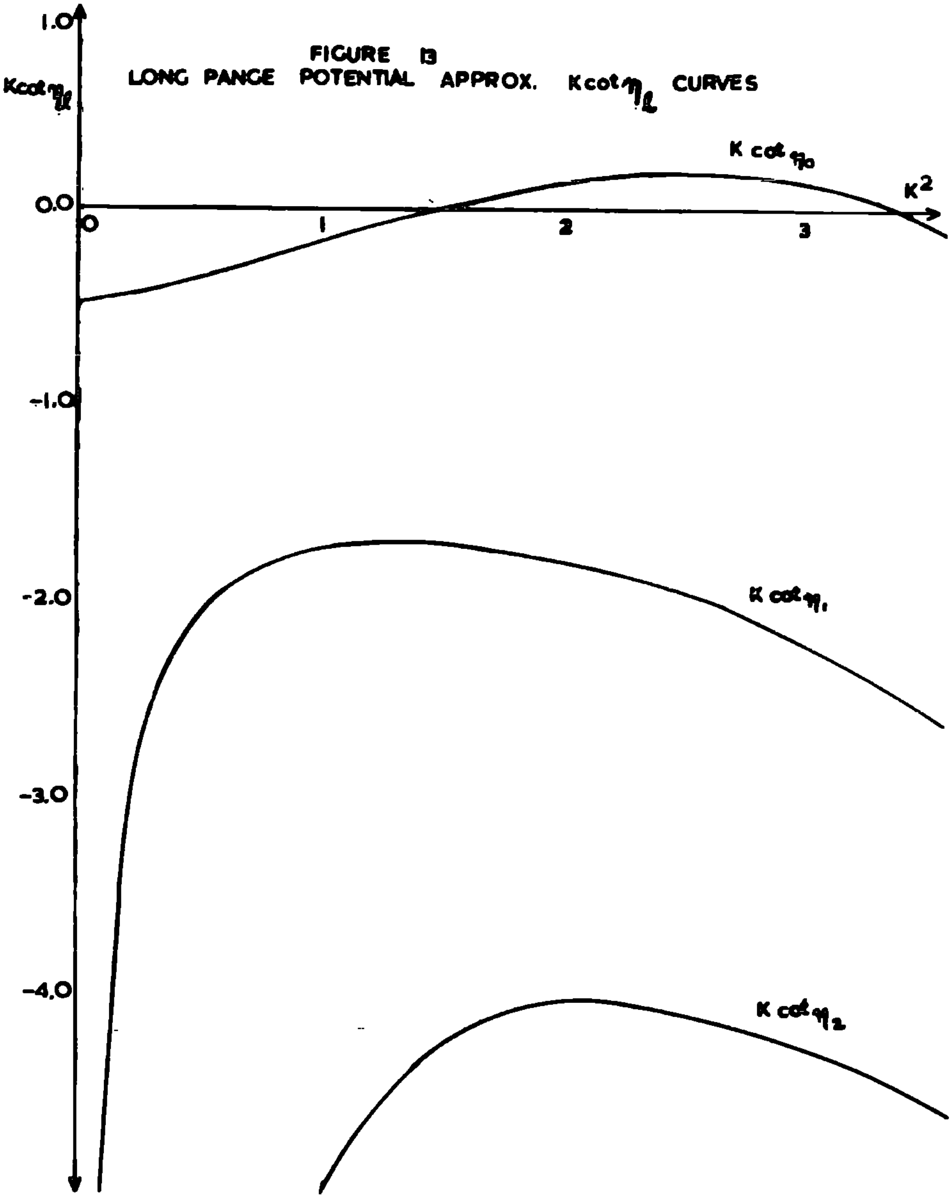


FIGURE 13

LONG PANGE POTENTIAL APPROX. $K\cot\eta_\ell$ CURVES

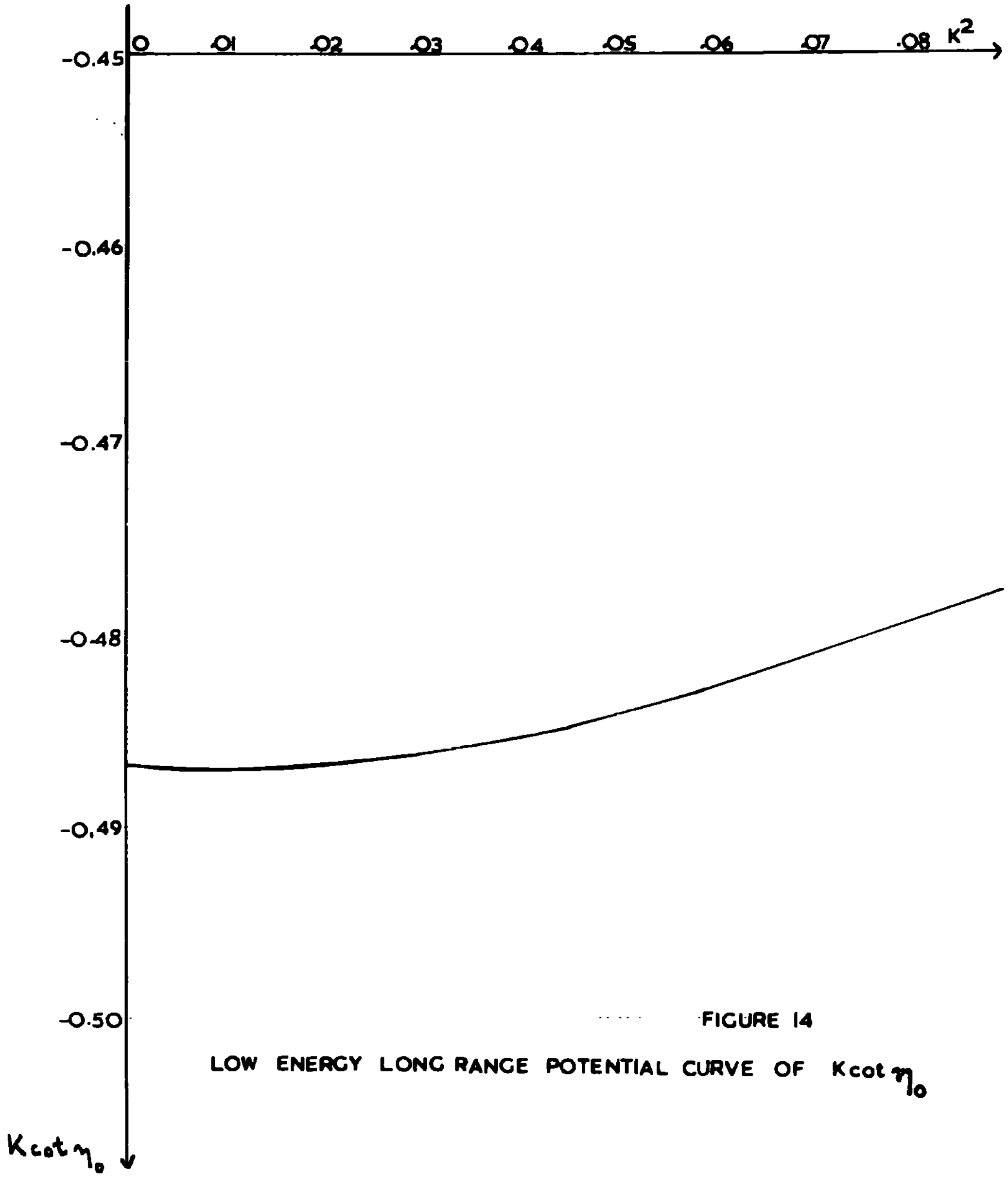


FIGURE 14

LOW ENERGY LONG RANGE POTENTIAL CURVE OF $K\cot\eta_0$

TABLE IV

Calculated values of Z_{eff} with k in the defined atomic units

k	A	B	C	D	A	B	C	D
0	0.0347	0.0347	0.0347	0.0347	0.0455	0.0455	0.0455	0.0455
0.01	0.0347	0.0348	0.0348	0.0348	0.0455	0.0456	0.0456	0.0456
0.05	0.0347	0.0357	0.0360	0.0373	0.0452	0.0463	0.0469	0.0481
0.06	0.0347	0.0361	0.0361	0.0374	0.0451	0.0467	0.0467	0.0480
0.07	0.0348	0.0366	0.0366	0.0379	0.0449	0.0471	0.0471	0.0484
0.1	0.0348	0.0384	0.0387	0.0400	0.0443	0.0486	0.0487	0.0499
0.15	0.0348	0.0426	0.0428	0.0441	0.0430	0.0523	0.0525	0.0538
0.2	0.0349	0.0480	0.0480	0.0497	0.0415	0.0572	0.0577	0.0590
0.3	0.0350	0.0605	0.0624	0.0638	0.0387	0.0690	0.0714	0.0727
0.4	0.0353	0.0732	0.0786	0.0803	0.0366	0.0811	0.0874	0.0891
0.5	0.0358	0.0851	0.0960	0.0987	0.0355	0.0919	0.1044	0.1070
0.6	0.0364	0.0959	0.1139	0.1187	0.0352	0.1012	0.1214	0.1262
0.7	0.0373	0.1057	0.1319	0.1405	0.1357	0.1094	0.1383	0.1469
0.8	0.0383	0.1152	0.1498	0.1644	0.0367	0.1172	0.1549	0.1694
0.9	0.0394	0.1245	0.1677	0.1905	0.0381	0.1251	0.1713	0.1941
1.0	0.0408	0.1338	0.1852	0.2186	0.0398	0.1333	0.1876	0.2210
1.1	0.0422	0.1432	0.2027	0.2491	0.0416	0.1416	0.2037	0.2501
1.2	0.0438	0.1527	0.2200	0.2803	0.0437	0.1503	0.2198	0.2800
1.3	0.0456	0.1623	0.2373	0.3129	0.0458	0.1519	0.2356	0.3112
1.4	0.0478	0.1722	0.2545	0.3464	0.0482	0.1683	0.2515	0.3433
1.5	0.0506	0.1856	0.2718	0.3804	0.0514	0.1783	0.2676	0.3762
1.6	0.0541	0.1935	0.2892	0.4146	0.0551	0.1887	0.2839	0.4093
1.7	0.0587	0.2049	0.3066	0.4491	0.0597	0.1996	0.3001	0.4427
1.8	0.0645	0.2163	0.3235	0.4827	0.0650	0.2102	0.3158	0.4750
1.9	0.0714	0.2271	0.3392	0.5146	0.0710	0.2199	0.3311	0.5066
2.0	0.0773	0.2363	0.3524	0.5435	0.0750	0.2258	0.3407	0.5318

Static Exchange

Long Range Potential

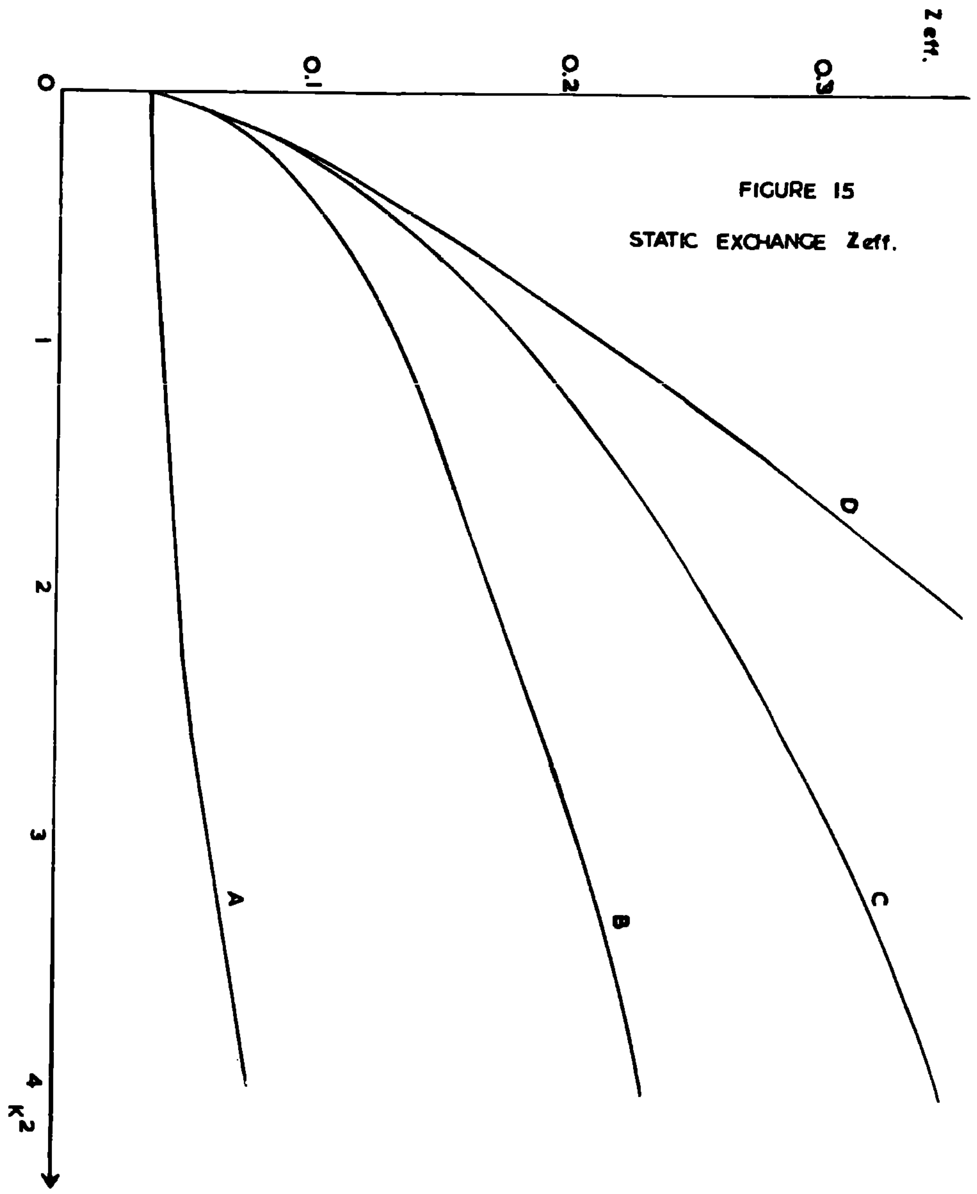


FIGURE 15

STATIC EXCHANGE Zeff.

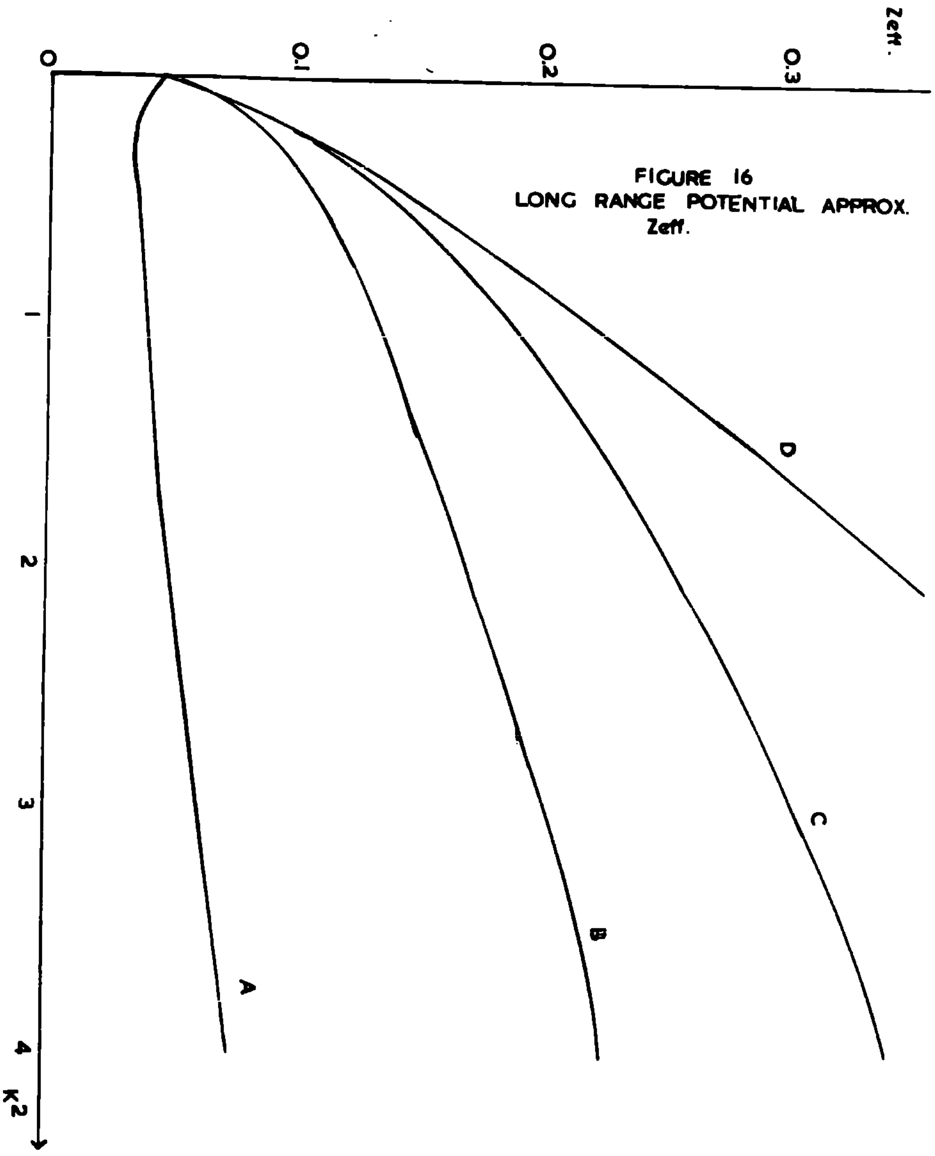


FIGURE 16
LONG RANGE POTENTIAL APPROX.
Zeff.

TABLE V

Variation in partial cross section and ${}^{A}Z_{eff}$ for $\ell = 0$, $k = 0.06$, with strength of the long range potential.

β	σ_0	${}^{A}Z_{eff}\ (\ell = 0)$
0	40.08	0.035
0.2	47.30	0.075
0.35	49.01	0.077
0.5	13.79	0.107
0.8	2.99	0.218
0.9	15.02	0.111
0.95	63.35	0.021
1.0	52.23	0.045
1.05	6.02	0.084
1.25	9.65	0.017
1.3	0.07	0.168
1.4	0.22	0.242
2.3	0.003	0.381
3.0	0.17	0.375
4.0	0.10	0.366
6.0	15.77	0.610

σ_0 is in a_o^2 units

CHAPTER 7

THE ATTACHMENT OF POSITRONS TO GASEOUS ATOMS

Introduction

Since the early work of (Deutsch, 1953) the possibility of positronium compounds has been postulated to explain anomalous rates in the study of quenching effects in gases. Also (Paul and St. Pierre, 1963) and (Green and Tao, 1963) interpreted their experimental results to show that compounds were formed between positrons which had failed to form positronium, and various gas atoms. In argon gas, to which small amounts of methane, ethane, propane, n-butane, isobutane or carbon tetrachloride had been added, the annihilation rates of positrons were found to be 3 to 700 times as fast as those predicted for free positrons. It was supposed that this was due to the positrons being in a region of higher electron density, i.e. bound to the gaseous atoms in forms like $e^+ CCl_4$ for example. As gas pressure was increased the lifetime of the free positrons decreased,as would be expected if compound formation was taking place. Discussions of positronium compound formation in the gaseous state are given by (Gittelman and Deutsch, 1956, 1958), (Gittleman, 1957, 1958) and Heymann, 1961).

The theoretical aspects of the problem were inaugerated by the work of (Hylleraas, 1947) and (Hylleraas and Ore, 1947), who investigated the stability of the system positronium plus electron or positronium plus positron and also the positronium molecule. These systems were found to be stable with binding energies in the 0.1 - 0.2 ev range.

(Ore, 1948) then investigated the possibility of the positron-hydrogen atom binding from a rough variational approach. The idea was to calculate the lower limit for the mass of a light positive particle which could replace a hydrogen nucleus in a molecule. Obviously this replacement in the hydrogen molecule itself would leave us with the positron-hydrogen atom system if the mass were the positron mass. Because of the general inaccuracy of the method the conclusion reached was indesisive for the positron-hydrogen case, but indications were present that other negative atomic ions could have a positive positron affinity.

The system positron-hydrogen atom, e^+H is the simplest of its kind and can be regarded as a positron coupled to a hydrogen atom or a positronium atom coupled to a proton. Two factors determine the stability of e^+H

(1) It should be stable against dissociation into fragments

i.e. $e^+ H \rightarrow e^+ + H$

or, $e^+ H \rightarrow e^+e^- + H^+$

The energy of the initial system must be lower than the fragmented system. The first mentioned above would be more favourable energetically and is the crucial reaction therefore.

(2) Thermal collisions at room temperature and atmospheric pressure occur with mean energy ~ 0.02 ev at a rate of $\sim 10^{10}$ sec^{-1} so the compound must have energy of at least ~ 0.05 ev below that of the fragments for it to be found in a significant amount under the conditions specified above.

If the wave function of the positron-atom system is Ψ and the energy E with total Hamitonian H, then a variational solution for the system is given by,

$$E = \frac{\int \Psi^* H \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau}$$

and where $\delta E = 0$

If H_A is the Hamiltonian of the system with the positron removed and E_A its energy in the ground state, we write,

$$H = H_A + H_B$$

and stability of the compound exists if,

$$E - E_A < 0$$

Evidently,

$$\int \Psi^* H_B \Psi \, d\tau < 0$$

which means physically that when a trial function is used in the variational calculation, stability will only be achieved if the energy of attraction of the positron by the electron exceeds the kinetic energy of the positron and the repulsive energy of the nucleus.

If also for simplicity the trial function is taken as angular independent the stability conditions reduce to

$$n < Z$$

where n is the number of electrons and Z the nuclear charge. The above arguments due to (Ore, 1952) demonstrate that for systems with $n = Z$, in particular the positron-hydrogen, positron helium systems, the simple variational treatment will not be adequate.

Because of this earlier calculations were performed on the binding of positron-hydride, $e^+ H^-$, by (Ore, 1952) which was found to be stable under three approximations with binding energy of ~ 0·1 ev.

The extension to positron-chloride was done by (Simons, 1948, 1949, 1953) and was found to be stable at ~ 1.6 ev. More refined calculations have been performed concerned with lifetimes and angular correlations in helium and molecular hydrogen with moderate success, (Lee Chang, 1957), (Basina et al, 1958), (Toptykin, 1962).

The work of (Khare et al, 1964) predicts a bound state of the positron-helium atom system with binding energy of 0.55 ev and they point out that since the bound state is formed in helium; with its characteristic and strong rigidity the least likely atom for bonding; then it is probable that bound states are possible with any atom or molecule.

In the case of the e^+H problem, variational methods due to (Inokuti, et al, 1960), (Baker and Handler, 1963) and (Fraser et al, 1964) show no bound state to exist. By varying the positron mass however it was found that a bound state would become possible for a mass of 2.635 times the electron mass.

Very recently, (Bransden and Jundi, 1967) a calculation was done of the cross section for positronium formation by positron impact on hydrogen in the two-state approximation taking into account the polarization of the hydrogen and positronium atoms in each channel. It was found that the polarization forces dominated the cross section near the positronium formation threshold and evidence showed the probable existence of a positronium proton, $(e^+e^-)H^+$, virtual bound state giving rise to a resonance in the elastic scattering of positrons on hydrogen atoms just below the formation threshold. This evidence together with a new projection operator technique for the resonant bound states, prompted a further investigation of the positron-hydrogen atom binding problem. We shall first discuss the method of projection operators and then outline the variational solution for the positron-hydrogen atom case.

The Projection Operator Method

If we have Hilbert space $\mathcal{E}$ and a subspace of this $\mathcal{S}$ with complementary subspace $\mathcal{S}^c$ then any ket vector $|u\rangle$ possesses a projection in $\mathcal{S}^c$, $|u_p^c\rangle$ and a projection in $\mathcal{S}$, $|u_p\rangle$, which are uniquely defined and where,

$$|u\rangle = |u_P\rangle + |u_P^c\rangle$$

The correspondence is thus linear and the linear operator, **P**, defined by,

$$P\,|u\rangle = |u_P\rangle$$

is called the projection operator or projector on ξ.

Evidently,

$$P^2|u\rangle = P.\,P\,|u\rangle = P\,|u_P\rangle$$

and obviously,

$$P\,|u_P\rangle = |u_P\rangle = P\,|u\rangle$$

Consequently,

$$P^2 = P \qquad (1)$$

Any Hermitian operator satisfying this equation is a projector. **P** is linear, Hermitian and an observable with two eigenvalues of 0 and 1. The eigenvalue 0 has subspace ξ^c and eigenvalue 1 has subspace ξ. Suppose p is an eigenvalue of **P** i.e. $P\,|u\rangle = p\,|u\rangle$

Because of equality (1),

$$0 = (P^2 - P)\,|u\rangle = (p^2 - p)\,|u\rangle$$

Since $|u\rangle$ does not vanish,

$$p^2 - p = 0$$

Hence, the eigenvalues are 0 or 1 only.

P is seen to be an observable since any vector $|u\rangle$ can be put in the form of a sum of eigenvectors of $\mathbf{P}$, i.e.

$$|u\rangle = P|u\rangle + (1-P)|u\rangle \qquad (2)$$

Now since,

$$P^2|u\rangle = P.P|u\rangle = P|u\rangle$$

then $P|u\rangle$ is an eigenvector of $\mathbf{P}$ belonging to eigenvalue 1.

On the other hand,

$$P(1-P)|u\rangle = (P-P^2)|u\rangle = 0$$

So $(1-P)|u\rangle$ is an eigenvector of $\mathbf{P}$ belonging to eigenvalue 0.

In equation (2) since,

$$P|u\rangle = |u_P\rangle$$

then evidently,

$$(1-P)|u\rangle = |u_P^c\rangle$$

let, $\quad Q = 1 - P \quad , \quad |u_P^c\rangle = |u_Q\rangle$

then,

$$Q|u\rangle = |u_Q\rangle$$

and $\mathbf{Q}$ is the projector on the complementary subspace ξ^c.

Finally then we have two projectors $\mathbf{P}$ and $\mathbf{Q}$ related by,

$$\mathbf{P} + \mathbf{Q} = 1$$

where,

$$P^2 = P$$

$$Q^2 = Q$$

which project any vector into its subspace and complementary subspace respectively i.e. they project out orthogonal parts of Hilbert space. It is obvious also that,

$$PQ = QP = 0$$

Now (Feshbach, 1958, 1962) applied these projectors to the study of nuclear reactions. The idea was to apply a projection operator to the wave function of the system which would project out the open channel configurations. Thence it was possible to partition the total wave function into closed and open channel segments and to obtain a Shrodinger equation for the open channel part by eliminating the closed channels. The projection operator which selects the open channels was not unique since it was possible to define open channels only in terms of the asymptotic behaviour of the wave function when the reaction products were far apart. This gave great flexibility to the method since one could choose that projector most convenient for the problem under investigation.

The formation was extended to atomic scattering by (Hahn et al, 1962) where they defined an operator P which projects onto the ground state of the target and a complementary projector Q projecting on all the excited states of the target including the continuum states. In this case then $P + Q$ is again the unit operator since the sum projects on all possible states.

If the Schrodinger equation for the system is,

$$H \Psi = E \Psi$$

then we operate with P and $Q = 1 - P$ on this equation to obtain the coupled equations, (Feshbach, 1962),

$$\left.\begin{aligned} (E - PHP)P\Psi &= PHQ . Q\Psi \\ (E - QHQ)Q\Psi &= QHP . P\Psi \end{aligned}\right\} \quad (3)$$

Considering the case of an isolated resonance, then when the compound state has a long lifetime, the probability of a particle re-entering an open channel is very small. To a first approximation the wave function describing the compound state is a bound state solution of the homogeneous form of (3) i.e.,

$$(E_R - QHQ)\Phi_R = 0$$

Φ_R is not the exact compound state wave function since it has an infinite lifetime due to dropping the right hand side of (3), which allows the decay from $Q\Psi$ to $P\Psi$ but we assume the approximation to be close and that E_R is here a reasonable quess at the resonant energy.

Justification for this approximation is given by the work of (O'Malley and Geltman, 1965) and (Bhatia et al, 1967) who estimate the energy difference and find it very small in the case of two-electron systems.

The Variational Calculation

The problem is to evaluate the eigenvalues of the equation,

$$Q\, H\, Q\, \Phi_R = E_R\, \Phi_R$$

for the positron-hydrogen atom system where in atomic units,

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}}$$

where the coordinates are illustrated in figure 17.

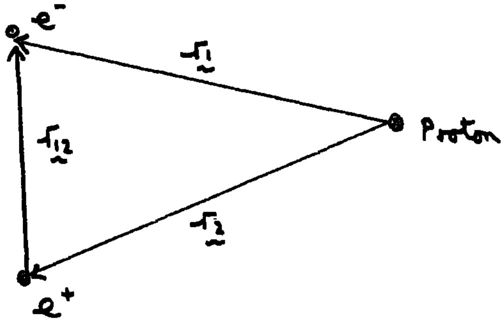


FIGURE 17

The method adopted is to assume a trial function for $Q\,\Phi_R$ and perform a Rayleigh-Ritz type of calculation. We multiply the eigenvalue equation by $\Phi_R^{*}\, Q = \Phi_R^{*}\, Q^2$ and integrate, giving,

$$\int \Phi_R^{*}\, Q\, H\, Q\, \Phi_R\, d\tau = E_R \int \Phi_R^{*}\, Q^2\, \Phi_R\, d\tau$$

Due to the Hermitian nature of Q and $Q\,H$ then,

$$E_R = \frac{\int (Q\,\Phi_R)^{*}\, H\, (Q\,\Phi_R)\, d\tau}{\int (Q\,\Phi_R)^{*}\, (Q\,\Phi_R)\, d\tau}$$

Whereas we had intially an eigenvalue equation with effective Hamitonian **QHQ** and eigenfunctions Φ_R we now have an equation with the usual Hamiltonian **H** and trial functions $Q\,\Phi_R$. The two standard choice of coordinates in the evaluation of the integrals invloved is , r_1, r_2 and r_{12} or, r_1, r_2 and θ, where θ is the angle between r_1 and r_2, where we assume that the trial function is a function of one set of the three coordinates mentioned. We choose the set r_1, r_2 and θ since it is easier to choose $Q\,\Phi_R^*$, the trial wave function, to be orthogonal to the hydrogenic ground state as required by the form of the projectors and also it makes it easier to generalize to higher partial waves. The Hamiltonian in the coordinates choosen reduces to the form, (Hahn and Spruch, 1965),

$$H = -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} + \frac{L^2}{2}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) - \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}}$$

where,

$$L^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

The functional, I, is now set up, namely,

$$I = \int (Q\,\Phi_R^*)\,[H - E_R]\,(Q\,\Phi_R^*)\,d\tau$$

and the trial function for $Q\,\Phi_R^*$ substituted.

On the basis of trial functions used in the corresponding two electron problem by (O'Malley and Geltman, 1965) and in the phase-shift calculation of (Hahn, and Spruch, 1965), we assume the form,

$$Q\,\Phi_R^{*} = \frac{1}{r_1 r_2}\Big\{ u_{200}(r_1)\, e^{-\lambda r_2} \sum_{n=1}^{N} B_n\, r_2^{\,n} + e^{-\lambda r_2}\, e^{-\mu r_1} \sum_{l=1}^{L} \sum_{n=1}^{N} \sum_{m=0}^{M} C_{lmn}\, r_1^{(m+2l)}\, r_2^{(n+2l)}\, P_l(\cos\theta) \Big\}$$

where the B_n and C_{lmn} are constants and $u_{200}(r_1)$ is the 2s hydrogenic function and is included explicitely as it is one of the lowest hydrogenic states containable in the trial function and so is likely to contribute to the energy in a substantial manner. This function is normlised as,

$$\int u_{200}^{2}(r_1)\, r_1^{2}\, dr_1 = 1$$

so in fact,

$$u_{200}(r_1) = \frac{1}{2\sqrt{2}}\,(2 - r_1)\, e^{-\frac{r_1}{2}}$$

and this satisfies,

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial r_1^2} + \frac{L^2}{2}\frac{1}{r_1^2} - \frac{1}{r_1} \right] u_{200}(r_1) = -\frac{1}{4}\, u_{200}(r_1)$$

We substitute the trial function in the functional equation and using the equations for $u_{100}(r_1)$ and the properties of the Legendre polynomials we evaluate all the integrals. This is outlined in Appendix C.

Finally as seen in the Appendix C we arrive at,

$$I = \sum B_n B_{n'} f_1(n, n') + \sum C_{lmn} C_{l'm'n'} f_2(l, m, n, l', m', n')$$

$$- E_A \Big\{ \sum B_n B_{n'} f_3(n, n') + \sum C_{lmn} C_{l m' n'} f_4(l, m, n, m', n')$$

the summations ranging over all the variables in the terms following them.

If we now order the terms C_{lmn} with respect to one subscript i, where,

$$i = m L N + l N + n$$

and here L, N, M are the maximum values used by each summation over l, n and m.

This means,

$$C_{lmn} = C_i$$

We also see that,

$$C_{00n} = B_n$$

So that the B_n are included in the total of the C_i. Obviously i ranges from 1 to MLN + LN + N.

The condition of the Rayleigh-Ritz method is that,

$$\frac{\partial I}{\partial C_i} = 0$$

Performing this differentiation we arrive at a set of simultaneous equations which are solved by the determinant of the coefficients of the terms $C_i C_j$ being equated to zero, i.e.

$$\mathrm{DET}\left(\mathcal{H} - E_R \mathcal{N}\right) = 0$$

where the matrix elements of the $\mathcal{H}$ and $\mathcal{N}$ are the coefficients of the various $C_i C_j$ in the expression for I. This determinant is in this problem asymmetrical and its solution for the lowest eigenvalue of E_R is discussed in the next chapter where the computational techniques used are explained.

CHAPTER 8

THE NUMERICAL SOLUTION OF THE POSITRON-HYDROGEN ATOM PROBLEM.

Introduction

In this chapter we present the numerical and computational techniques for solving the secular equation,

$$\mathrm{DET}\ (\mathcal{H} - E_R \mathcal{N}) = 0$$

for the lowest eigenvalue of E_R.

We then present the results and a discussion with regard to the recent work of other workers.

Numerical and Computational Techniques

A programme was written to evaluate the matrix elements of $\mathcal{N}$ and $\mathcal{H}$ for any value of μ, λ and L, M or N. This necessitated subprogramming for factorials and the required Clebsch-Gordan coefficients. The accuracy of the programme was tested by setting μ and λ equal to unity and evaluating for small L, M and N analytically and checking with the results of the programme.

With μ and λ equal to unity again the determinant could be solved analytically in the 3 x 3 form, with L, M and N unity and the three values of E_R obtained. We expect the lowest to be the most likely candidate for any physical bound state. The 3 x 3 matrix elements indicate a value of $E_R \sim -2.0$. From the electron-hydrogen atom problem we expect a lowest value of E_R in the region -0.5.

Using the value $E_R \sim -2.0$ as a starting value a zero-

-finding programme was written based on Newton's method for the roots of a polynomial which is in this case the expanded determinant.

This programme was tested with known determinants and with the small values of L, M, N equal to unity and gave exact agreement under about ten interations of the searching technique.

The proceedure was to set $E_R = -2.0$ and the zero-finding programme would work from this initial guess to the nearest zero.

It was found that the minimum value of E_R was most sensitive to changes in L as would be expected, so for each L value tried μ and λ were minimised independently.

First λ was set equal to unity, L, M and N fixed at some low value each and the minimum of E_R found for a range of μ. This proceedure pinpointed μ_{min} the value of μ giving the smallest value of E_R.

μ was taken then fixed at μ_{min} and λ varied to give λ_{min}. Fixing μ and λ at μ_{min} and λ_{min} the values of M and N were increased to gradually larger values and with $M = N$ or $M \neq N$ to indicate the variation of the lowest E_R value with M and N.

The whole proceedure could then be repeated with a different value of L.

Even for quite large sizes of the determinant the zero could be pinpointed due to the sudden sign change in the value of the determinant as E_R was varied through the zero by the Newton's searching programme.

Results and Discussion

The different values of L used were L = 1, 2 and 3. For L = 1, M = 1, N = 1 the value of minimum E_R was given by

$$\mu_{min} = 1.015$$

$$\lambda_{min} = 0.850$$

Consequently, $E_{R_{min}} = +1.6292$ in this approximation. For L = 2, M = 1, N = 1,

$$\mu_{min} = 1.665$$

$$\lambda_{min} = 0.885$$

and $E_{R_{min}} = +1.2184$.

The increase in L from 1 to 2 had decreased $E_{R_{min}}$ and we could safely assume a successive decrease with increasing L.

In fact for L = 3, M = 1, N = 1,

$$\mu_{min} = 2.701$$

$$\lambda_{min} = 1.000$$

and $E_{R_{min}} = +0.9517$, a further decrease as assumed. Since (O'Malley and Geltman, 1965) had choosen L = 2 i n their evaluation of the electron-hydrogen-atom problem we decided to try this value first to see the comparison in the present positron-hydrogen atom case.

The various values tried for M and N are indicated below and the size of the determinant (n x n) resulting.

L	M	N	(n x n)	$E_{R_{min}}$
2	1	1	(5 x 5)	+1.2184
2	2	2	(14,14)	+0.5857
2	1	3	(15,15)	+0.6076
2	2	3	(21,21)	+0.6023
2	3	3	(27,27)	+0.5828
2	4	4	(44,44)	+0.5820

Using values of $M \neq N$ gives an unequal preference to various powers of r_1 and r_2 in the trial fucntion so we expect the values of $M = N$ to give the best approximation to $E_{R_{min}}$. The convergence for these values is quite reasonable and in this approximation i.e. up to terms in $\ell = 2$ we can say $E_{R_{min}} \sim +0.58$.

This indicated a total system of energy E_S where,

$$E_S = 0\cdot33 \sim 4\cdot49\,\mathrm{ev}$$

This is to be compared to the values given for the electron -hydrogen atom case (O'Malley and Geltman, 1965); as would be expected from the sign of the charge on the different particles, the positron is less tightly bound than the electron. We now continued the approximation to values with $L = 3$. With the same values of μ_{min} and λ_{min} the value of $E_{R_{min}}$ for $L = 3$, $M = 1$, $N = 1$,

$(n \times n) = (7,7)$ was obviously too large a variation, so μ_{min} and λ_{min} were redetermined for the new value of L. The results with L = 3 are given below,

L	M	N	(nxn)	E_{Rmin}
3	1	1	(7,7)	+0.9517
3	2	2	(20,20)	+0.5205
3	3	3	(39,39)	+0.5190

This indicates, $E_{Rmin} \sim +0.52$ and the total energy of the system is, taking account of the hydrogen 2s state energy of -0.25,

$$E_S \sim +0.27 = 3.67 \text{ ev}$$

Now the positronium formation threshold is at energy 0.25 and so the positron-hydrogen atom system is unbound with energy +0.02 = 0.27 ev above the positronium formation threshold. Very recently (Drachman, 1968) has considered the problem of a resonance in positron-hydrogen scattering in which he uses a trial wave function containing the positronium atom wave function explicitly and a function allowing for adiabatic distortion of the positronium atom.

Using this in a non-variational adiabatic calculation he finds a resonance at 0.1 ev below the positronium formation threshold.

He then extends his method to include non-adiabatic terms by a variational calculation and this acts in such a way as to eliminate the possibility of a resonance and bringing both our conclusions into agreement.

APPENDIX A

THE VARIATIONAL CALCULATION AND THE KERNAL

The variational procedure is performed on the equation

$$\frac{I_t}{3} = \int d\underset{\sim}{\sigma_1}\, d\underset{\sim}{\rho_1}\, d\underset{\sim}{r_2}\, d\underset{\sim}{r_3}\; v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) \left[H - E_t\right] \left[v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) - v_l(\sigma_2)\, \phi(\rho_2)\, \psi_t(\underset{\sim}{r_3}, \underset{\sim}{r_1}) \right]$$

i. e.

$$\frac{\delta I_t}{3} = \int d\underset{\sim}{\sigma_1}\, d\underset{\sim}{\rho_1}\, d\underset{\sim}{r_2}\, d\underset{\sim}{r_3} \Big\{ \delta v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) \left[H - E_t\right] \left[v(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) - v_l(\sigma_2)\, \phi(\rho_2)\, \psi_t(\underset{\sim}{r_3}, \underset{\sim}{r_1}) \right] + v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) \left[H - E_t\right] \left[\delta v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) - \delta v_l(\sigma_2)\, \phi(\rho_2)\, \psi_t(\underset{\sim}{r_3}, \underset{\sim}{r_1}) \right] \Big\}$$

Because of the symmetry of the various terms we can change the coordinates in the last term such that,

$$\frac{\delta I_t}{3} = \int d\underset{\sim}{\sigma_1}\, d\underset{\sim}{\rho_1}\, d\underset{\sim}{r_2}\, d\underset{\sim}{r_3} \Big\{ \delta v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) \left[H - E_t\right] \left[v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) - v_l(\sigma_2)\, \phi(\rho_2)\, \psi_t(\underset{\sim}{r_3}, \underset{\sim}{r_1}) \right] + v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) \left[H - E_t\right] \delta v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_2}, \underset{\sim}{r_3}) - v_l(\sigma_2)\, \phi(\rho_2)\, \psi_t(\underset{\sim}{r_1}, \underset{\sim}{r_3}) \left[H - E_t\right] \delta v_l(\sigma_1)\, \phi(\rho_1)\, \psi_t(\underset{\sim}{r_3}, \underset{\sim}{r_1}) \Big\} \quad (1$$

We remember that the coordinates in **H** in the last term must be cyclically inter-changed too of course.

Writing,

$$V = -\frac{2}{r_{2p}} - \frac{2}{r_{3p}} + \frac{4}{r_p} - \frac{4}{r_1} + \frac{2}{r_{12}} + \frac{2}{r_{13}}$$

The Hamiltonian becomes,

$$H = -\frac{1}{2}\nabla_{\sigma_1}^2 - 2\nabla_{\rho_1}^2 - \frac{2}{\rho_1} - \nabla_2^2 - \nabla_3^2 - \frac{4}{r_2} - \frac{4}{r_3} + \frac{2}{r_{23}} + V$$

We know also that,

$$\left(-2\nabla_{\rho_1}^2 - \frac{2}{\rho_1}\right)\phi(\rho_1) = -\frac{1}{2}\phi(\rho_1)$$

$$\left(-\nabla_2^2 - \nabla_3^2 - \frac{4}{r_2} - \frac{4}{r_3} + \frac{2}{r_{23}}\right)\Psi(\mathbf{r}_2, \mathbf{r}_3) = E_0^{He}\,\Psi(\mathbf{r}_2, \mathbf{r}_3)$$

and also,

$$E_\kappa = \frac{1}{2}k^2 - \frac{1}{2} - 2\mu^2$$

We also know, (Massey and Mohr, 1954), that in first approximation there is no direct interaction between the positronium and heliumatom, i.e.,

$$\int d\boldsymbol{\rho}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\; \phi(\rho_1)\,\Psi_\kappa(\mathbf{r}_2, \mathbf{r}_3)\, V\, \phi(\rho_1)\,\Psi_\kappa(\mathbf{r}_2, \mathbf{r}_3) = 0$$

By expressing **V** in terms of $\boldsymbol{\sigma}_1$ and $\boldsymbol{\rho}_1$ this is evident from symmetry considerations.

We also need to know the effect of operating on $\Psi_\kappa(\mathbf{r}_2, \mathbf{r}_3)$ with ∇_2^2 and ∇_3^2, this is easily seen to be,

$$(\nabla_2^2 + \nabla_3^2)\,\Psi_\kappa(\mathbf{r}_2, \mathbf{r}_3) = \Psi_\kappa(\mathbf{r}_2, \mathbf{r}_3)\left\{-\frac{2\mu}{r_2} - \frac{2\mu}{r_3} + 2\mu^2\right\}$$

Evidently then, using the above formulae, and the assumption that $E_0^{He} = -2\mu^2$,

$$(H - E_*)\,\phi(\rho_1)\,\psi_*(\underline{r}_2, \underline{r}_3) = \psi_*(\underline{r}_2, \underline{r}_3)\,\phi(\rho_1)\left[-\tfrac{1}{2}\nabla_{\sigma_1}^2 - \tfrac{1}{2}k^2 + \frac{2\mu-4}{r_2} + \frac{2\mu-4}{r_3} + \frac{2}{r_{23}} + V\right]$$

and similarly with the other terms in (1), so,

$$\frac{\delta I_*}{3} = \int d\underline{\sigma}_1\, d\underline{\rho}_1\, d\underline{r}_2\, d\underline{r}_3 \Big\{ \delta v_\ell(\sigma_1)\,\phi^2(\rho_1)\,\psi_*^2(\underline{r}_2, \underline{r}_3)\left[-\tfrac{1}{2}\nabla_{\sigma_1}^2 - \tfrac{1}{2}k^2\right] v_\ell(\sigma_1) - \delta v_\ell(\sigma_1)\,\phi(\rho_1)\,\phi(\rho_2)\,\psi_*(\underline{r}_2, \underline{r}_3)$$

$$\psi_*(\underline{r}_3, \underline{r}_1)\left[-\tfrac{1}{2}\nabla_{\sigma_2}^2 - \tfrac{1}{2}k^2 + \frac{2\mu-4}{r_1} + \frac{2\mu-4}{r_2} + \frac{2}{r_{23}} + V\right] v_\ell(\sigma_2)$$

$$+ v_\ell(\sigma_1)\,\phi^2(\rho_1)\,\psi_*^2(\underline{r}_2, \underline{r}_3)\left[-\tfrac{1}{2}\nabla_{\sigma_1}^2 - \tfrac{1}{2}k^2\right]\delta v_\ell(\sigma_1) - v_\ell(\sigma_2)\,\phi(\rho_2)$$

$$\phi(\rho_1)\,\psi_*(\underline{r}_1, \underline{r}_3)\,\psi_*(\underline{r}_2, \underline{r}_3)\left[-\tfrac{1}{2}\nabla_{\sigma_1}^2 - \tfrac{1}{2}k^2 + \frac{2\mu-4}{r_2} + \frac{2\mu-4}{r_3} + \frac{2}{r_{23}} + V\right]\delta v_\ell(\sigma_1) \qquad (2)$$

With the appropriate coordinate changes in **V** in the last term.

Consider now,

$$D = \int d\underline{\sigma}_1\, v_0(\sigma_1)\,\nabla_{\sigma_1}^2\,\delta v_0(\sigma_1) = \int d\underline{\sigma}_1\, \frac{f_0(\sigma_1)}{\sigma_1}\,\frac{1}{\sigma_1^2}\,\frac{\partial}{\partial\sigma_1}\left(\sigma_1^2\frac{\partial}{\partial\sigma_1}\right)\frac{\delta f_0(\sigma_1)}{\sigma_1}$$

where we use $\ell = 0$ to simplify the algebra. The generalisation to any ℓ will be obvious.

$$\therefore\ D = 4\pi\int_0^\infty d\sigma_1\, f_0(\sigma_1)\,\frac{\partial^2}{\partial\sigma_1^2}\,\delta f_0(\sigma_1)$$

By using Green's theorem,

$$D = 4\pi \int_0^\infty d\sigma_1 \, \delta f_0(\sigma_1) \frac{\partial^2}{\partial \sigma_1^2} f_0(\sigma_1) + 4\pi \Big[f_0(\sigma_1) \frac{\partial}{\partial \sigma_1} \delta f_0(\sigma_1)$$

$$- \delta f_0(\sigma_1) \frac{\partial}{\partial \sigma_1} f_0(\sigma_1) \Big]_0^\infty$$

But,

$$f_0(0) = 0$$

and,

$$f_0(\sigma_1) \underset{\sigma_1 \to \infty}{\sim} \sin k\sigma_1 + a_0^{*} \cos k\sigma_1$$

and,

$$\delta f_0(\sigma_1) \underset{\sigma_1 \to \infty}{\sim} \delta a_0^{*} \cos k\sigma_1$$

Substitution in the equation for D gives,

$$D = 4\pi \int d\sigma_1 \, \delta f_0(\sigma_1) \frac{\partial^2}{\partial \sigma_1^2} f_0(\sigma_1) - 4\pi k \, \delta a_0^{*}$$

$$\therefore D = \int d\underset{\sim}{\sigma_1} \, \delta v_0(\sigma_1) \nabla_{\sigma_1}^2 v_0(\sigma_1) - 4\pi k \, \delta a_0^{*}$$

Generally then,

$$\int d\underset{\sim}{\sigma_1} \, v_l(\sigma_1) \nabla_{\sigma_1}^2 \delta v_l(\sigma_1) = \int d\underset{\sim}{\sigma_1} \, \delta v_l(\sigma_1) \nabla_{\sigma_1}^2 v_l(\sigma_1)$$

$$- 4\pi k \, \delta a_l^{*}$$

Using this in (2), we arrive at

$$\frac{1}{3}\left[\delta I_+ - 6\pi k \, \delta a_l^{*} \right] = \int d\underset{\sim}{\sigma_1} \, \delta v_l(\sigma_1) \left\{ -\nabla_{\sigma_1}^2 - k^2 \right\}$$

$$v_l(\sigma_1) - \int d\underset{\sim}{\sigma_1} \, d\underset{\sim}{\rho_1} \, d\underset{\sim}{r_2} \, d\underset{\sim}{r_3} \Big\{ \delta v_l(\sigma_1) \phi(\rho_1) \phi(\rho_2) \psi_+(\underset{\sim}{r_2}, \underset{\sim}{r_3})$$

$$\psi_+(\underset{\sim}{r_3}, \underset{\sim}{r_1}) \left[-\frac{1}{2}\nabla_{\sigma_2}^2 - \frac{1}{2}k^2 + \frac{2\mu-4}{r_1} + \frac{2\mu-4}{r_3} + \frac{2}{r_{23}} + V \right] v_l(\sigma_2)$$

$$+ v_l(\sigma_2) \phi(\rho_2) \phi(\rho_1) \psi_+(\underset{\sim}{r_1}, \underset{\sim}{r_3}) \psi_+(\underset{\sim}{r_2}, \underset{\sim}{r_3}) \left[-\frac{1}{2}\nabla_{\sigma_1}^2 - \frac{1}{2}k^2 \right.$$

$$\left. + \frac{2\mu-4}{r_2} + \frac{2\mu-4}{r_1} + \frac{2}{r_{23}} + V \right] \delta v(\sigma_1) \Big\}$$

We now change the coordinate space from $(\underset{\sim}{\sigma_1}, \underset{\sim}{\rho_1}, \underset{\sim}{r_2}, \underset{\sim}{r_3})$ to $(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2}, \underset{\sim}{r_\ell}, \underset{\sim}{r_3})$ the Jacobian for this transformation being 4^3. Because of the asymptotic nature of $f_\ell(\sigma_2)$ and consequently $v_\ell(\sigma_2)$ Green's theorem shows that,

$$\int d\underset{\sim}{\sigma_1}\, d\underset{\sim}{\sigma_2}\, d\underset{\sim}{r_\ell}\, d\underset{\sim}{r_3}\, v_\ell(\sigma_2)\, \phi(\rho_2)\, \psi_x(\underset{\sim}{r_1}, \underset{\sim}{r_3})\, \phi(\rho_1)\, \psi_x(\underset{\sim}{r_2}, \underset{\sim}{r_3}) \left[-\tfrac{1}{2}\nabla_{\sigma_1}^2\right] \delta v_\ell(\sigma_1) = \int d\underset{\sim}{\sigma_1}\, d\underset{\sim}{\sigma_2}\, d\underset{\sim}{r_\ell}\, d\underset{\sim}{r_3}\, v_\ell(\sigma_2)$$

$$\delta v_\ell(\sigma_1) \left[-\tfrac{1}{2}\nabla_{\sigma_1}^2\right] \phi(\rho_2)\, \phi(\rho_1)\, \psi_x(\underset{\sim}{r_1}, \underset{\sim}{r_3})\, \psi_x(\underset{\sim}{r_2}, \underset{\sim}{r_3})$$

and similarly for the term containing the operator $-\frac{1}{2}\nabla_{\sigma_2}^2$

This gives,

$$\tfrac{1}{3}\left[\delta I_t - 6\pi k\, \delta a_\ell^t\right] = \int d\underset{\sim}{\sigma_1}\, \delta v_\ell(\sigma_1) \left[\left\{-\nabla_{\sigma_1}^2 - k^2\right\} v_\ell(\sigma_1) + \int d\underset{\sim}{\sigma_2}\, L(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2})\, v_\ell(\sigma_2)\right]$$

and,

$$L(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2}) = 4^3 \int d\underset{\sim}{r_\ell}\, d\underset{\sim}{r_3} \left\{ k^2 + \tfrac{1}{2}\left(\nabla_{\sigma_1}^2 + \nabla_{\sigma_2}^2\right) - \frac{(2\mu-8)}{r_1} - \frac{(2\mu-8)}{r_2} \right.$$

$$\left. - \frac{(4\mu-8)}{r_3} - \frac{4}{r_{13}} + \frac{2}{r_{1\rho}} + \frac{2}{r_{2\rho}} + \frac{4}{r_{3\rho}} - \frac{8}{r_\rho} - \frac{4}{r_{12}} - \frac{4}{r_{23}} \right\} \phi(\rho_1)\, \phi(\rho_2)$$

$$\psi_x(\underset{\sim}{r_1}, \underset{\sim}{r_3})\, \psi_x(\underset{\sim}{r_2}, \underset{\sim}{r_3})$$

or, in the new coordinates,

$$L(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2}) = 4^3 \int d\underset{\sim}{r_\ell}\, d\underset{\sim}{r_3} \left\{ k^2 + \tfrac{1}{2}\left(\nabla_{\sigma_1}^2 + \nabla_{\sigma_2}^2\right) + \frac{1}{|\underset{\sim}{\sigma_1} - \underset{\sim}{r_\ell}|} \right.$$

$$+ \frac{1}{|\underset{\sim}{\sigma_2} - \underset{\sim}{r_\ell}|} - \frac{(2\mu-8)}{|2\underset{\sim}{\sigma_1} - \underset{\sim}{r_\ell}|} - \frac{(2\mu-8)}{|2\underset{\sim}{\sigma_2} - \underset{\sim}{r_\ell}|} - \frac{8}{r_\rho} - \frac{2}{|\underset{\sim}{\sigma_1} - \underset{\sim}{\sigma_2}|}$$

$$\left. - \frac{(4\mu-8)}{r_3} + \frac{4}{|\underset{\sim}{r_3} - \underset{\sim}{r_\ell}|} - \frac{4}{|2\underset{\sim}{\sigma_1} - \underset{\sim}{r_\ell} - \underset{\sim}{r_3}|} - \frac{4}{|2\underset{\sim}{\sigma_2} - \underset{\sim}{r_\ell} - \underset{\sim}{r_3}|} \right\}$$

$$\phi\left(2|\underset{\sim}{\sigma_1} - \underset{\sim}{r_\ell}|\right) \phi\left(2|\underset{\sim}{\sigma_2} - \underset{\sim}{r_\ell}|\right) \psi_x\left(\underset{\sim}{r_3}, |2\underset{\sim}{\sigma_1} - \underset{\sim}{r_\ell}|\right)$$

$$\psi_x\left(|2\underset{\sim}{\sigma_2} - \underset{\sim}{r_\ell}|, \underset{\sim}{r_3}\right)$$

We now require,

$$\nabla^2_{\sigma_1}\ \phi\left(2|\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\right)\,\psi_k\left(\underset{\sim}{r}_3,\ |2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\right)$$

This is easiest done by expressing the various coordinates in their Cartesian components, on evaluation we find,

$$\nabla^2_{\sigma_1}\ \phi\left(2|\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\right)\psi_k\left(\underset{\sim}{r}_3, |2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\right) = \phi\left(2|\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\right)$$

$$\psi_k\left(\underset{\sim}{r}_3, |2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\right)\Bigg\{1 + 4\mu^2 + \frac{4\mu\,(\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p).(2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p)}{|\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\,|2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|}$$

$$- \frac{2}{|\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|} - \frac{8\mu}{|2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|}\Bigg\}$$

A similar formula results with the $\nabla^2_{\sigma_2}$ operator on the corresponding wave functions.

So,

$$L(\underset{\sim}{\sigma}_1, \underset{\sim}{\sigma}_2) = 4^3\int d\underset{\sim}{r}_p\, d\underset{\sim}{r}_3\,\Bigg\{k^2 + 1 + 4\mu^2 +$$

$$\frac{2\mu(\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p).(2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p)}{|\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\ \ |2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p)} + \frac{2\mu(\underset{\sim}{\sigma}_2 - \underset{\sim}{r}_p).(2\underset{\sim}{\sigma}_2 - \underset{\sim}{r}_p)}{|\underset{\sim}{\sigma}_2 - \underset{\sim}{r}_p|\,|2\underset{\sim}{\sigma}_2 - \underset{\sim}{r}_p|} - \frac{(6\mu - 8)}{|2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|}$$

$$- \frac{(6\mu - 8)}{|2\underset{\sim}{\sigma}_2 - \underset{\sim}{r}_p|} - \frac{8}{r_p} - \frac{2}{|\underset{\sim}{\sigma}_1 - \underset{\sim}{\sigma}_2|} - \frac{(4\mu - 8)}{r_3} + \frac{4}{|\underset{\sim}{r}_3 - \underset{\sim}{r}_p|}$$

$$- \frac{4}{|2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p - \underset{\sim}{r}_3|} - \frac{4}{|2\underset{\sim}{\sigma}_2 - \underset{\sim}{r}_p - \underset{\sim}{r}_3|}\Bigg\}\ \phi\left(2|\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\right)\phi\left(2|\underset{\sim}{\sigma}_2 - \underset{\sim}{r}_p|\right)$$

$$\psi_k\left(\underset{\sim}{r}_3, |2\underset{\sim}{\sigma}_1 - \underset{\sim}{r}_p|\right)\psi_k\left(|2\underset{\sim}{\sigma}_2 - \underset{\sim}{r}_p|, \underset{\sim}{r}_3\right)$$

This expression is now integrated over $\underset{\sim}{r}_3$. We find straightforwardly that, dropping the subscript on $\underset{\sim}{r}_p$,

$$L(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2}) = \frac{8\mu^3}{\pi^2} \int d\underset{\sim}{\xi} \left\{ k^2 + 1 + 8\mu + \frac{2\mu (\underset{\sim}{\sigma_1} - \underset{\sim}{\xi}).(2\underset{\sim}{\sigma_1} - \underset{\sim}{\xi})}{|\underset{\sim}{\sigma_1} - \underset{\sim}{\xi}|\,|2\underset{\sim}{\sigma_1} - \underset{\sim}{\xi}|} \right.$$

$$+ \frac{2\mu (\underset{\sim}{\sigma_2} - \underset{\sim}{\xi}).(2\underset{\sim}{\sigma_2} - \underset{\sim}{\xi})}{|\underset{\sim}{\sigma_2} - \underset{\sim}{\xi}|\,|2\underset{\sim}{\sigma_2} - \underset{\sim}{\xi}|} - (6\mu - 4)\left[\frac{1}{|2\underset{\sim}{\sigma_1} - \underset{\sim}{\xi}|} + \frac{1}{|2\underset{\sim}{\sigma_2} - \underset{\sim}{\xi}|}\right]$$

$$- \frac{8}{\tau} - \frac{2}{|\underset{\sim}{\sigma_1} - \underset{\sim}{\sigma_2}|} + 4\left[\frac{1}{\tau} - \left(\frac{1}{\tau} + \mu\right) e^{-2\mu\tau}\right]$$

$$+ \frac{4 e^{-2\mu|2\underset{\sim}{\sigma_1} - \underset{\sim}{\xi}|}}{|2\underset{\sim}{\sigma_1} - \underset{\sim}{\xi}|} + \frac{4 e^{-2\mu|2\underset{\sim}{\sigma_2} - \underset{\sim}{\xi}|}}{|2\underset{\sim}{\sigma_2} - \underset{\sim}{\xi}|} + 4\mu e^{-2\mu|2\underset{\sim}{\sigma_1} - \underset{\sim}{\xi}|}$$

$$\left. + 4\mu e^{-2\mu|2\underset{\sim}{\sigma_2} - \underset{\sim}{\xi}|} \right\} e^{-|\underset{\sim}{\sigma_1} - \underset{\sim}{\xi}|} e^{-|\underset{\sim}{\sigma_2} - \underset{\sim}{\xi}|} e^{-\mu|2\underset{\sim}{\sigma_1} - \underset{\sim}{\xi}|}$$

$$e^{-\mu|2\underset{\sim}{\sigma_2} - \underset{\sim}{\xi}|}$$

which is the required kernal for the integro-differential equation.

APPENDIX B.

THE FUNCTIONAL I_t

The functional I_t is reduced in appendix A to,

$$\frac{I_t}{3} = \int d\boldsymbol{\sigma}_1\, d\boldsymbol{\rho}_1\, d\boldsymbol{r}_2\, d\boldsymbol{r}_3\, v_\ell(\sigma_1)\, \phi(\rho_1)\, \psi_t(\boldsymbol{r}_2, \boldsymbol{r}_3)$$

$$[H - E_t]\left[v_\ell(\sigma_1)\, \phi(\rho_1)\, \psi_t(\boldsymbol{r}_2, \boldsymbol{r}_3) - v_\ell(\sigma_2)\, \phi(\rho_2)\right.$$

$$\left.\psi_t(\boldsymbol{r}_3, \boldsymbol{r}_1)\right]$$

Proceeding through the derivation of δI_t in appendix A we see that a similar process will yield for I_t,

$$\frac{I_t}{3} = \int d\boldsymbol{\sigma}_1\, d\boldsymbol{\rho}_1\, d\boldsymbol{r}_2\, d\boldsymbol{r}_3 \left\{ v_\ell(\sigma_1)\, \phi^2(\rho_1)\, \psi_t^2(\boldsymbol{r}_2, \boldsymbol{r}_3)\right.$$

$$\left[-\tfrac{1}{2}\nabla_{\sigma_1}^2 - \tfrac{1}{2}k^2\right] v_\ell(\sigma_1) - 4^3 \int d\boldsymbol{\sigma}_1\, d\boldsymbol{\sigma}_2\, d\boldsymbol{\rho}\, d\boldsymbol{r}_3\, v_\ell(\sigma_1)$$

$$\phi(\rho_1)\, \psi_t(\boldsymbol{r}_2, \boldsymbol{r}_3)\, \phi(\rho_2)\, \psi_t(\boldsymbol{r}_3, \boldsymbol{r}_1) \left[-\tfrac{1}{2}\nabla_{\sigma_2}^2 - \tfrac{1}{2}k^2\right.$$

$$\left. + \frac{(2\mu-4)}{r_1} + \frac{(2\mu-4)}{r_2} + \frac{2}{r_{23}} + V\right] v_\ell(\sigma_2)$$

We now assume that the values $v_\ell(\sigma)$ satisfy the integro-differential equation,

$$(\nabla_{\sigma_1}^2 + k^2)\, v_\ell(\sigma_1) = \int d\sigma_2\, L(\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2)\, v_\ell(\sigma_2)$$

Substituting back in the above we get, for the first term in the expression for $I_t/3$,

$$\int d\boldsymbol{\sigma}_1\, v_\ell(\sigma_1) \left(-\tfrac{1}{2}\right) \int d\boldsymbol{\sigma}_2\, L(\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2)\, v_\ell(\sigma_2)$$

If we now substitute the expression for $L(\underset{\sim}{\sigma_1}, \underset{\sim}{\sigma_2})$ the full equation becomes,

$$\frac{I_t}{3.4^3} = \int v_\ell(\sigma_1)\, v_\ell(\sigma_2)\, d\underset{\sim}{\sigma_1}\, d\underset{\sim}{\sigma_2}\, dr_\rho\, d\underset{\sim}{r_3} \Big[(-\tfrac{1}{2})$$

$$\Big\{ k^2 + \tfrac{1}{2} (\nabla_{\sigma_1}^2 + \nabla_{\sigma_2}^2 - \frac{(2\mu-8)}{r_1} - \frac{(2\mu-8)}{r_2} - \frac{(4\mu-8)}{r_3}$$

$$- \frac{4}{r_{13}} + \frac{2}{r_{1\rho}} + \frac{2}{r_{2\rho}} + \frac{4}{r_{3\rho}} - \frac{8}{r_\rho} - \frac{4}{r_{12}} - \frac{4}{r_{23}} \Big\} + \tfrac{1}{2} \nabla_{\sigma_2}^2 + \tfrac{1}{2} k^2$$

$$- \frac{(2\mu-4)}{r_1} - \frac{(2\mu-4)}{r_2} - \frac{2}{r_{23}} - V \Big] \phi(\rho_1)\, \phi(\rho_2)\, \psi_*(\underset{\sim}{r_1}, \underset{\sim}{r_3})$$

$$\psi_*(\underset{\sim}{r_2}, \underset{\sim}{r_3})$$

Substitution of V leads to,

$$\frac{I_t}{3.4^3} = \int v_\ell(\sigma_1)\, v_\ell(\sigma_2)\, d\underset{\sim}{\sigma_1}\, d\underset{\sim}{\sigma_2}\, dr_\rho\, d\underset{\sim}{r_3} \Big[-\tfrac{1}{4} \nabla_{\sigma_1}^2$$

$$+ \tfrac{1}{4} \nabla_{\sigma_2}^2 - \frac{1}{r_{1\rho}} + \frac{1}{r_{2\rho}} - \frac{(\mu-4)}{r_1} - \frac{\mu}{r_2} + \frac{2\mu-4}{r_3} \Big] \phi(\rho_1)\, \phi(\rho_2)$$

$$\psi_*(\underset{\sim}{r_1}, \underset{\sim}{r_3})\, \psi_*(\underset{\sim}{r_2}, \underset{\sim}{r_3})$$

$$\therefore \frac{I_*}{3.4^3} = \int v_\ell(\sigma_1)\, v_\ell(\sigma_2)\, d\underset{\sim}{\sigma_1}\, d\underset{\sim}{\sigma_2}\, dr_\rho\, d\underset{\sim}{r_3} \Big[-\tfrac{1}{4} \nabla_{\sigma_1}^2 + \tfrac{1}{4} \nabla_{\sigma_2}^2$$

$$- \frac{1}{2|\underset{\sim}{\sigma_1} - r_\rho|} + \frac{1}{2|\underset{\sim}{\sigma_2} - r_\rho|} - \frac{(\mu-4)}{|2\underset{\sim}{\sigma_1} - r_\rho|} - \frac{\mu}{|2\underset{\sim}{\sigma_2} - r_\rho|} + \frac{2\mu-4}{|2\underset{\sim}{\sigma_3} - r_\rho|} \Big]$$

$$\phi(\rho_1)\, \phi(\rho_2)\, \psi_*(\underset{\sim}{r_1}, \underset{\sim}{r_3})\, \psi_*(\underset{\sim}{r_2}, \underset{\sim}{r_3})$$

The antisymmetry in σ of the square bracketed expression leads to the disappearence of the integral so we can finally say, if $\mathcal{S}_{\ell}(\sigma)$ satisfies the integro-differential equation defined earlier, then

$$I_{*} = 0$$

which is what we wished to demonstrate.

APPENDIX C

EVALUATION OF THE INTEGRALS IN THE POSITRON-HYDROGEN ATOM PROBLEM

The functional **I** in Chapter 7 is written as,

$$I = \int dr_1\, dr_2\, d(\cos\theta)\; r_1 r_2\, Q\, \Phi_R^* \left[-\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} + \frac{L^2}{2}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) - \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}} - E_R \right] r_1 r_2\, Q\, \Phi_R^*$$

We have the expression for $Q\,\Phi_R^*$ and we write,

$$r_1 r_2\, Q\, \Phi_R^* = S_1 + S_2$$

where S_1 is the summation with coefficients B_n and S_2 the summation with coefficients C_{lmn}.

Substituting back,

$$I = \int dr_1\, dr_2\, d(\cos\theta)\,(S_1 + S_2)\left\{ -\frac{1}{2}\frac{\partial^2}{\partial r_2^2} + \frac{L^2}{2}\frac{1}{r_2^2} + \frac{1}{r_2} - \frac{1}{r_{12}} - E_R \right\}(S_1 + S_2) + \int dr_1\, dr_2\, d(\cos\theta)\,(S_1 + S_2)\left\{ -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} + \frac{L^2}{2}\frac{1}{r_1^2} - \frac{1}{r_1} \right\} S_2 +$$

$$\int dr_1\, dr_2\, d(\cos\theta)\,(S_1 + S_2)\left(-\frac{1}{4}\right) S_1$$

The last term comes from the use of the equation satisfied by $u_{200}(r_1)$ presented in chapter 7.

In evaluating the integrals it is useful to observe that since the function $P_\ell(\cos\theta)$ is proportional to the spherical harmonic $Y_\ell^0(\theta,\phi)$ and that,

$$L^2\, Y_\ell^0(\theta,\phi) = \ell(\ell+1)\, Y_\ell^0(\theta,\phi)$$

then clearly,

$$L^2\, P_\ell(\cos\theta) = \ell(\ell+1)\, P_\ell(\cos\theta)$$

We now present a listing of the various integrals required.

Let,

$$I_1 = \int d\tau\, (S_1+S_2)\left[-\frac{1}{2}\frac{\partial^2}{\partial r_2^2}\right](S_1+S_2)$$

$$I_2 = \int d\tau\, (S_1+S_2)\,\frac{L^2}{2r_2^2}\,(S_1+S_2)$$

$$I_3 = \int d\tau\, (S_1+S_2)\,\frac{1}{r_2}\,(S_1+S_2)$$

$$I_5 = \int d\tau\, (S_1+S_2)\,(-E_n)\,(S_1+S_2)$$

$$I_6 = \int d\tau\, (S_1+S_2)\left[-\frac{1}{2}\frac{\partial^2}{\partial r_1^2}\right]S_2$$

$$I_7 = \int d\tau\, (S_1+S_2)\,\frac{L^2}{2r_1^2}\,S_2$$

$$I_8 = \int d\tau\, (S_1+S_2)\left(-\frac{1}{r_1}\right)S_2$$

$$I_9 = \int d\tau\, (S_1+S_2)\left(-\frac{1}{4}\right)S_1$$

These integrals are straightforward but tedious to evaluate and result in summations over the various integers involved. We use one summation sign to indicate summation over the total number of integers for brevity.

$$I_1 = -\frac{1}{4}\sum B_n B_{n'}\left\{\frac{\lambda^2(n+n')!}{(2\lambda)^{n+n'+1}} - \frac{2n'\lambda(n+n'-1)!}{(2\lambda)^{n+n'}} + \frac{n'(n'-1)(n+n'-2)!}{(2\lambda)^{n+n'-1}}\right\} - \sum C_{lmn}C_{lm'n'}\cdot\frac{1}{2l+1}\cdot$$

$$\frac{(m+m'+4l)!}{(2\mu)^{m+m'+4l+1}}\left\{\frac{\lambda^2(n+n'+4l)!}{(2\lambda)^{n+n'+4l+1}} - \frac{2\lambda(n'+2l)(n+n'+4l-1)!}{(2\lambda)^{n+n'+4l}} + \frac{(n'+2l)(n'+2l-1)(n+n'+4l-2)!}{(2\lambda)^{n+n'+4l-1}}\right\}$$

$$I_2 = \sum C_{lmn}C_{lm'n'}\,\frac{l(l+1)}{2l+1}\,\frac{(m+m'+4l)!}{(2\mu)^{m+m'+4l+1}}\,\frac{(n+n'+4l-2)!}{(2\lambda)^{n+n'+4l-1}}$$

$$I_3 = \frac{1}{2}\sum B_n B_{n'}\,\frac{(n+n'-1)!}{(2\lambda)^{n+n'}} + 2\sum C_{lmn}C_{lm'n'}\cdot\frac{1}{2l+1}\cdot\frac{(m+m'+4l)!}{(2\mu)^{m+m'+4l+1}}\,\frac{(n+n'+4l-1)!}{(2\lambda)^{n+n'+4l}}$$

$$I_5 = - E_R \left\{ \frac{1}{2} \sum B_n B_{n'} \frac{(n+n')!}{(2\lambda)^{n+n'+1}} + 2 \sum C_{lmn} C_{lm'n'} \right.$$

$$\left. \cdot \frac{1}{2l+1} \cdot \frac{(m+m'+4l)!}{(2\mu)^{m+m'+4l+1}} \quad \frac{(n+n'+4l)!}{(2\lambda)^{n+n'+4l+1}} \right\}$$

$$I_6 = - \sum C_{lmn} C_{lm'n'} \cdot \frac{1}{2l+1} \cdot \frac{(n+n'+4l)!}{(2\lambda)^{n+n'+4l+1}}$$

$$\left\{ \frac{\mu^2 (m+m'+4l)!}{(2\mu)^{m+m'+4l+1}} - \frac{2\mu (m'+2l)(m+m'+4l-1)!}{(2\mu)^{m+m'+4l}} \right.$$

$$\left. + \frac{(m'+2l)(m'+2l-1)(m+m'+4l-2)!}{(2\mu)^{m+m'+4l-1}} \right\}$$

$$I_7 = \sum C_{lmn} C_{lm'n'} \cdot \frac{l(l+1)}{2l+1} \cdot \frac{(m+m'+4l-2)!}{(2\mu)^{m+m'+4l-1}}$$

$$\frac{(n+n'+4l)!}{(2\lambda)^{n+n'+4l+1}}$$

$$I_8 = -2 \sum C_{lmn} C_{lm'n'} \cdot \frac{1}{2l+1} \cdot \frac{(m+m'+4l-1)!}{(2\mu)^{m+m'+4l}}$$

$$\frac{(n+n'+4l)!}{(2\lambda)^{n+n'+4l+1}}$$

$$I_9 = - \frac{1}{8} \sum B_n B_{n'} \frac{(n+n')!}{(2\lambda)^{n+n'+1}}$$

Consider now,

$$I_4 = \int d\tau \, (S_1 + S_2)\left(-\frac{1}{r_{12}}\right)(S_1 + S_2)$$

$$\therefore I_4 = -\int d\tau \, (S_1^2 + S_2^2 + 2S_1S_2) \sum_{l=0}^{\infty} \frac{r_<^{\,l}}{r_>^{\,l+1}} P_l(\cos\theta)$$

where we have used the expansion of $\frac{1}{r_{12}}$ in terms of Legendre polynomials and $r_<$, $r_>$ are the smaller and greater of r_1 and r_2 respectively.

Let,

$$I_{4A} = -\int d\tau \; S_1^2 \sum_l \frac{r_<^{\,l}}{r_>^{\,l+1}} P_l(\cos\theta)$$

$$\therefore I_{4A} = -2\int d\tau \; S_1^2 \, \frac{1}{r_>}$$

We must note now the important point that because of the form of S_1^2, in particular the square of $u_{100}(r_1)$, we must have $r_2 \gg r_1$ to avoid a singularity in the integral. This is, from the physical point of view, assuming that the positron favours that region of space where it is further from the nucleus than the electron, a reasonable assumption considering the various charges involved. With this in mind,

$$I_{4A} = -\frac{1}{2}\sum B_n B_{n'} \left\{ \frac{(n+n'-1)!}{(2\lambda)^{n+n'}} + \frac{(n+n')!}{(2\lambda+1)^{n+n'+1}} - \frac{(n+n'-1)!}{(2\lambda+1)^{n+n'}} - \frac{(n+n'+1)!}{2(2\lambda+1)^{n+n'+2}} \right\}$$

Let,

$$I_{4B} = -2\int d\tau \; S_1 S_2 \sum_{l=0}^{\infty} \frac{r_<^{l}}{r_>^{l+1}} \; P_l(\cos\theta)$$

Because of the relative complexity of the result we write,

$$\left.\begin{aligned} \alpha &= m' + 3l' \\ \beta &= n' + n + l' \\ \upsilon &= \mu + \tfrac{1}{2} \\ \Lambda &= \frac{\alpha!\,(2\upsilon - \alpha - 1)}{\upsilon^{\alpha+2}} \end{aligned}\right\}$$

whence,

$$I_{4B} = -\sqrt{2}\;\sum B_n\, C_{l'm'n'} \cdot \frac{1}{2l+1} \cdot \left\{ \frac{\Lambda\,(\beta-1)!}{(2\lambda)^{\beta}} + \frac{(\alpha+\beta)!}{\upsilon\,(2\lambda+\upsilon)^{\alpha+\beta+1}} - \Lambda \sum_{k=0}^{\alpha} \frac{(k+\beta-1)!\;\upsilon^{k}}{(2\lambda+\upsilon)^{k+\beta}\;k!} \right\}$$

The summation over k arises from the integration over r_1 from 0 to some arbitrary value of r_2, and then integrating r_2 over the interval 0 to ∞. The incongruous $\sqrt{2}$ arises from the normalisation coefficient of $u_{200}(r_1)$.

Let,

$$I_{4c} = -\int d\tau \; S_2^{2} \sum_{l''=0}^{\infty} \frac{r_<^{l''}}{r_>^{l''+1}} \; P_{l''}(\cos\theta)$$

We are confronted here with a term of the form,

$$\int_{-1}^{1} d(\cos\theta)\ P_{\ell}(\cos\theta)\ P_{\ell'}(\cos\theta)\ P_{\ell''}(\cos\theta)$$

This is evaluated in (Brink and Satchler, 1962) and it is equivalent to,

$$\frac{2}{2\ell+1}\ \mathcal{C}^{2}(\ell''\ell'\ell\,;\,0\,0)$$

where the $\mathcal{C}$ is the Clebsh-Gordan coefficient and in fact, (Rose, 1957),

$$\mathcal{C}^{2}(\ell''\ell'\ell\,;\,0\,0) = \frac{(-1)^{\ell''+\ell'-\ell}\ (2\ell+1)\ F^{2}(\ell''+\ell'+\ell)}{(\ell''+\ell'+\ell+1)\ F^{2}(\ell''+\ell'-\ell)}$$

$$\cdot\ \frac{1}{F^{2}(\ell''-\ell'+\ell)\ F^{2}(-\ell''+\ell'+\ell)}$$

Non-vanishing values of $\mathcal{C}^{2}$ occur from $\ell''+\ell'+\ell$ even only.

Also, $\ell'' \leqslant \ell'+\ell$

and, $F(L) = \dfrac{(L/2)!}{\sqrt{L!}}$

Define,

$$\left.\begin{aligned} m+m'+2\ell+2\ell' &= J \\ n+n'+2\ell+2\ell' &= K \\ \text{and,}\quad V &= \frac{(J+\ell'')!}{(2\mu)^{J+\ell''+1}} \end{aligned}\right\}$$

Then,

$$I_{4c} = -2 \sum C_{lmn} C_{l'm'n'} \mathcal{C}^2(l''l'l;00) \cdot \frac{V}{2l+1} \cdot$$

$$\left\{ \frac{(K-l''-1)!}{(2\lambda)^{K-l''}} - \sum_{k=0}^{J+l''} \frac{(2\mu)^k}{k!} \frac{(k-l''-1+K)!}{\{2(\lambda+\mu)\}^{K-l''+k}} \right\}$$

and the summation over l'' is from 0 to $l'+l$.

Evidently,

$$I = \sum I_i \qquad (i = 1, 2 \cdots 9)$$

and is of the form,

$$I = \sum B_n B_{n'} f_1(n, n') + \sum C_{lmn} C_{l'm'n'}$$

$$f_2(l, m, n, l', m', n') - E_R \left\{ \sum B_n B_{n'} f_3(n, n') \right.$$

$$\left. + \sum C_{lmn} C_{lm'n'} f_4(l, m, n, m', n') \right\}$$

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