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THE $2p^{2\,1}D$ AND $(2p3p \pm 2s3d)\,^3D$ AUTOIONIZING RESONANCES OF THE HELIUM ISOELECTRONIC SEQUENCE

by

John M. Cullen

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER I

1.0 Introduction

A doubly-excited atomic state is produced by the simultaneous excitation of two electrons from the ground electronic state of the atom. Typically such states are imbedded in the ionization continuum associated with single excitation as shown in Fig.1. The configuration interaction of the doubly-excited state with the continuum allows the state to decay to the ground state of the parent ion with the emission of an electron. A well studied example is the $2s2p\,^1P$ state of helium which can be produced by photoabsorption from the ground $1s^2\,^1S$ state (Madden and Codling, 1965). The $2s2p\,^1P$ state tends to decay to $He^+(1s)$ ground state plus an outgoing continuum P electron. The above process of electron emission from a doubly-excited state is known as autoionization.

Autoionization can be regarded as the outgoing half of an elastic scattering event by the parent ion. The inverse process, dielectronic recombination, is also possible with the autoionizing state appearing as a resonance in the elastic scattering of the electrons by the ground state of the parent ion. The incoming electron as reviewed by Taylor (1970) excites one of the target ion's electrons into an outer orbit leaving a hole or potential well near the centre of the atomic system through which the incoming electron tunnels and becomes temporarily trapped by the screened nuclear potential. The resulting 'compound state' decays either by autoionization or by the emission of radiation in the absence of collisions with a third body. The fundamental events leading to the formation of autoionizing states are summarized in Fig. 2.

k, ($k^2 = 2mE/\hbar^2$) is a continuous variable and l the angular momentum quantum number is l = 0,1,2,3,..., ∞

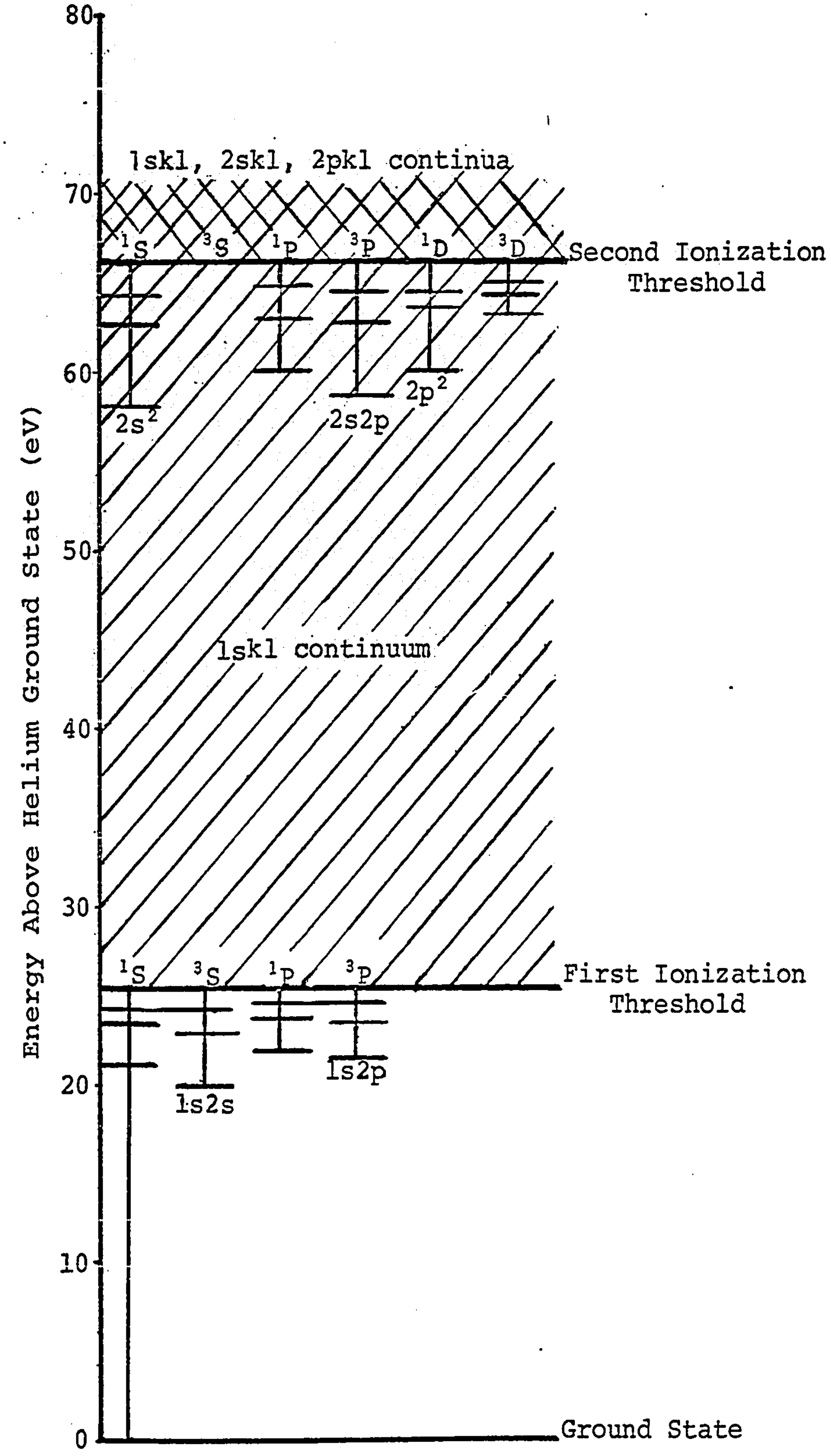

Fig. 1: Energy Levels In Helium

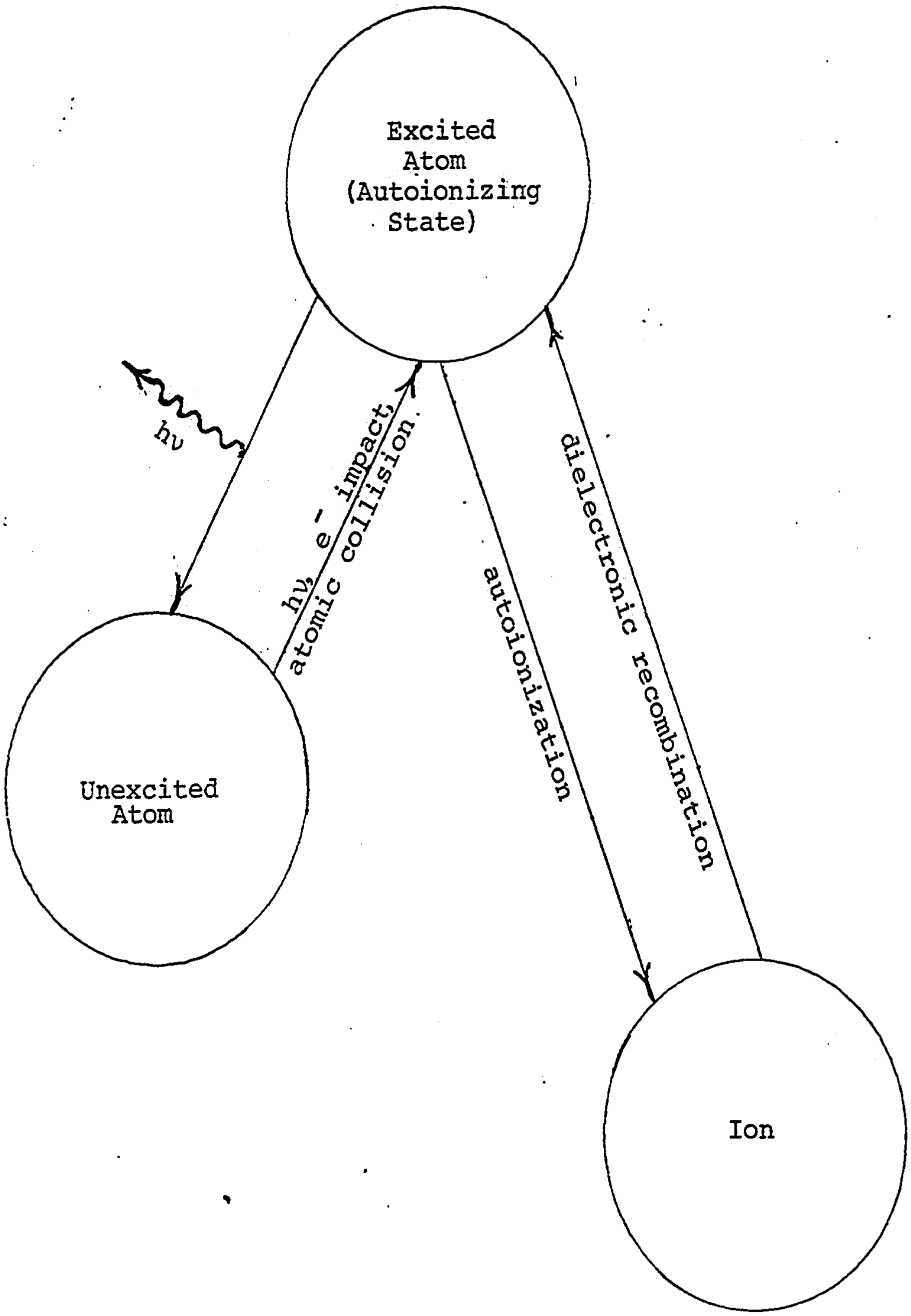

Fig. 2: Formation of Autoionizing States

1.1 Historical Survey

Pierre Auger (1923, 1925) was the first to observe autoionization. Passing X-rays into a cloud chamber that was filled with a gas, he observed the tracks left by the electrons which were emitted by the atoms in the gas. Studying hydrogen, argon, chlorine, iodine, krypton, he found that many short range tracks diverged from points of impact at lower concentrations. He concluded that each primary ionization was accompanied by one or two secondary ionizations. Auger interpreted this phenomenon as being caused by the emission of one inner electron from the atom, leaving the parent ion in an autoionizing state.

Later Compton and Boyce (1928) observed the ultraviolet spectra when helium, neon and argon were bombarded by electrons. In helium, lines at 320.38 Å and 309.04 Å were tentatively identified as transitions from the doubly excited states 2p2s, 2p2p to the continuum states 1s2s, 1s2p respectively.

Kruger (1930) further studied the ultraviolet spectum of helium. Although he did not find any line at 309.04 Å, he observed lines at 320.329 Å (the 320.38 Å line of Compton and Boyce), at 321.186 Å, at 322.517 Å. The transitions he assigned to these lines were $2p^{2}\,{}^{3}P-1s2p\,{}^{3}P$, $2p^{2}\,{}^{1}S-1s2p\,{}^{1}P$, $2p^{2}\,{}^{1}D-1s2p\,{}^{1}P$ respectively.

Predissociation, which is the molecular analog of autoionization, was first examined by Rice (1933). Above the dissociation limit of a molecule there lie quasi-discrete band spectra, giving rise to weakly quantized states embedded in a continuum. Excitation of the molecule into these states is followed by either a radiative transition to a lower state or dissociation of the molecule. Rice found that the rotation levels were broadened, distorted out of shape, shifted in position and had rather complicated secondary structures.

In 1934, Whiddington and Priestly (1934) observed the energy loss spectrum of a beam of electrons passing through helium. Using electron beams having energies ranging from 100 volts to 600 volts, energy losses of 59.25 ±.12 volts were observed. Since the energy absorbed by a transition from the $1s^2$ ground state to the $2p^2$ doubly-excited state is approximately 58.6 electron volts, Whiddington and Priestly concluded that this was the transition being observed. They also noted that there seemed to be indications of structure in the energy loss spectrum, although it was not completely resolved by their apparatus.

In 1935, Massey and Mohr (1935) calculated cross sections for the electron impact excitation of doubly-excited states of helium, using the Born approximation and approximate wave functions for the initial and final states. The calculated relative intensities and angular distributions agreed qualitatively, but not quantitatively with the experimental results of Priestly and Whiddington (1934, 1935) for the transitions from the ground state to the $2s2p\,{}^1P$ and $3s2p\,{}^1P$ doubly-excited states.

From the late 1930's to the mid 1950's little progress was made, either experimentally or theoretically. But in the late 1950's computers came into general use and a revival of interest in the theory of doubly-excited states occurred. Also the experimental techniques necessary to resolve the resonances became available. By the mid 1960's both theoretical and experimental fields were progressing at a rapid rate. In 1958, Holøien (1958) introduced the multiconfiguration stabilization method (MCS) for calculating the positions of doubly-excited states, and in 1961, Fano further developed and applied Rice's theory of 1933.

A major theoretical advance occurred in 1962, when Feshbach (1958, 1962) presented a unified theory of nuclear reactions in terms of projection operators P and Q (see Section 2.0.3). As shown by O'Malley and Geltman (1965), and Fano and Cooper (1965), the Feshbach projection operator formalism can be applied directly to autoionizing resonances in atoms. Also during this time, Burke and co-workers (see Burke, 1968 for a review) obtained a number of resonances directly from close-coupling scattering calculations. A large number of calculations using the above techniques have since been published as reviewed by Burke (1968) and Taylor (1970). The very accurate projection operator calculations by Bhatia and Temkin (1969) and Bhatia (1972) are of particular interest. This thesis is an extension and application of the 1/Z expansion perturbation technique developed by Drake and Dalgarno (1971) as described in Chapter II.

Much of the above theoretical work was stimulated by the very accurate measurements of Madden and Codling (1963). Using the National Bureau of Standards 180-Mev electron synchrotron as their continuum light source, they were able to obtain accurate measurements of the positions, widths, line shapes, and oscillator strengths of transitions from the ground state to the radiatively allowed ^1P autoionizing resonances of helium and other inert gases.

In 1964, Lassettre and his co-workers began to publish a number of papers on the electron-impact spectra of a variety of gases such as He, H_2, methane, ethane, cyclohexane, ethylene, water, nitrogen, carbon monoxide, oxygen, using an extremely accurate electron spectrometer.

Recently, results from beam-foil spectroscopy have come into prominence. In this work, an ion beam is accelerated through a thin exciter foil causing further ionization, excitation and electron pickup in the beam (Bickel et al, 1969). The rapid multiple collisions occurring are efficient in producing multi-excited electronic states. Many doubly-excited states decaying to singly-excited states by photon emission can be observed in this way (Berry et al, 1972a)

Also in experiments involving a gas target instead of a thin foil, resonances such as in electron-helium (Simpson et al, 1965) and ion-helium (Rudd, 1965) inelastic scattering were observed. (For a review, see also McGowan, 1970.)

1.2 Astrophysical Importance

Autoionizing resonances are important in astrophysical problems for two reasons. First, they serve as indicators of the physical conditions present in a given region. Second, they function as decay modes or channels through which a stellar region can leak its energy to the outside.

Because transitions involving autoionizing resonances are typically broad with characteristic line shapes, they are readily and uniquely identifiable (Goldberg, 1966). Such lines by their absence or presence can indicate which species of atoms are not or are present in a stellar plasma and in what ionized states they exist. Also the relative intensities of those lines excited by the stellar continuum indicate the relative abundances of the species present in the plasma. Conversely if the abundances are known, then the observations of transitions involving autoionizing states can be used to deduce the intensity of the stellar continuum and the electron temperature (Burgess, 1966). The process of dielectronic recombination through an autoionizing state has been found to be of great importance in determining the ionization balance in the high temperature stellar plasmas such as the Solar Corona (Walker and Runge, 1971). In fact, before autoionizing transitions were taken into account, there was a discrepancy between the temperature of the Solar Corona as deduced from the observed Doppler widths of the "forbidden" emission lines to Fe^{+9}, Fe^{+13}, Ca^{+14} and as deduced from ionization balance calculations. The Doppler width method gave a temperature that was twice the temperature resulting from ionization balance calculations (Burgess, 1966).

Until recently it has not been possible to observe many of these transitions in astrophysical spectra because the earth's upper atmosphere is opaque to ultraviolet light. However the advent of orbiting satelite observatories has now made it possible to observe these valuable spectra.

1.3 Outline of Thesis

The remainder of the thesis is divided into two chapters: one containing the formal theory of autoionization, the other describing the calculations, results and conclusions.

In Chapter II the S-matrix formulation of scattering theory is presented. This is followed by a discussion of a particular problem of scattering, -autoionizing resonances. The scattering resonance problem is then formulated in terms of the Feshbach Q,P projection operator formalism and an expression for the resonant phase shift is derived. From this, an expression for the resonance width and an interpretation of the resonance energy is made.

The specific method used to calculate the resonances in this thesis: the 1/Z expansion perturbation method is then presented in detail for zero-order nondegenerate and degenerate cases. Also an appropriately modified formula for the resonance width is described.

In Chapter III, numerical methods used to calculate the positions and widths of the nondegenerate $2p^{2\,1}D$ and the zero-order degenerate $(2d3d \pm 2p3p)^3D$ states are outlined. The results obtained are tabulated and compared with results found by other authors. The advantages of the method are discussed and compared with other methods. Finally suggestions for future work are proposed.

CHAPTER II

2.0 Resonance Scattering Theory

2.0.1 S-Matrix Formulation of Scattering Theory

In general the time-independent Schrödinger equation for the total system of target atom and incident electron is

$$\{H_o(\vec{r}_1) + H_a(\vec{r}_j) + V(\vec{r}_1, \vec{r}_j) - E\} \Psi(\vec{r}_i, s_i) = 0 \qquad (2.0)$$

where H_a is the atomic Hamiltonian, H_o is that of the incident electron, V is the interaction, $\vec{r}_i$ is the position coordinate of the ith electron relative to the fixed nucleus, and s_i is its spin coordinate.

The asymptotic solution for the equation is a linear combination of all possible asymptotic solutions satisfying the Pauli exclusion principle. The Pauli principle is satisfied if Ψ is antisymmetric in the interchange of any pair of $\vec{r}_i$, s_i. Since

$$\lim_{r_1 \to \infty} V(\vec{r}_1, \vec{r}_j) \doteq 0 \qquad (2.1)$$

It follows that the asymptotic solutions will be products of the independent electron and atomic systems respectively. Before collision, the electron is a free particle with wave function

$$\psi_e = e^{i\vec{k}_o \cdot \vec{r}_1} \chi_{S_o}(s_1) \qquad (2.2)$$

where $\vec{k}_o = \vec{p}_o/\hbar$, $\vec{p}_o$ being the momentum of the incident electron. $\chi_{S_o}(s_1)$ is the initial spin state of the incident electron. Similarly the target atom will initially be in a state $\psi_o(\vec{r}_j, s_j)$. Therefore a possible asymptotic solution is

$$\psi\ (\vec{r}_i, s_i) \xrightarrow[r_1\to\infty]{} \chi_{S_o}\ (s_1)\ e^{i\vec{k}_o\cdot\vec{r}_1}\ \psi_o\ (\vec{r}_j, s_j) \tag{2.3}$$

After collision the target atom can be in any energetically accessible state ψ_γ. If the change in kinetic energy of the scattered electron is ΔK.E. then

$$\Delta K.E. = \left[E_\gamma - E_o\right] = \frac{1}{2m}\left[p_\gamma^2 - p_o^2\right] \tag{2.4}$$

where p_γ is the momentum of the scattered electron. Since $\vec{k}\gamma = \frac{\vec{p}_\gamma}{\hbar}$ then

$$\left[k_\gamma^{\ 2} - k_o^{\ 2}\right] = \frac{2m}{\hbar^2}\left[E_\gamma - E_o\right] \tag{2.5}$$

The scattered electron can be represented asymptotically by an outgoing spherical wave multiplied by an angle-dependent function $f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma)$. Therefore the asymptotic wave function of the scattered electron is written in the form

$$\psi_e = f_{o\gamma}\ (\hat{k}_o, \hat{k}_\gamma)\ \frac{e^{ik_\gamma r_1}}{r_1}\ \chi_S(s_1) \tag{2.6}$$

where $f_{o\gamma}\ (\hat{k}_o, \hat{k}_\gamma)$ is called the scattering amplitude. The quantity $|f_{o\gamma}\ (\hat{k}_o, \hat{k}_\gamma)|^2$ represents the probability of the electron being scattered from $\hat{k}_o$ into the direction $\hat{k}_\gamma$. The scattering amplitude $f_{o\gamma}\ (\hat{k}_o, \hat{k}_\gamma)$ can be related to the differential cross section dσ which is defined as

$$d\sigma = \frac{\text{number of particles scattered into solid angle } d\Omega \text{ per unit time}}{\text{incident flux}} \tag{2.7a}$$

$$d\sigma_{o\gamma}(\hat{k}_o, \hat{k}_\gamma) = \frac{\frac{\hbar k_\gamma}{m}\left|\frac{f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma)}{r_1^2}\right|^2 r_1^2 \, d\Omega}{\frac{\hbar k_o}{m}} \tag{2.7b}$$

$$d\sigma_{o\gamma}(\hat{k}_o, \hat{k}_\gamma) = \frac{k_\gamma}{k_o}\left| f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma)\right|^2 d\hat{k}_\gamma \tag{2.7c}$$

$f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma)$ depends on the interaction for its functional form.

Therefore the general asymptotic form for the wave function of the electron-atom system is

$$\Psi(\vec{r}_i, s_i) \xrightarrow[r_1 \to \infty]{} \chi_{S_o}(s_1)\, e^{i\vec{k}_o \cdot \vec{r}_1}\, \psi_o(\vec{r}_j, s_j) + \sum_{\gamma}\sum_{S} \chi_S(s_1)\, \frac{e^{ik_\gamma r_1}}{r_1}\, f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma)\, \psi_\gamma(\vec{r}_j, s_j) \tag{2.8a}$$

$$\Psi(\vec{r}_i, s_i) = \Psi_{k_o}(\vec{r}_i, s_i) + \Psi_{\mathrm{SCAT.}}(\vec{r}_i, s_i) \tag{2.8b}$$

where Ψ_{k_o} is the incoming plane wave and $\Psi_{\mathrm{SCAT.}}$ is the scattered wave. $\Psi_{\mathrm{SCAT.}}$ vanishes if there is no interaction.

Usually the wave function is expanded in terms of the complete set of target eigenfunctions

$$\Psi(\vec{r}_i, s_i) = \sum_{\gamma}\sum_{S} F_\gamma(\vec{r}_1)\, \chi_S(s_1)\, \psi_\gamma(\vec{r}_j, s_j) \tag{2.9}$$

Expanding in terms of the angular momentum eigenfunctions is called a partial wave expansion. The plane wave $e^{i\vec{k}_o \cdot \vec{r}_1}$ can be expanded as

$$e^{i\vec{k}_o \cdot \vec{r}_1} = 4\pi \sum_{l_o} i^{l_o}\, j_{l_o}(k_o r_1) \sum_{m_o} Y^*_{l_o m_o}(\hat{k}_o)\, Y_{l_o m_o}(\hat{r}_1) \tag{2.10}$$

where $j_{l_o}(k_o r_1)$ is the spherical Bessel function with the asymptotic form

$$\lim_{k_o r_1 \to \infty} j_{l_o}(k_o r_1) \longrightarrow \frac{\sin(k_o r_1 - l_o \pi/2)}{k_o r_1} \tag{2.11}$$

Therefore

$$\lim_{r_1 \to \infty} e^{i\vec{k}_o \cdot \vec{r}_1} = \frac{2\pi}{k_o r_1} \sum_{l_o} \sum_{m_o} Y^{*}_{l_o m_o}(\hat{k}_o)\, Y_{l_o m_o}(\hat{k}_\gamma)$$

$$\times \{e^{-i(k_o r_1 - l_o \pi/2)} - e^{i(k_o r_1 - l_o \pi/2)}\}\, i^{l_o+1} \tag{2.12}$$

where $\hat{r}_1 = \hat{k}_\gamma$. Similarly we expand

$$f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma) = \sum_{lm}\sum c_{lm}(\hat{k}_o)\, Y_{lm}(\hat{k}_\gamma) \tag{2.13a}$$

with

$$c_{lm}(\hat{k}_o) = \langle f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma) |\, Y_{lm}(\hat{k}_\gamma)\rangle \tag{2.13b}$$

or

$$c_{lm}(\hat{k}_o) = \sum_{l_o} \sum_{m_o} b_{l_o m_o}\, Y^{*}_{l_o m_o}(\hat{k}_o) \tag{2.14a}$$

where

$$b_{l_o m_o} = \langle Y_{l_o m_o}(\hat{k}_o)\, f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma) |\, Y_{lm}(\hat{k}_\gamma)\rangle \tag{2.14b}$$

A matrix T, the transition matrix, can be defined as

$$T(\gamma_o s_o l_o m_o | \gamma s l m) = \frac{\sqrt{k_o k_\gamma}}{2\pi}\, i^{l-l_o-1} \langle Y_{l_o m_o}(\hat{k}_o) f_{o\gamma} | Y_{lm}(\hat{k}_\gamma)\rangle \tag{2.15}$$

so that

$$f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma) = \frac{2\pi}{\sqrt{k_o k_\gamma}} \sum_{l_o} \sum_{m_o} \sum_{l} \sum_{m} i^{l_o - l + 1}\, T(\gamma_o s_o l_o m_o | \gamma s l m)$$

$$\times Y^{*}_{l_o m_o}(\hat{k}_o)\; Y_{lm}(\hat{k}_\gamma) \tag{2.16}$$

Also a matrix S can be defined as

$$T(\gamma_o s_o l_o m_o|\gamma slm) = \delta(\gamma_o s_o l_o m_o|\gamma slm) - S(\gamma_o s_o l_o m_o|\gamma slm) \qquad (2.17)$$

where $\delta(\gamma_o s_o l_o m_o|\gamma slm)$ is a kronecker delta

$$\delta(\gamma_o s_o l_o m_o|\gamma slm) = \delta_{\gamma_o,\gamma} \ \delta_{s_o,s} \ \delta_{l_o,l} \ \delta_{m_o,m}$$

Using the S matrix formulation for $f_{o_\gamma}(\hat{k}_o,\hat{k}_\gamma)$ and the asymptotic form for $e^{i\vec{k}_o\cdot\vec{r}_1}$ and substituting into $\psi(\vec{r}_i,s_i)$ as $r_1 \to \infty$ leads after rearrangement to (Geltman, 1969)

$$\Psi(\vec{r}_i,s_i) \xrightarrow[r_1\to\infty]{} 2\pi \sum_{\gamma}\sum_{s}\sum_{l_o}\sum_{m_o}\sum_{l}\sum_{m} \frac{i^{l_o+1}}{(k_\gamma k_o)^{\frac{1}{2}}\, r_1} Y^{*}_{l_o m_o}(\hat{k}_o)\, Y_{lm}(\hat{k}_\gamma)$$
$$\times\, \chi_S(s_1)\psi_\gamma(\vec{r}_j,s_j)\Big[\delta(\gamma_o s_o l_o m_o|\gamma slm)\, e^{-i(k_\gamma r_1 - l\pi/2)}$$
$$- S(\gamma_o s_o l_o m_o|\gamma slm)\, e^{i(k_\gamma r_1 - l\pi/2)}\Big] \qquad (2.18)$$

Physically the wave function has been expanded in terms of the complete set of scattering state eigenfunctions with the absolute squares of the amplitude coefficients representing the probabilities of finding the electron-atom system in the corresponding scattering state. The difference between the complete solution $\psi(\vec{r}_i,s_i)$ given by (2.18) and the incoming plane wave Ψ_{k_o} is the scattered wave $\Psi_{SCAT}(\vec{r}_i,s_i)$ given by the second term of (2.8), i.e.

$$\Psi(\vec{r}_i,s_i) - \Psi_{ko} = \sum_{\gamma s} \chi_S(s_1)\, \frac{e^{ik_\gamma r_1}}{r_1}\, f_{o_\gamma}(\hat{k}_o,\hat{k}_1)\, \Psi_\gamma(\vec{r}_j,s_j) \qquad (2.19)$$

Using the partial wave expansion for ψ_{k_o} and comparing with (2.18) shows that

$$f_{o\gamma}(\hat{k}_o, \hat{k}_\gamma) = 2\pi i \sum_{l_o m_o l m}\sum\sum\sum \{\delta(\gamma_o s_o l_o m_o|\gamma s l m) - S(\gamma_o s_o l_o m_o|\gamma s l m)\} \times Y^*_{l_o m_o}(\hat{k}_o)\, Y_{lm}(\hat{k}_\gamma) \tag{2.20}$$

The scattering amplitude is related to the cross-section by (2.7c).

Since physical laws are invariant under time reversal it follows that

$$S(\gamma_o s_o l_o m_o|\gamma s l m) = S(\gamma s l {-m}|\gamma_o s_o l_o {-m_o}) \tag{2.21}$$

S can also be shown to be unitary from the conservation of total flux.

2.0.2 Scattering Resonances

Physically resonances correspond to the temporary trapping of the scattered particle by the target. Scattering resonances can be divided into two basic types.

First, the interaction potential may have a well, caused for example, by the repulsive angular momentum barrier. The incoming particle may then "tunnel through" the barrier and be temporarily trapped. Since this type of resonance depends on the shape of the interaction potential it is called a shape resonance. A second type of resonance occurs when the incoming particle excites the target causing a structural change which temporarily binds the particle. Such a resonance is called a closed channel resonance if the excited target state is energetically forbidden. The resonances considered in this thesis are of the latter type. For example, the $2s2p^1P$ resonance of helium lies below the excitation threshold for the n=2 states of He^+. Closed channel resonances of this type appear in the elastic scattering cross-section of electrons by the parent ion, and so $|\vec{k}_\gamma|=|\vec{k}_o|$. Furthermore, the S-matrix does not connect states of different angular momentum since the interaction potential is spherically symmetric. It is also diagonal in spin if spin-orbit interactions are neglected. We may thus write $S(\gamma_o s_o l_o m_o|\gamma slm) = \delta(\gamma_o s_o l_o m_o|\gamma slm)\ S_l(k)$, where $S_l(k)$ is an analytic function of k and $\frac{\hbar^2 k^2}{2m}$ is the energy of the incoming electron. It follows from the unitary and time-reversal properties of $S_l(k)$ that

$$S_l^{-1}(k) = S_l(-k) \tag{2.21}$$

$$\text{and } S_l^*(k) = S_l(-k^*) \tag{2.22}$$

Thus a pole at k is accompanied by a second pole at $-k^*$ and a zero at -k. Poles along the positive imaginary k-axis correspond to bound states and those in the lower k-plane correspond to scattering resonances.

Consider an autoionizing resonance under elastic scattering conditions where an atom is excited from its ground state into a resonant state by a free electron, and after a period of time decays back to its ground state and ejects the electron.

If a pole lies at $k=k_R$ and is of the resonance state type, then $S_l(k)$ has an associated pole $-k_R^*$ and zeroes $k_R^*, -k_R$. $S_l(k)$ can be rewritten as

$$S_l(k) = \frac{1}{(k-k_R)(k+k_R^*)}\, g_l(k) \tag{2.23}$$

where $g_1(k)$ is an analytic function of k near the pole. In order to ensure $S_1(k_R) = o$ let $g_1(k)$ be redefined as $(k+k_R)\ g_1(k)$. Therefore

$$S_1(k) = \frac{k + k_R}{(k-k_R)\ (k+k_R^*)}\ g_1(k) \tag{2.24}$$

Expanding the analytic function $g_1(k)$ in a Taylor series about $k=k_R^*$ results in

$$S_1(k) = \frac{k+k_R}{(k-k_R)(k+k_R^*)}\ \{g_1(k_R^*) + (k-k_R^*)\ g_1'(k)\Big|_{k=k_R^*} + \ldots\} \tag{2.25}$$

Since $S_1(k_R^*) = 0$ therefore $g_1(k_R^*) = 0$, thus

$$S_1(k) = \frac{(k + k_R)\ (k - k_R^*)}{(k + k_R^*)\ (k - k_R)}\ e^{2i\delta_1'} = e^{2i\delta_1} \tag{2.26}$$

where the phase shifts δ_1', δ_1 are defined by the relations

$$S_1(k) = e^{2i\delta_1(k)} \tag{2.27a}$$

$$g_1'(k)\Big|_{k=k_R^*} = e^{2i\delta_1'(k)} \tag{2.27b}$$

If $k_R = \beta - i\gamma$ then

$$e^{2i\delta_1(k)} = \frac{(k + \beta - i\gamma)\ (k - \beta - i\gamma)}{(k - \beta + i\gamma)\ (k + \beta + i\gamma)}\ e^{2i\delta_1'(k)} \tag{2.28a}$$

Therefore

$$e^{2i\delta_1(k)} = \frac{k^2 - (\beta^2 + \gamma^2) - 2ik\gamma}{k^2 - (\beta^2 + \gamma^2) + 2ik\gamma}\, e^{2i\delta_1'(k)} \tag{2.28b}$$

which can be solved for $\delta_1(k)$ to obtain

$$\delta_1(k) = \delta_1'(k) - \tan^{-1} \frac{\Gamma_R}{2\ (E-E_R)} \tag{2.29}$$

where $E_R = \frac{\hbar^2}{2m} (\beta^2 + \gamma^2)$, $\frac{\Gamma_R}{2} = \frac{\hbar^2}{m} \gamma k$

The above is well known as the Breit-Wigner one-level resonance formula for a resonance at energy E_R and width Γ_R. By definition k is real and positive and lies close to the zero at k_R^*.

2.0.3 The Projection Operator Formalism

The projection operator formalism allows one to calculate the positions and widths of scattering resonances without finding a detailed solution to the scattering problem. Following Feshbach (1962) and O'Malley and Geltman (1965) the complete Hilbert space of bound and scattering states may be split into two subspaces P space and Q space such that if P and Q are the corresponding projection operators then

$$\Psi(\vec{r}_1,s_1;\ \vec{r}_2,s_2) \equiv (P + Q)\ \Psi(\vec{r}_1,s_1;\ \vec{r}_2,s_2) \tag{2.30}$$

P space and Q space are defined so that as $r_1 \to \infty$ the asymptotic wave function has no components in Q space and lies entirely in P space. That is

$$P\Psi(\vec{r}_1,s_1;\ \vec{r}_2,s_2) \xrightarrow[r_1 \text{ or } r_2 \to \infty]{} \Psi(\vec{r}_1,s_1;\ \vec{r}_2,s_2)_{\text{ASYMPTOTIC}} \tag{2.31a}$$

and

$$Q\Psi(r_1,s_1;\ r_2,s_2) \xrightarrow[r_1 \text{ or } r_2 \to \infty]{} 0 \tag{2.31b}$$

In general (H-E) $\Psi = 0$, so that

$$Q(H-E)\ (P + Q)\ \Psi = 0 \tag{2.32a}$$

Therefore $Q\Psi = Q \dfrac{1}{Q(E-H)\ Q}\ QHP\ \Psi$ (2.32b)

where the relations

$$Q^2 = Q \tag{2.33a}$$

$$P^2 = P \tag{2.33b}$$

$$QP = PQ = 0 \tag{2.33c}$$

have been used. Similiarly

$$P(H - E)\ (P + Q)\ \Psi = 0 \tag{2.34}$$

or on substitution for $Q\Psi$

$$P\{H + HQ \frac{1}{Q(E - H)\ Q} QH - E\}\ P\Psi = 0 \tag{2.35}$$

Since $Q\Psi$ asymptotically vanishes (eq. 2.31b), it then follows that Q space can be spanned by a complete set of bound state functions $Y_n(\vec{r}_1,\vec{r}_2)$ such that

$$H_{QQ} Y_n (\vec{r}_1, \vec{r}_2) = \varepsilon_n Y_n (\vec{r}_1, \vec{r}_2) \tag{2.36}$$

where Q, H_{QQ} are defined as

$$Q = \sum_n | Y_n \rangle \langle Y_n | \tag{2.37a}$$

$$H_{QQ} = QHQ \tag{2.38a}$$

Similiarly defining H_{PP}, H_{QP}, H_{PQ} as

$$H_{PP} = PHP \tag{2.38b}$$

$$H_{QP} = QHP \tag{2.38c}$$

$$H_{PQ} = PHQ \tag{2.38d}$$

it follows that

$$PHQ \frac{1}{Q(E - H)Q} QHP = H_{PQ} \frac{\sum_n | Y_n \rangle \langle Y_n | H_{QP}}{E - \varepsilon_n} . \tag{2.39}$$

and therefore

$$\{H_{PP} + \sum_n H_{PQ} \frac{| Y_n \rangle \langle Y_n | H_{QP}}{E - \varepsilon_n} - E\} P\Psi = 0 \tag{2.40}$$

Let E lie closest to ε_s in the set of ε_n's and consider the Hamiltonian equation rewritten in the form

$$\{H_{PP} + \sum_{n \neq s} H_{PQ} \frac{| Y_n \rangle \langle Y_n | H_{QP}}{E - \varepsilon_n} - E\} P\Psi = -H_{PQ} \frac{| Y_s \rangle \langle Y_s | H_{QP}}{E - \varepsilon_s} P\Psi \tag{2.41a}$$

Let $P\Psi'$ be the solution of the homogeneous equation

$$(H' - E)\, P\Psi' = 0 \tag{2.41b}$$

where $$H' = H_{PP} + \sum_{n \neq s} \frac{H_{PQ}|Y_n\rangle\langle Y_n|H_{QP}}{E-\varepsilon_n} \tag{2.41c}$$

which is the background scattering problem in the absence of the resonance. O'Malley and Geltman (1965) showed that the solution to (2.41a) can be written in the form

$$\begin{aligned} P\Psi(\vec{r}_1{}',\vec{r}_2{}') \xrightarrow[r_1\to\infty]{} & \sum_{l_o} \sum_{m_o} \psi_{\gamma_o}(\vec{r}_2{}',s_2{}')\, \chi_{S_o}(s_1{}') \\ & \times Y^*_{l_o m_o}(\hat{k}_o)\, Y_{l_o m_o}(\hat{r}_1{}')\, i^{l_o+1}\, e^{i\delta_{l_o}(k_o)} \left[\frac{\sin\{k_o r_1{}' - l_o\pi/2 + \delta_{l_o}{}'(k_o)\}}{k_o r_1{}'} \right. \\ & \left. - \frac{2mk_o}{\hbar^2} \frac{|\langle\Psi', H_{PQ}Y_S\rangle|^2}{E-\varepsilon_s-\Delta_s} \frac{\cos\{k_o r_1{}' - l_o\pi/2 + \delta_{l_o}{}'(k_o)\}}{k_o r_1{}'} \right] \end{aligned} \tag{2.42}$$

where $$\Delta_S = \langle Y_S|H_{QP}\, G\, H_{PQ}|Y_S\rangle \tag{2.43}$$

and G is the Green's function satisfying the equation

$$\begin{aligned} \{H_{PP} + \sum_{n \neq s} H_{PQ}|Y_n\rangle\langle Y_n|\, H_{QP} - E\}\, G\,(\vec{r}_1, \vec{r}_2 \cdot \vec{r}_1{}', \vec{r}_2{}') \\ = \delta(\vec{r}_1 - \vec{r}_1{}')\, \delta(\vec{r}_2 - \vec{r}_2{}') \end{aligned} \tag{2.44}$$

Defining a new phase shift $\eta(k_o)$ where

$$\tan \eta(k_o) = \frac{-2mk_o}{\hbar^2} \frac{|\langle\Psi', H_{PQ}\, Y_S\rangle|^2}{E-\varepsilon_S-\Delta_S} \tag{2.45}$$

it follows that

$$P\Psi(\vec{r}_1,\vec{r}_2) = \sum_{l_o m_o}\sum \psi_\gamma(\vec{r}_2, s_2)\, \chi_{S_o}(s_1)\, Y^*_{l_o m_o}(\hat{k}_o)\, Y_{l_o m_o}(\hat{r}_1) \tag{2.46}$$

$$\times\, i^{l_o+1}\, e^{i\delta_{l_o}(k_o)}\, \frac{\sin \{k_o r_1 - \frac{l_o \Pi}{2} + \delta'_{l_o}(k_o) + \eta(k_o)\}}{k_o r_1 \cos \eta(k_o)}$$

But since $\Psi(\vec{r}_1,\vec{r}_2) \xrightarrow[r_1 \rightarrow \infty]{} P\Psi(\vec{r}_1,\vec{r}_2)$ it follows that $\delta_{l_o}(k_o) = \delta_{l_o}'(k_o) + \eta(k_o)$ and from the Breit-Wigner one level resonance formula

$$\tan\{\delta_{l_o}(k_o) - \delta_{l_o}'(k_o)\} = -\frac{\Gamma_R}{2\,(E-E_R)}$$

therefore it follows that

$$\frac{2mk_o}{\hbar^2} \frac{|\langle\Psi', H_{PQ}\, Y_s\rangle|^2}{E-\varepsilon_s-\Delta_s} = \frac{\Gamma_R}{2\,(E-E_R)} \tag{2.47}$$

In the vicinity of a resonance the wave function will have a very large amplitude and this can only happen if $\cos \eta(k_o) \rightarrow 0$ or $\tan \eta\,(k_o) \rightarrow \infty$. $\tan \eta\,(k_o) \rightarrow \infty$ when E approaches $\varepsilon_s + \Delta_s$. Therefore $(\varepsilon_s + \Delta_s)$ must indeed be the resonance position E_R. Therefore

$$\frac{\Gamma_R}{2} = \frac{2mk_o}{\hbar^2} |\langle\Psi', H_{PQ}\, Y_s\rangle|^2 \tag{2.48}$$

where $\frac{\Gamma_R}{2}$ is the half-width as shown by the relation

$$\{\tan \eta(k_o)\}\{E-E_R\} = \frac{\Gamma_R}{2} \tag{2.49}$$

Far from resonance $P\Psi \simeq P\Psi'$ therefore $\eta(k_o)$ must be small and rise to $\frac{\pi}{2}$ at resonance. At the halfway point $\eta(k_o) = \frac{\pi}{4}$ therefore $\tan \frac{\pi}{4}(E-E_R) = E-E_R = \frac{\Gamma_R}{2}$ and thus the halfwidth $(E-E_R)$ at $\eta(k_o) = \frac{\pi}{4}$ is indeed $\frac{\Gamma_R}{2}$.

2.0.4. Methods of Calculating Resonances

Methods of calculating resonance positions and widths can be divided into three categories as follows:

1. Detailed Scattering Calculations: In principle one can simply calculate scattering cross-sections as a function of energy, using, for example, the close-coupling method introduced by Massey and Mohr (1932) and extensively developed by Burke (for recent reviews see Burke, 1968 and Taylor, 1970). Any resonances then appear when the cross-section is plotted as a function of energy, provided that the appropriate closed channels are included in the calculation. Although electron-atom scattering resonances were first discovered by Burke and co-workers in this way, the method is extremely time consuming and becomes completely impractical when more than a few channels are involved.

2. Q-Projection Operator Methods: By definition the eigenvalue spectrum of QHQ is entirely discrete at least up to and just above the resonance position. It follows that the eigenvalues ε_s of QHQ can be bounded by a standard variational calculation. If the resonance is narrow, then the configuration interaction of Q space with the continuum P space is weak and the compound state wave function is well described

in the region of physical space near the nucleus by a bound state type trial solution. In addition, the residual energy shift $\Delta_s = E_s - \varepsilon_s$ arising from the interaction with P space, though difficult to evaluate, is small. Recent calculations by this method are referenced by Bhatia and Temkin (1969) and Bhatia (1972). The major disadvantages are that the exact target eigenfunctions must be known in order to construct the Q operator and the energy shift Δ_s is not included.

3. Energy Stabilization Methods: An alternative procedure introduced by Holøien and Midtdal (1966) and Miller (1966) does not require a knowledge of the exact target eigenfunctions. In essence, one simply diagonalizes the Hamiltonian in a finite basis set and looks for roots which stabilize in energy as an exponential parameter is varied. Perkins (1969) has shown that recent configuration interaction calculations by Holøien and Midtdal (1971a, 1971b) yield upper bounds to the eigenvalues of QHQ in this way, although their results are of low accuracy. The accuracy can in principle be improved by use of a correlated basis set, but the resulting eigenvalues are no longer bounds to the resonance positions since components of the continuum P space are automatically included and an additional criterion must be introduced to eliminate spurious results. Essentially, the difficulty is that one is not sure whether a given solution to the variational problem is an approximation to an autoionizing state, or to a scattering state lying near by. Drake and Dalgarno (1971) have suggested a 1/Z expansion perturbation procedure with an adjustable screening parameter to circumvent this difficulty. The advantages of the method are that the exact target eigenstates need not be known, and a substantial part of the energy shift is included. In addition, the variational root corresponding to the autoionizing state can be uniquely identified. The

If the corresponding energy eigenvalues are re-expressed in units which are $\left[\frac{1}{Z-\sigma}\right]^2$ the size of the old units, then the proper form of the Hamiltonian in terms of the $\frac{1}{Z}$ expansion results

$$H = H_o + Z_\sigma^{-1} V \tag{2.52a}$$

where

$$H_o = \sum_{i=1}^{N} \left\{ -\frac{\nabla_i^2}{2} - \frac{1}{r_i} \right\} \tag{2.52b}$$

$$V = \sum_{i>j} \frac{1}{r_{ij}} - \sigma \sum_{i=1}^{N} \frac{1}{r_i} \tag{2.52c}$$

$$Z_\sigma = Z - \sigma \tag{2.52d}$$

The choice of Q space is arbitrary provided that the eigenfunctions spanning it vanish in the limit as r_1 or $r_2 \rightarrow \infty$. The 1/Z perturbation expansion method is generated by choosing Q space to contain only one eigenfunction Φ_s^o of H_o. Φ_s^o is just the product of hydrogenic orbitals which describe the autoionizing state in zero-order and is therefore known exactly. Then

$$Q = |\Phi_s^o\rangle \langle\Phi_s^o| \tag{2.53}$$

where $H_o\Phi_s^o = E_s^o \Phi_s^o$. Also it follows that

$$H_{QQ}\, \Phi_s^o = (E_s^o + Z_\sigma^{-1} E_s^1)\, \Phi_s^o \quad , \; E_s^1 = \langle\phi_s^o|V|\phi_s^o\rangle \tag{2.54}$$

Since H_{QQ} has no other eigenfunctions (by this particular definition of Q space), it follows that $H' = H_{PP}$ (from eq. 2.41c). Also since $H_oQ = E_s^oQ$ and $PQ = 0$ it follows that

$$H_{PQ} = Z_\sigma^{-1} V_{PQ} \tag{2.55a}$$

$$H_{QP} = Z_\sigma^{-1} V_{QP} \tag{2.55b}$$

Therefore the total resonance energy eigenvalue E_s, $E_s = \varepsilon_s + \Delta_s$ is

$$\begin{aligned} E_s &= E_s^{\,o} + Z_\sigma^{-1} E_s^{\,1} + Z_\sigma^{-2} \langle \Phi_s^{\,o} | VP(E_s - H_{PP})^{-1} PV | \Phi_s^{\,o} \rangle \\ &= \langle \Phi_s^{\,o} | H | \Phi_s^{\,o} \rangle + Z_\sigma^{-1} \langle \Phi_s^{\,o} | V | \xi_s \rangle \end{aligned} \tag{2.56}$$

where $$|\xi_s\rangle = Z_\sigma^{-1} P (E_s - H_{PP})^{-1} PV | \Phi_s^{\,o} \rangle \tag{2.57}$$

Multiply through by $(E_s - H_{PP})$ to obtain

$$(E_s - H_{PP}) |\xi_s\rangle = Z_\sigma^{-1} PV | \Phi_s^{\,o} \rangle \tag{2.58}$$

Thus $$E_s \langle \xi_s | \xi_s \rangle = \langle \xi_s | H | \xi_s \rangle + Z_\sigma^{-1} \langle \xi_s | V | \Phi_s^{\,o} \rangle \tag{2.59}$$

Add equation (2.59) to equation (2.56) to obtain

$$E_s \{ \langle \Phi_s^{\,o} | \Phi_s^{\,o} \rangle + \langle \xi_s | \xi_s \rangle \} = \langle \Phi_s^{\,o} + \xi_s | H | \Phi_s^{\,o} + \xi_s \rangle \tag{2.60}$$

Define $\Psi_s = \Phi_s^{\,o} + \xi_s$. Note that $\Phi_s^{\,o} = Q\psi_s$ and $\xi_s = P\psi_s$. Then (2.60) becomes

$$E_s = \frac{\langle \psi_s | H | \psi_s \rangle}{\langle \psi_s | \psi_s \rangle} \tag{2.61}$$

If ψ_s is taken to be a trial function $\tilde{\psi}_s$, then equation (2.61) is the starting point for a standard Rayleigh-Ritz variational calculation in which the trial function is varied to find the stationary values of $\widetilde{E}_s$. However unlike the situation for bound states, autoionizing states are imbedded in the scattering continuum and the trial value of the energy $\widetilde{E}_s$ is not an upper bound to the exact energy. One cannot even say that the stationary values of $\widetilde{E}_s$ become more accurate (i.e. closer to the exact resonance position) as the trial function becomes more flexible. We therefore impose the subsidiary condition that $<\psi_s|\psi_s> \equiv 1 + <\xi_s|\xi_s>$ be a minimum with respect to variations in the screening parameter σ. This minimizes the perturbation corrections and guarantees that ψ_s resembles as closely as possible (on the average) the zero-order function $\Phi_s{}^o$, which is known a priori. In this way, spurious results can be eliminated and the variational eigenvalue belonging to the autoionizing state corresponding to $\Phi_s{}^o$ can be uniquely identified.

The method of calculation is as follows. We introduce a finite orthonormal correlated M dimensional basis set ϕ_i satisfying

$$<\phi_i|H_o|\phi_j> = \varepsilon_i \, \delta_{ij} \quad i,j = 1,\ldots, M \tag{2.62}$$

The ϕ_i's are constructed from linear combinations of correlated functions of the form $r_1{}^a \, r_2{}^b \, r_{12}{}^c \, e^{-\alpha r_1 - \beta r_2}$ with α and β set equal to their hydrogenic values. One of the ϕ_i, say ϕ_s will then be the exact hydrogenic reference state $\Phi_s{}^o$ with eigenvalue $\varepsilon_s = E_s{}^o$ and the trial function $\widetilde{\psi}_s$ may be written

$$\widetilde{\psi}_s = \Phi_s{}^o + \sum_{i \neq s} a_i \phi_i \tag{2.63}$$

Thus automatically satisfying the normalization condition $<\psi_s|\Phi_s{}^o> = 1$. The variational coefficients a_i are determined by substituting (2.63) into (2.61) and setting $\frac{\delta E_s}{\delta a_i} = 0$, $i \neq s$. This gives rise to the set of non-linear equations (where $V_{ij} = \langle\phi_i|V|\phi_j\rangle$)

$$\sum_{i \neq s}^{M} a_i V_{ij} + a_j Z_\sigma (\varepsilon_j - \tilde{E}_S) = -V_{sj}, \qquad j \neq s \tag{2.64}$$

which must be solved iteratively since $\tilde{E}_s$ is given in terms of the a_i by equations (2.61) and (2.63). The resulting value of $\tilde{E}_s$ is identical to the value that would be obtained by the direct diagonalization of the total Hamiltonian H in the same basis set, but the above procedure is much more efficient once the orthonormal functions ϕ_i have been constructed. Results for the ^1D and ^3D resonances of helium will be presented in the next chapter.

2.1.2 The Perturbation Expansion

The method described above can be re-expressed as a perturbation series involving powers of Z_σ^{-1}. The advantages of doing so are that results are obtained for the entire helium isoelectronic sequence in a single calculation, and a direct connection is established between the doubly excited zero-order states Φ_s^o and the autoionizing resonances. We will assume for the moment that the zero-order states are non-degenerate. The degenerate case is discussed in the following section.

The correlated basis set $\phi_i (i \neq s)$ spans a subspace of P space defined by

$$P_1 = \sum_{i \neq s} |\phi_i\rangle\langle\phi_i| \tag{2.65}$$

P_1 space contains functions approximating both bound and continuum states in the region of physical space near the nucleus where the amplitude of the resonant scattering function is large. Thus part of the shift arising from the interaction of Φ_s^o with the continuum can be taken into account. However, the spectrum P_1HP_1 remains entirely discrete and the solution to the modified problem specified by

$$|\tilde{\psi}_s\rangle = |\Phi_s^o\rangle + Z_\sigma^{-1} P_1 (E_s - H_{P_1P_1})^{-1} P_1 V|\Phi_s^o\rangle \tag{2.66}$$

which was obtained iteratively in the previous section, can also be generated in terms of a standard Rayleigh-Schrödinger perturbation expansion in powers of Z_σ^{-1}. The method is summarized by Löwdin (1966) for bound states and can be applied directly to equation (2.66). Writing

$$\tilde{\Psi}_s = \Phi_s^o + \sum_{n=1}^{N_{max}} Z_\sigma^{-n} \psi_s^{(n)} \tag{2.67}$$

$$\tilde{E}_s = E_s^o + \sum_{n=1}^{N_{max}} Z_\sigma^{-n} E_s^{(n)} \tag{2.68}$$

the results may be expressed in terms of the recursion relations (Drake and Dalgarno, 1971)

$$\psi_s^{(n)} = \sum_{i \neq s} \frac{\langle\psi_s^{(n-1)}|V|\phi_i\rangle\langle\phi_i|}{E_s^o - \varepsilon_i} - \sum_{i \neq s} \sum_{p=1}^{n} E_s^{(p)} \frac{\langle\psi_s^{(n-p)}|\phi_i\rangle\langle\phi_i|}{E_s^o - \varepsilon_i} \tag{2.69}$$

$$E_s^{(n)} = \langle\psi_s^{(n-1)}|V|\Phi_s^o\rangle - \sum_{p=1}^{n-1} E_s^{(p)}\langle\psi_s^{(n-p)}|\Phi_s^o\rangle \tag{2.70}$$

The direct iterative calculation of (2.64) in effect sums the perturbation series for a particular value of Z while avoiding possible divergence difficulties arising from the use of a finite basis set. The advantages of the perturbation expression approach above are that a direct connection is established between the zero-order solution Φ_s^o and the autoionizing state, and results are obtained for the entire isoelectronic sequence in a single calculation.

2.1.3 The Zero-Order Degenerate Case

Consider for example the $2p3p\,^3D$ and $2s3d\,^3D$ resonances. These states are degenerate in zero-order and the perturbation theory must be appropriately modified. In the case of an m-fold zero-order degeneracy such that

$$\underline{H}_o \Phi_{s_j}^o = E_s^o \Phi_{s_j}^o , \qquad j = 1, 2, 3, \ldots, m \tag{2.71}$$

Q space must be extended to include the complete degenerate subspace of the m zero-order eigenfunctions $\Phi_{s_j}^o$. Therefore

$$Q = \sum_{j=1}^{M} |\Phi_{s_j}^o\rangle \langle\Phi_{s_j}^o| \tag{2.72}$$

If the Q space degenerate eigenfunctions are to be eigenfunctions of H_{QQ} then

$$H_{QQ}|\Phi_{s_k}^o\rangle = (E_s^o + Z_\sigma^{-1} E_{s_k}^1)|\Phi_{s_k}^o\rangle \quad , \quad E_{S_K}^1 = \langle\Phi_{S_K}^o|V|\Phi_{S_K}^o\rangle \tag{2.73a}$$

or

$$\sum_{j=1}^{M} |\Phi_{s_j}^o\rangle \langle\Phi_{s_j}^o|H_o + Z_\sigma^{-1} V|\Phi_{s_k}^o\rangle = (E_s^o + Z_\sigma^{-1} E_{s_k}^1)|\Phi_{s_k}^o\rangle \tag{2.73b}$$

Thus we must impose the condition that $<\Phi_{s_j}^{o}|V|\Phi_{s_k}^{o}> = E_{s_k}^{1}\,\delta_{jk}$. In other words the eigenfunctions must diagonalize the perturbation V. In general the perturbation V will remove the zero-order degeneracy of the m eigenfunctions of H_o and cause m autoionization resonances to be formed. The set $\Phi_{s_j}^{o}$ can be redefined as m linearly independent linear combinations of the old set $\Phi_{s_j}^{o}$. The new set $\Phi_{s_j}^{o}$ can be chosen to diagonalize V and be orthonormal. Since any linear combination of degenerate eigenfunctions is itself a degenerate eigenfunction, the new set $\Phi_{s_j}^{o}$ will still be m-fold degenerate for H_o. Consider H' defined in the discussion of the Feshbach P,Q projector formalism

$$H' = H_{PP} + \sum_{n \neq s} \frac{H_{PQ}\, Y_n> <Y_n\, H_{QP}}{E - \varepsilon_n} \qquad (2.41c)$$

In the nondegenerate case H' reduced to H_{PP} since Q space spanned only the eigenfunction space $|Y_s> <Y_s| = |\Phi_s^{o}> <\Phi_s^{o}|$. In the m-fold zero-order degenerate case

$$H' = H_{PP} + \sum_{j \neq k} \frac{P|H_o + Z_\sigma^{-1}\, V|\Phi_{s_j}^{o}> <\Phi_{s_j}\; |H_o + Z_\sigma^{-1}\, V|P}{E - E_s^{o} - E_{s_j}^{1}} \qquad (2.74a)$$

$H_o\,\Phi_{s_j}^{o} = E_s^{o}\,\Phi_{s_j}^{o}$ and $P|\Phi_{s_j}^{o}> = 0$. But $V_{QQ}\,\Phi_{s_j}^{o} = E_{s_j}^{1}\,\Phi_{s_j}^{o}$ and in general

$$PVQ\,\Phi_{s_j}^{o} \neq 0 \qquad (2.75)$$

Therefore

$$H' = H_{PP} + \sum_{j \neq k} Z_\sigma^{-2}\, \frac{V_{PQ}|\Phi_{s_j}^{o}> <\Phi_{s_j}^{o}|V_{QP}}{E - E_s^{o} - E_{s_j}^{1}} \qquad (2.74b)$$

Also in the nondegenerate case $H_{PQ} = Z_\sigma^{-1} V_{PQ}$, $H_{QP} = Z_\sigma^{-1} V_{QP}$. Since Q space is still spanned by eigenfunctions of H_o then

$$H_{PQ} = Z_\sigma^{-1} V_{PQ} \tag{2.55a}$$

$$H_{QP} = Z_\sigma^{-1} V_{QP} \tag{2.55b}$$

holds for the degenerate case. Therefore the total resonant energy E_{s_k} may be written as

$$E_{s_k} = E_s^o + Z_\sigma^{-1} E_{s_k}^1 + Z_\sigma^{-2} \langle \Phi_{s_k}^o | VP(E_s - H_{PP}')^{-1} PV | \Phi_{s_k}^o \rangle \tag{2.76}$$

where $H_{PP}' = H'$ as defined in equation (2.74c) and the total wave function is

$$| \Psi_{s_k} \rangle = | \Phi_{s_k}^o \rangle + Z_\sigma^{-1} P (E_s - H_{PP}')^{-1} PV | \Phi_{s_k}^o \rangle \tag{2.77}$$

Using the same argument as for the non-degenerate case, E_{s_k} may be written in the standard variational form

$$E_{s_k} = \frac{\langle \Psi_{s_k} | H | \Psi_{s_k} \rangle}{\langle \Psi_{s_k} | \Psi_{s_k} \rangle} \tag{2.78}$$

where $\langle \Psi_{s_k} | \Phi_{s_k}^o \rangle = 1$

As in the nondegenerate case $\tilde{\Psi}_{s_k}$ can be represented by the expansion

$$\tilde{\Psi}_{s_k} = \Phi_{s_k}^o + \sum_{i \neq s} a_i \phi_i \tag{2.79}$$

Thus, the zero-order degenerate case can be treated in exactly the same way as the non-degenerate case, provided that V is diagonalized in zero-order. M zero-order degenerate states give rise to M non-degenerate distinct resonances when the perturbation V is switched on.

2.1.4 Calculation of the Width

From Section 2.0.3 it was determined that the width Γ_R in the P, Q projection operator formalism is

$$\Gamma_R = \frac{4mk_o}{\hbar^2} \left|\langle \Psi', H_{PQ} Y_S \rangle\right|^2 \tag{2.48}$$

where $P\Psi'$ is normalized to unit asymptotic amplitude, i.e.

$$P\Psi'(\vec{r}_1, s_1; \vec{r}_2, s_2) \xrightarrow[r_1 \to \infty]{} \sum_{l_o m_o} \sum_{S_o} \chi_{S_o}(s_1)\, \psi_\gamma(\vec{r}_2, s_2) \times i^{l_o+1}\, Y^*_{l_o m_o}(\hat{k}_o)\, Y_{l_o m_o}(\hat{r}_1)\, e^{i\delta_{l_o}'(k_o)} \times \frac{\sin\{k_o r_1 - l_o \frac{\Pi}{2} + \delta_{l_o}'(k_o)\}}{k_o r_1} \tag{2.80}$$

The formula for the width assumes a more familiar form if $P\Psi'$ is re-normalized to unit density of states on the energy scale; i.e. so that

$$\int (P\Psi')^* P\Psi' \, dr_1 \, dr_2 = \delta(E - E_o) \tag{2.81}$$

with $E = \frac{\hbar^2 k^2}{2m}$

This is accomplished by the replacement of $P\Psi'$ by the following:

$$P\Psi' \longrightarrow \left[\frac{2k_o m}{\pi\hbar^2}\right]^{\frac{1}{2}} P\Psi' \tag{2.82}$$

so that

$$P\Psi'(\vec{r}_1,s_1;\ \vec{r}_2,s_2) \xrightarrow[r_1\to\infty]{} \left[\frac{2k_o m}{\pi\hbar^2}\right]^{\frac{1}{2}} \sum_{l_o}\sum_{m_o} \chi_{S_o}(s_1)\ \psi_{\gamma_o}(\vec{r}_2,\ s_2)$$

$$\times\ i^{l_o+1}\ Y^*_{l_o m_o}(\hat{k}_o)\ Y_{l_o m_o}(\hat{r}_1)\ e^{i\delta_{l_o}'(k_o)}$$

$$\times\ \frac{\sin\{k_o r_1 - l_o \frac{\pi}{2} + \delta_{l_o}'(k_o)\}}{k_o r_1} \tag{2.83}$$

and
$$\Gamma_R = 2\pi|\langle\Psi',\ H_{PQ}\ Y_S\rangle|^2 \tag{2.84}$$

which is Fermi's well known "Golden Rule" for unit density of states on the energy scale.

The above result cannot be applied directly in the present work because the trial function used to construct the autoionizing state is not constrained to lie in Q space, even though it vanishes asymptotically. An appropriately modified expression for the width can be obtained from time-dependent perturbation theory as follows. Let ψ_s be the variational approximation to the autoionizing state obtained previously and let χ_k be a solution to the background scattering problem in the absence of the resonance specified by

$$P'\ (H-E_k)\ P'\ \chi_k = 0 \qquad P'\chi_k = \chi_k \tag{2.85}$$

with
$$P' = 1 - |\psi_s\rangle\langle\psi_s| \tag{2.86}$$

An arbitrary solution to the complete time-dependent Schrödinger equation

$$i\hbar\,\frac{\partial\Psi}{\partial t} = H\Psi \tag{2.87}$$

can then be written in the form

$$\Psi = c_s(t)\psi_s\, e^{-iE_s t/\hbar} + \sum_{k'} c_{k'}(t)\, \chi_{k'} e^{-E_{k'} t/\hbar} \tag{2.88}$$

Substitution of (2.88) into (2.87) then leads to the set of equations for the expansion coefficients (after multiplying by $\langle\chi_k|\, e^{iE_k t/\hbar}$)

$$i\hbar \frac{dc_k}{dt} + i\hbar \langle\chi_k|\psi_s\rangle \frac{dc_s}{dt} e^{i\omega_{ks}t}$$

$$= \sum_{k'} \langle\chi_k|H - E_k|\chi_{k'}\rangle c_{k'}\, e^{i\omega_{kk'}t} + \langle\chi_k|H - E_s|\psi_s\rangle c_s e^{i\omega_{ks}t} \tag{2.89}$$

with $\omega_{kn} = \dfrac{E_k - E_n}{\hbar}$

where we have not assumed that $\langle\chi_k|\psi_s\rangle = 0$. The first-order perturbation result is obtained by setting $c_s = 1$, $c_k = 0$. Also $\frac{dc_s}{dt}$ is related to the width of the resonance by

$$-\hbar \frac{dc_s}{dt} = \frac{-\hbar}{2c_s} \frac{d}{dt} (c_s^{\,2}) \simeq \frac{\Gamma_R}{2} \tag{2.90}$$

With the above substitutions (2.89) becomes

$$i\hbar \frac{dc_k}{dt} = \langle\chi_k|H - E_s + \frac{i\Gamma_R}{2}|\,\psi_s\rangle\ e^{i\omega_{ks}t} \tag{2.91}$$

For narrow resonances $\frac{\Gamma_R}{2} << |E_S|$ and can be neglected. As shown by Merzbacher (1970) equation (2.91) can be integrated and the quantity $\frac{d}{dt} \sum_k |c_k(t)|^2$ approximated to obtain

$$\Gamma_R = 2\pi|\langle\chi_k|H-E_s|\psi_s\rangle|^2 \; \rho_f(E_s) \tag{2.92}$$

with $\quad k = \left[\frac{2mE}{h^2}\right]^{\frac{1}{2}}$

in agreement with (2.84), but with H_{PQ} replaced by $H-E_s$ and $\rho_f(E_s) = 1$. An advantage of (2.92) is that χ_k need not be orthogonalized to ψ_s since the replacement $\chi_k' = \chi_k + \alpha\psi_s$ does not change Γ_R.

χ_k is itself a difficult function to evaluate since it satisfies the scattering equation (2.85), but since $(H-E_s)\,\psi_s \simeq 0$ near the nucleus, χ_k need only be known in the asymptotic region in evaluating (2.92) (Miller, 1970). The solution for the Schroedinger equation in the asymptotic region closely resembles a product of screened hydrogenic functions since the $\frac{1}{r_{12}}$ term in H is closely approximated by $\frac{1}{r_1}$ as $r_1 \rightarrow \infty$.

Therefore

$$H\psi_T \simeq \{-\frac{\nabla_1^{\,2}}{2} - \frac{\nabla_2^{\,2}}{2} + \frac{1}{r_{12}} - \frac{(Z-1)}{r_1}\}\psi_T = E_s\,\psi_T \tag{2.93}$$

and

$$\chi_k = P\Psi_T = \Psi_T \simeq \frac{1}{\sqrt{2}}\,\{1s(Z)kd(Z-1) \pm kd(Z-1)1s(Z)\} \tag{2.94}$$

where 1s(Z), kd(Z-1) are the hydrogenic functions for the ground state and continuum state with nuclear charge Z and Z - 1 respectively. The continuum state kd(Z) is a hypergeometric function which when normalized to unit energy density has the asymptotic form (Bhatia and Temkin, 1969).

$$kd(Z) \underset{r_1\rightarrow\infty}{\sim} \left[\frac{2}{\pi k}\right]^{\frac{1}{2}} \frac{\sin\,(kr + \eta_1 - 1\pi/2)}{r_1}\, Y_{10}\,(\Omega) \tag{2.95}$$

where $\eta_1 = (1-\delta_{Z,0})\,\arg\,(1 + 1 - \frac{iZ}{k}) + \frac{Z}{k}\ln 2kr$, $\quad$ with 1=2

The necessary integrals involving Coulomb functions occurring in (2.92) can be calculated analytically in closed form with formulas summarized by Bransden and Dalgarno (1953).

CHAPTER III

In this chapter we first describe how the theory developed in Section 2.1 was applied to the $2p^{2\,1}D$ and $(2p\ 3p \pm 2S\ 3d)\ {}^3D$ resonances of two-electron ions. The results are then presented and compared with other theoretical and experimental data.

3.0 Description of the Calculations

The calculations performed in this work can be divided into the following steps.

3.0.1 Definition of the Basis Sets

The trial functions for the D states of even parity were constructed from linear combinations of functions of the form

$$\phi = (1+P_{12}) \sum_{i}\sum_{j}\sum_{k}^{N} a_{ijk}\, r_1^{\,i}\, r_2^{\,i}\, r_{12}^{\,k}\, e^{-\alpha r_1-\beta r_2}\; Y_{2_{02}}^{M}(\hat{r}_1, \hat{r}_2) \tag{3.1}$$

$$+ (1 \pm P_{12}) \sum_{i'}\sum_{j'}\sum_{k'}^{N'} a'_{i'j'k'}\, r_1^{\,i} r_2^{\,j} r_{12}^{\,k}\, e^{-\alpha r_1-\beta r_2}\, Y_{2_{11}}^{M}(\hat{r}_1,\hat{r}_2)$$

where $$Y_{L_{l_1 l_2}}(\hat{r}_1,\hat{r}_2) = \sum_{m_1 m_2} \langle l_1 m_1 l_2 m_2 | LM\rangle\, Y_{l_1 m_1}(\hat{r}_1)\, Y_{l_2 m_2}(\hat{r}_2) \tag{3.2}$$

and $\langle l_1 m_1 l_2 m_2 | LM\rangle$ is a vector coupling coefficient (Edmonds, 1957) and P_{12} in (3.1) denotes the interchange of the labels 1 and 2, with the (+) sign being used for singlet states and the (-) sign being used for triplet states. The first set of terms in (3.1) represents the vector coupling of an s and a d electron to form a D state, and the second set represents the vector coupling of two p electrons to form a D state. In the following, the former terms are called sd-type and the latter are called pp'-type. Both kinds of angular functions must be included in the expansion to obtain completeness, even if the basis set contains powers of r_{12}. The powers of r_1, r_2 and r_{12} were chosen to satisfy the relations

$$i \geq 0,\ j \geq 2,\ k \geq 0,\ i+j+k \leq N$$

$$i' \geq 1,\ j' \geq 1,\ k' \geq 0,\ i'+j'+k' \leq N'$$

All integral combinations of (i, j, k) and (i', j', k') were included for given values of N and N'.

The non-linear parameters α and β were set equal to their hydrogenic values so that the exact zero-order states would be included in the basis sets.

3.0.2 Diagonalization of the Zero-Order Hamiltonian

If the expansion (3.1) contains (N+N') linearly independent terms, then (N+N') linearly independent functions ϕ_n, n=1,..., N+N' can be constructed by imposing the requirements

$$\langle\phi_n|\phi_{n'}\rangle = \delta_{n,n'} \tag{3.2}$$

$$\langle\phi_n|H_o|\phi_{n'}\rangle = E_n\delta_{n,n'} \tag{3.3}$$

as demanded by equation (2.62). Our choice of basis set implies that one of the ϕ_n, say ϕ_s is the exact hydrogenic reference state Φ_s^o while the remaining ϕ_n, $n \neq s$ form a variational approximation to the orthogonal complement in Hilbert space (see eq. 2.63). The integrals required in the evaluation of the matrix elements (3.2) and (3.3) are calculated analytically as described in appendix I and the matrix diagonalizations performed by Jacobi's method.

3.0.3 Iterative Calculation of Autoionizing Resonances

After calculating the perturbation matrix elements $V_{ij} = \langle\phi_i|V|\phi_j\rangle$, the resonance positions are obtained from the iterative solution of equations (2.64). If a trial value of $\tilde{E}_s$ is substituted, then (2.64) becomes a set of $N+N'$ linear inhomogeneous equations in $N+N'$ unknowns which can be solved for the coefficients a_i in (2.63) and (2.64). A new value of $\tilde{E}_s$ is then calculated from (2.61) and the procedure is repeated until convergence is reached. Since the approximate resonance position is known in advance, only a few iterations are usually required. The coefficients a_i determine a variational approximation to the resonance wave function $\tilde{\psi}_s$ in the form

$$\tilde{\psi}_s = \Phi_s^{\,o} + \sum_{i \neq s} a_i \phi_i$$

As discussed following eq. (2.61), an additional condition must be imposed to avoid spurious results. The procedure followed is to calculate

$$\eta = \langle\tilde{\psi}_s|\tilde{\psi}_s\rangle = 1 + \sum_{i \neq s} a_i^{\,2}$$

and then minimize η with respect to changes in the screening parameter σ. The iterative calculation is therefore repeated for several values of σ and the optimum value found graphically.

3.0.4 Perturbation Calculation of Autoionizing Resonances

Alternatively, the iterative procedure can be expanded in a $1/Z$ expansion perturbation series as explained in Section 2.1.2. The equations for each order in $1/Z$ are then linear and can be solved directly, rather than iteratively. The coefficients in the perturbation expansions (2.67) and (2.68) for $\tilde{\psi}_s$ and $\tilde{E}_s$ are generated step by step from the recursion relations (2.69) and (2.70). Once the expansion coefficients are known, the perturbation series can be summed for any value of Z.

3.0.5 Calculation of the Resonance Width

After calculating the resonance wave function by the iterative or 1/Z expansion procedure, the width Γ_R is obtained from (2.92). However, since ψ_s is not normalized to unity, the equation should be corrected to read

$$\Gamma_R = 2\pi|W|^2/|\langle\psi_s|\psi_s\rangle|^2 \tag{3.5}$$

where $$W = \langle\tilde{\psi}_s|H - E_s|\chi_k\rangle \tag{3.6}$$

and χ_k is the symmetrized (or anti-symmetrized hydrogenic product).

$$\chi_k = \frac{1}{\sqrt{2}}\{\chi_k(\vec{r}_1, \vec{r}_2) \pm \chi_k(\vec{r}_2, \vec{r}_1)\} \tag{3.7}$$

$$\chi_k(\vec{r}_1,\vec{r}_2) = 1s(\vec{r}_1, Z)\, kd(\vec{r}_2, Z-1) \tag{3.8}$$

with $$1s(\vec{r},Z) = \frac{2}{\sqrt{4\pi}} Z^{3/2} e^{-Zr} \tag{3.9}$$

and $$kd(r,Z) \underset{r\to\infty}{\sim} \sqrt{\frac{2}{\pi k}} \sin\{kr + \frac{Z}{k}\ln 2kr - \pi + \eta_1\} \tag{3.10}$$

This continuum function corresponds physically to an inner hydrogenic 1s electron with eigenvalue $-Z^2/2$ moving in the field of the full nuclear charge Z and an outer hydrogenic continuum electron moving in the field of the screened nuclear charge Z-1. The momentum $\hbar k$ of the continuum electron is adjusted so that the total energy equals the resonance energy; i.e.

$$\frac{-Z^2}{2} + \frac{k^2}{2} = E_s \tag{3.11}$$

in atomic units. In this approximation the evaluation of W simplifies as follows. The total Hamiltonian H can be written

$$H = H_o(\vec{r}_1,\vec{r}_2) + V(\vec{r}_1,\vec{r}_2) = H_o(\vec{r}_2,\vec{r}_1) + V(\vec{r}_2,\vec{r}_1) \tag{3.12}$$

where $$H_o(\vec{r}_1,\vec{r}_2) = \frac{-1}{2}\nabla_1^2 \frac{-1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z-1}{r_2} \tag{3.13}$$

and $$V(\vec{r}_1,\vec{r}_2) = \frac{1}{r_{12}} - \frac{1}{r_2}$$

Then since $H_o(\vec{r}_1,\vec{r}_2)\ \chi_k(\vec{r}_1,\vec{r}_2) = E_s\ \chi_k(\vec{r}_1,\vec{r}_2)$ and $H_o(\vec{r}_2,\vec{r}_1)\ \chi_k(\vec{r}_2,\vec{r}_1)$ $= E_s\ \chi_k(\vec{r}_2,\vec{r}_1)$, the matrix element W becomes

$$W = \frac{1}{\sqrt{2}} \langle\tilde{\psi}_s| V(r_1,r_2)\ \chi_k(r_1,r_2) \pm V(r_2r_1)\ \chi_k(r_2,r_1)\rangle \tag{3.15}$$

The necessary integrals can be calculated analytically in closed form with formulas summarized by Bransden and Dalgarno (1953).

3.1 Results

Energy eigenvalues and widths were calculated for the three D autoionizing resonances: $2p^{2\,1}D$, $(2p\ 3p \pm 2s\ 3d)\ ^3D$. The results for $2p^{2\,1}D$ resonance are discussed first.

A considerable amount of theoretical and experimental data on the $2p^{2\,1}D$ resonance is available for comparison with our work. Results from our largest basis sets (10sd, 33pp) and (43pp) are given in tables 1, 2, 3. The optimum value for the screening parameter $\sigma = .430$ for the iteration method was found by plotting the normalization versus σ for several values of the screening parameter (see table 5). However this value could not be used in the 1/Z expansion approach because the perturbation series was poorly convergent. Much better results were obtained with the smaller values of $\sigma = 0.0$ and 0.1 used to obtain the resonance positions given in Table 2. The expansion coefficients are given in Table 3.

Table 5 shows that the energy is relatively insensitive to the screening parameter over the range of values tabulated. In contrast the width Γ_R depends much more sensitively on the value of the screening parameter as shown by the H^- results in Table 5. Fortunately as shown in Table 6 this sensitivity decreases very rapidly with increasing Z. For Z = 2 the width of the He resonance more than doubles as σ ranges between 0.0 and 0.1. However for Z=3 the change in the width is less than 6%. For larger values of Z, the 1/Z expansion for the resonance energies are estimated to be accurate to better than ± .05 eV and the widths to ±6%.

Examination of Table 4 reveals that the proportions of the sd and pp'-type angular momentum eigenfunctions within the basis sets, have a significant effect on the resonance positions. For example

TABLE 1

$2p^2\ {}^1D$ RESONANCE

ITERATION RESULTS FOR H- AND He

Parent Ion	Basis Used	Screening Parameter Used	Norm of Wave Function	Resonance Energy (In eV) Above Ground State	Width (In eV)
H-	(10sd,33pp)	.4275	1.4625	10.147	1.05×10^{-2}
	(43pp)	.4175	1.3548	10.130	1.34×10^{-2}
He	(10sd,33pp)	.4300	1.0998	59.946	7.37×10^{-2}
	(43pp)	.4300	1.0774	59.817	7.12×10^{-2}

TABLE 2

$2p^2\ {}^1D$ RESONANCE

1/Z EXPANSION RESULTS FOR THE HELIUM ISOELECTRONIC SEQUENCE

(10sd,33pp) Basis

Parent Ion	Resonance Energy (In eV) Above Ground State	Width (In eV)
He I	59.883	5.21×10^{-2}
Li II	150.0550	9.72×10^{-2}
Be III	280.934	1.27×10^{-1}
B IV	452.635	1.47×10^{-1}
C V	665.152	1.61×10^{-1}
N VI	918.485	1.72×10^{-1}
O VII	1212.633	1.81×10^{-1}
F VIII	1547.597	1.87×10^{-1}
Ne IX	1923.374	1.93×10^{-1}

Screening Parameter used was $\sigma = .100$

(43pp) Basis

Parent Ion	Resonance Energy (In eV) Above Ground State	Width (In eV)
He I	59.822	7.13×10^{-2}
Li II	149.746	1.09×10^{-1}
Be III	280.545	1.34×10^{-1}
B IV	452.190	1.52×10^{-1}
C V	664.669	1.65×10^{-1}
N VI	917.967	1.75×10^{-1}
O VII	1212.090	1.82×10^{-1}
F VIII	1547.034	1.89×10^{-1}
Ne IX	1922.794	1.94×10^{-1}

Screening Parameter used was $\sigma = 0.0$

TABLE 3

$2p^2\ {}^1D$ RESONANCE

1/Z EXPANSION ENERGY COEFFICIENTS

(10sd,33pp) Basis		(43pp) Basis	
Order	Energy Coefficient (In Z_σ^2 A.U.)	Order	Energy Coefficient (In Z_σ^2 A.U.)
0	-2.500000×10^{-1}	0	-2.500000×10^{-1}
1	1.351562×10^{-1}	1	1.851563×10^{-1}
2	-5.547969×10^{-2}	2	-9.910277×10^{-2}
3	-1.166245×10^{-2}	3	5.930965×10^{-2}
4	6.374751×10^{-2}	4	-2.316759×10^{-2}
5	9.397231×10^{-2}	5	-9.853327×10^{-3}
6	9.796411×10^{-2}	6	2.043806×10^{-2}
7	-4.480858×10^{-2}	7	-7.743570×10^{-3}
8	-1.410917×10^{-1}	8	-1.204465×10^{-2}
9	5.672820×10^{-1}	9	1.674555×10^{-2}
10	-1.290572	10	-1.390922×10^{-3}
11	2.107047	11	-1.732526×10^{-2}
12	-2.151426	12	1.679837×10^{-2}
13	-6.769245×10^{-1}	13	5.143362×10^{-3}
14	1.007573×10^{-1}	14	-2.485771×10^{-2}
15	-3.025612×10^{1}	15	1.668032×10^{-2}
16	6.082279×10^{1}	16	1.527151×10^{-2}
17	-8.375565×10^{1}	17	-3.527463×10^{-2}
18	3.981212×10^{1}	18	1.388390×10^{-2}
19	1.989354×10^{2}	19	3.216994×10^{-2}
20	-8.261710×10^{2}	20	-4.86772×10^{-2}
Screening Parameter used was $\sigma = 1.00$		Screening Parameter used was $\sigma = 0.0$	

$$E = Z_\sigma^2 E_0 + Z_\sigma E_1 + E_2 + E_3 Z_\sigma^{-1} + \ldots$$

TABLE 4

$2p^2\ {}^1D$ RESONANCE

COMPARISON OF ITERATION RESULTS FOR VARIOUS BASIS SETS USED FOR A GIVEN VALUE OF THE SCREENING PARAMETER

Parent Ion + Screening Parameter Used	Basis Set Used	Norm of Wave Function	Resonance Energy (In eV) Above Ground State	Width (In eV)
H^- Screening Parameter used was σ = .42750	(10sd,10pp)	1.39471	10.165	
	(20pp)	1.33518	10.133	1.31×10^{-2}
	(10sd,20pp)	1.45930	10.149	9.92×10^{-3}
	(30pp)	1.34231	10.131	1.34×10^{-2}
	(10sd,22pp)	1.49736	10.148	1.01×10^{-2}
	(32pp)	1.34267	10.131	1.34×10^{-2}
	(10sd,33pp)	1.46247	10.147	1.05×10^{-2}
	(43pp)	1.35890	10.130	1.33×10^{-2}
He Screening Parameter used was σ = .4300	(10sd,10pp)	1.10905	59.975	7.12×10^{-2}
	(20pp)	1.07712	59.819	7.07×10^{-2}
	(10sd,20pp)	1.10045	59.950	7.21×10^{-2}
	(30pp)	1.07736	59.817	7.11×10^{-2}
	(10sd,22pp)	1.10047	59.950	7.25×10^{-2}
	(32pp)	1.07737	59.817	7.11×10^{-2}
	(10sd,33pp)	1.09975	59.946	7.37×10^{-2}
	(43pp)	1.07740	59.817	7.12×10^{-2}

TABLE 5

$2p^2\ {}^1D$ RESONANCE

COMPARISON OF ITERATION RESULTS FOR VARIOUS VALUES OF THE SCREENING PARAMETER FOR A GIVEN BASIS SET

Parent Ion + Basis Set Used	Screening Parameter Used	Norm of Wave Function	Resonance Energy (In eV) Above Ground State	Width (In eV)
H^- (10sd,33pp) Basis used	.20000	1.83954	10.139	8.38×10^{-3}
	.30000	1.57673	10.132	1.16×10^{-2}
	.35000	1.50443	10.135	1.16×10^{-2}
	.40000	1.46684	10.141	1.10×10^{-2}
	.41750	1.46260	10.145	1.05×10^{-2}
	.42750	1.46247	10.147	1.05×10^{-2}
	.43750	1.46412	10.149	1.05×10^{-2}
	.44200	1.46547	10.150	1.01×10^{-2}
	.50000	1.52244	10.166	8.58×10^{-3}
He (10sd,10pp) Basis used	.35000	1.12000	59.977	6.96×10^{-2}
	.40000	1.11129	59.975	7.08×10^{-2}
	.42750	1.10915	59.975	7.13×10^{-2}
	.43000	1.10905	59.975	7.12×10^{-2}
	.43750	1.10883	59.975	7.14×10^{-2}
	.44000	1.10878	59.975	7.13×10^{-2}
	.45000	1.10876	59.976	7.14×10^{-2}
	.50000	1.11227	59.981	7.14×10^{-2}

TABLE 6

$2p^{2}\ {}^{1}D$ RESONANCE

COMPARISON OF THE 1/Z EXPANSION WIDTHS FOR VARIOUS VALUES OF THE SCREENING PARAMETER FOR A GIVEN BASIS SET (10sd,33pp)

Parent Ion		Width (In eV) For σ = 0.0	Width (In eV) For σ = .05	Width (In eV) For σ = .1
He	I	2.336×10^{-2}	4.068×10^{-2}	5.206×10^{-2}
Li	II	8.244×10^{-2}	9.097×10^{-2}	9.714×10^{-2}
Be	III	11.803×10^{-2}	12.288×10^{-2}	12.669×10^{-2}
B	IV	14.121×10^{-2}	14.432×10^{-2}	14.689×10^{-2}
C	V	15.739×10^{-2}	15.955×10^{-2}	16.138×10^{-2}
N	VI	16.930×10^{-2}	17.088×10^{-2}	17.226×10^{-2}
O	VII	17.842×10^{-2}	17.962×10^{-2}	18.070×10^{-2}
K	VIII	18.562×10^{-2}	18.656×10^{-2}	18.742×10^{-2}
Ne	IX	19.144×10^{-2}	19.220×10^{-2}	19.290×10^{-2}

basis sets containing only pp'-type angular functions yield resonance positions near 10.13 eV and 59.82 eV for H^- and He respectively, while basis sets containing both pp' and sd type angular functions yield resonance positions near 10.15 eV and 59.95 eV respectively. The above results illustrate the necessity of including both kinds of angular function, even for a state which is described in zero-order as a $2p^{2\cdot 1}D$ configuration. The latter results are to be taken as more accurate. Similar effects appear also in the resonance widths.

Our results are compared with other experimental and theoretical data in Tables 7 and 8. The overall agreement is very good for all the members of the helium sequence. For H^-, McGowan (1969) has measured the resonance position to be at 10.13 eV ± .015 eV. Close coupling calculations by McGowan showed a ^1D resonance at 10.149 eV which agrees well with our result of 10.147 eV, however, Burke's (1968) result is 10.125 eV. For He, Berry et al (1972) have tentatively identified transitions to the $2p^{2\,1}D$ state from $2p3d\,^1D$ and $2p3d\,^1P$ states. Although our predicted wavelengths 3334.5 Å and 2934 Å are closer to the experimental wavelengths 3372±2 Å, 2285±1 Å for the $2p^2\ ^1D$-$2p3d\,^1D$, $2p^{2\,1}D$- $2p3d\,^1P$ transitions respectively than the theoretical results given by Berry et al (1972a) they appear still too far from the experimental results. Also the 0.07 eV width of the $2p^{2\,1}D$ should give rise to a spectral line about 70 Å wide, while Berry et al quote their results to within a few Å. Such discrepancies would indicate that the transition assignments of $2p^{2\,1}D$ - $2p3d\,^1D$, $2p^{2\,1}D$ - $2p3d\,^1P$ for the respective lines at 3372 ± 2 Å, 2885 ± 1 Å are questionable.

We now present the results for the pair of states $(2p3p \pm 2s3d)\,^3D$. Although these are the lowest-lying ^3D resonances of even parity, relatively little data are available for comparison. Results for the

TABLE 7

He I ISOELECTRONIC SEQUENCE

COMPARISON OF MEASURED AND THEORETICAL WAVE LENGTHS (IN Å)

$1s2p\ ^1P - 2p^2\ ^1D$

Atom or Ion	Experiment	Our Result	Other Theoretical Results
He I		320.63	319.8[b]
Li II		141.14	141.2[b]
Be III	78.92[e]	78.83	78.87[b]
B IV	50.22[f]	50.177	50.17[b]
C V	34.70[f,h]	34.694	34.77[g]
N VI		25.406	25.46[g]
O VII	19.421[f,i]	19.401	19.43[g]
Ne IX	12.355[j]	12.369	12.345[j]
Mg XI	8.550[k]	8.522	8.548[k]
Si XIII	6.265[l]	6.281	6.263[k]

b Perrot and Stewart (1968)

g Goldberg and Clogston (1939)

j Peacock et al (1969)

k Walker and Rugge (1971)

e Goldsmith (1969)

f Edlen and Tyren (1939)

h Feldman and Cohen (1969)

i Roth and Elton (1968)

l Meekins et al (1970)

TABLE 8

COMPARISON OF THEORETICAL RESULTS FOR THE $2p^2\ ^1D$ RESONANCE OF He

Resonance Parameters	Our Result	Bhatia (1972)	Cooper et al (1967)	Altick and Moore (1967)	Burke and Taylor (1967)
Resonance Energy (In eV) Above Ground State	59.946	59.902	60.025	60.115	59.911
Width (In eV)	7.374×10^{-2}	7.29×10^{-2}	7.32×10^{-2}	7.48×10^{-2}	6.62×10^{-2}

lower state are presented in Tables 9, 10. In this case the optimum value for the screening parameter σ = .4000 found by the iteration method also produced a 1/Z expansion series with good convergence (see Table 10).

The width for the lower lying state of He was calculated to be 1.58 X 10^{-6} eV. Thus the autoionization probability is so small that radiative transitions to lower states should be observable.

Our results for He are in good agreement with other theoretical results as shown in Table 11. Berry (1972b) has observed lines at 125.8 Å and 955 Å in Li II identified as transitions from the lower ^{3}D resonance to the 1s2p^{3}P and 2s2p^{3}P states respectively. The wavelengths agree with our predicted values of 125.8 Å and 959.9 Å.

These identifications appear reasonable since the width of the resonance is so small. That is, the resonance is almost completely decoupled from the continuum and is thus more likely to undergo a radiative transition than an autoionizing one. However the 0.01 eV width of the 2s2p^{3}P state raises some doubt to the correctness of the second transition assignment (Drake, 1972). In the case of helium Berry et al (1972a) have assigned to the lines 293.8 Å and 2577 Å the transitions 1s2p^{3}P - pp 23-^{3}D, 2s2p^{3}P - pp23-^{3}D respectively. Our theoretical results of 294.1 Å and 2580 Å agree quite well.

The higher (2p3p ± 2s3d) D state has not yet been observed. Results for the higher state are presented in Tables 12, 13. Again the optimum σ found from the iteration procedure produced a convergent 1/Z expansion. The width for the He resonance was calculated to be 2.23 X 10^{-4} eV. Our results for He are in close agreement with other theoretical calculations as shown in Table 14.

The 1/Z expansion method is computationally simpler than that

TABLE 9

THE LOWER (2p3p ± 2s3d) ^3D RESONANCE

ITERATION AND 1/Z EXPANSION RESULTS FOR THE HELIUM ISOELECTRONIC SEQUENCE USING A (25sd, 25pp) BASIS WITH $\sigma = .4000$

Parent Ion	Resonance Energy (In eV) Above Ground State
*He I	63.119
He I	63.126
Li II	159.841
Be III	301.139
B IV	487.027
C V	717.507
N VI	992.580
O VII	1312.246
F VIII	1676.506
Ne IX	2085.362
**H	10.32

* Iteration Result

** Screening Parameter $\sigma = 0.0$

TABLE 10

THE LOWER (2p3p ± 2s3d) ^3D RESONANCE

1/Z EXPANSION ENERGY COEFFICIENTS FOR THE (25sd, 25pp) BASIS WITH $\sigma = .4000$

Order	Energy Coefficient (In Z_σ^2 A.U.)
0	-1.805556×10^{-1}
1	-6.307417×10^{-2}
2	-2.219984×10^{-2}
3	4.219645×10^{-3}
4	-3.364130×10^{-3}
5	1.160912×10^{-3}
6	-2.402681×10^{-4}
7	-9.861181×10^{-5}
8	2.001833×10^{-4}
9	-9.468510×10^{-5}
10	6.958154×10^{-5}
11	-6.496531×10^{-5}
12	6.050782×10^{-5}
13	-4.198586×10^{-5}
14	-7.570341×10^{-6}
15	4.762316×10^{-5}
16	-5.743411×10^{-5}
17	3.465624×10^{-5}
18	5.881102×10^{-6}
19	3.673783×10^{-5}
20	4.302018×10^{-5}

TABLE 11

COMPARISON OF THEORETICAL RESULTS FOR THE LOWER (2p3p ± 2s3d) ^3D RESONANCE OF He

Resonance Parameters	Our Result	Bhatia (1972)	Cooper et al (1967)	Altick and Moore (1967)
Resonance Energy (In eV) Above Ground State	63,119	63,118	63,141	63.157
Width (In eV)	1.584×10^{-6}	2.715×10^{-6}	1.44×10^{-6}	1.2×10^{-6}

TABLE 12

THE HIGHER (2p3p ± 2s3d) ^{3}D RESONANCE

ITERATION AND 1/Z EXPANSION RESULTS FOR THE HELIUM ISOELECTRONIC SEQUENCE USING A (25sd, 25pp) BASIS WITH $\sigma = .4300$

Parent Ion	Resonance Energy (In eV) Above Ground State
*He I	63.750
He I	63.757
Li II	161.001
Be III	302.807
B IV	489.196
C V	720.175
N VI	995.744
O VII	1315.907
F VIII	1680.662
Ne IX	2090.012

*Iteration Result

TABLE 13

THE HIGHER (2p3p ± 2s3d) ^{3}D RESONANCE

1/Z EXPANSION ENERGY COEFFICIENTS FOR THE (25sd, 25pp) BASIS WITH $\sigma = .4300$

Order	Energy Coefficient (In Z_σ^2 A.U.)
0	-1.805556×10^{-1}
1	-5.575676×10^{-2}
2	-2.663710×10^{-2}
3	6.658920×10^{-4}
4	-4.630566×10^{-3}
5	-3.976807×10^{-4}
6	1.007597×10^{-3}
7	-8.339323×10^{-4}
8	1.648211×10^{-3}
9	3.402156×10^{-4}
10	6.147293×10^{-4}
11	1.339402×10^{-4}
12	4.597267×10^{-5}
13	-1.480566×10^{-3}
14	2.872248×10^{-4}
15	-1.567826×10^{-3}
16	1.210010×10^{-3}
17	-9.029224×10^{-4}
18	2.370231×10^{-3}
19	-1.253187×10^{-3}
20	2.909570×10^{-3}

TABLE 14

COMPARISON OF THEORETICAL RESULTS FOR THE UPPER (2p3p ± 2s3d) ^3D RESONANCE OF He

Resonance Parameters	Our Results	Bhatia (1972)	Cooper et al (1967)	Altick and Moore (1967)
Resonance Energy (In eV) Above Ground State	63.750	63.747	63.796	63.797
Width (In eV)	2.23×10^{-4}	1.91×10^{-4}	2.48×10^{-4}	2.53×10^{-4}

of Bhatia and Temkin (1969) and is capable of producing very accurate results. For example, the lower (2p3p ± 2s3d)^{3}D resonance of He was calculated in this work to lie 63.119 eV above the ground state, using a 50 term basis set. The experimental value is 63.116 ±.001 eV above the ground state (Berry et al, 1972). Bhatia's (1972) Q-projection operator calculation yielded 63.118 eV for the resonance position, but his calculation required a 112- term Hyleraas basis set and a separate evaluation of the energy shift.

3.2 Suggestions for Future Work

The experimental results of Berry et al should be re-examined in the light of our calculations and those of Bhatia (1972) especially those transitions involving the 2p$^{2\,1}$D state. Calculations of the oscillator strengths for transitions from the D states would be helpful in making identifications. Also the properties of the higher lying D states should be calculated.

The 1/Z expansion method can be extended to the Li isoelectronic sequences. In the case of Li, both doubly and triply excited resonances occur.

It has been shown that the proportion of sd and pp'-type angular functions in the basis set significantly affects the resonance position. Therefore some criterion is needed for optimizing the angular momentum composition of the basis set.

APPENDIX I

Calculation of Matrix Elements

All necessary matrix elements M, except those involving Coulomb functions, can be expressed as a sum of terms M_i

$$M = \sum_i M_i \tag{A.1}$$

with each term having the general form

$$M_i = \left< F(a,b,c,\alpha,\beta) \begin{vmatrix} m_1' & m_2' \\ l_1' & l_2' \end{vmatrix}^* \begin{vmatrix} m_1 & m_2 \\ l_1 & l_2 \end{vmatrix} \right> \tag{A.2}$$

where
$$F(a,b,c,\alpha,\beta) = r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} \tag{A.3}$$

$$\begin{vmatrix} m_1 & m_2 \\ l_1 & l_2 \end{vmatrix} = Y_{l_1 m_1}(\hat{r}_1)\, Y_{l_2 m_2}(\hat{r}_2) \tag{A.4}$$

and the angle brackets denote the complete six-dimensional integration

$$< \quad > = \int r_1^2 \sin\theta_1 dr_1 d\theta_1 d\phi_1 r_2^2 \sin\theta_2 dr_2 d\theta_2 d\phi_2 \tag{A.5}$$

Since the integrand contains powers of $r_{12} = |\vec{r}_1 - \vec{r}_2|$, the integration is most easily performed by changing the variables of integration so that (Margenau and Murphy, 1956)

$$< \quad > = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12} dr_{12} \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\chi \tag{A.6}$$

where χ is the angle of rotation about the direction of $\vec{r}_1$ as shown in Fig.3.

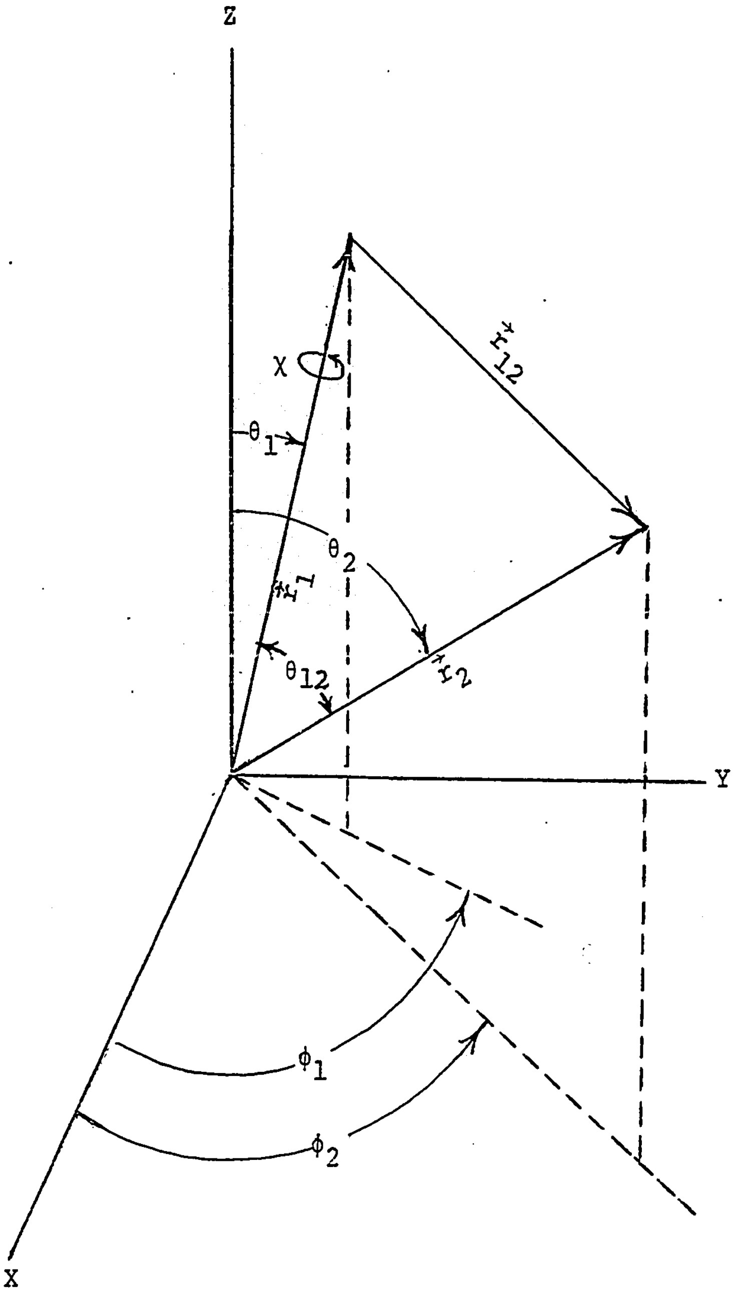

Fig. 3: 2 Electron Coordinate System

(A.6) now contains an explicit integration over r_{12} but the polar angles θ_2, ϕ_2 for electron 2 are no longer independent variables and must be re-expressed in terms of the independent variables $r_1, r_2, r_{12}, \theta_1, \phi_1, \chi$ as described below.

However, it is first necessary to re-express the products of four spherical harmonics in (A.2) as a sum of products of two spherical harmonics by use of the relation (Edmonds, 1957, eq. 4.6.5.)

$$Y_{l_1'm_1'}(1)^* \, Y_{l_1m_1}(1) = \sum_{L_1=|l_1'-l_1|}^{l_1'+l_1} (-1)^{M_1+m_1'} \frac{[(2l_1'+1)(2l_1+1)(2L+1)]^{\frac{1}{2}}}{\sqrt{4\pi}}$$

$$\times \begin{pmatrix} l_1' & l_1 & L_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & l_1 & L_1 \\ -m_1' & m_1 & M \end{pmatrix} Y_{L_1-M_1}(1) \qquad \text{(A.7)}$$

where $M_1 = m_1 - m_1'$ and $\begin{pmatrix} l' & l & L \\ -m' & m & M \end{pmatrix}$ is a 3-j symbol. Using the analogous expression for $Y_{l_2'm_2'}(2)^* \, Y_{l_2m_2}(2)$, the angular functions can be written

$$\begin{vmatrix} m_1' & m_2' \\ l_1' & l_2' \end{vmatrix}^* \begin{vmatrix} m_1 & m_2 \\ l_1 & l_2 \end{vmatrix}$$

$$= \sum_{L_1=|l_1'-l_1|}^{l_1'+l_1} \; \sum_{L_2=|l_2'-l_2|}^{l_2'+l_2} (-1)^{m_1'+M_2+m_2'} \frac{c(l_1',l_2,L_1)\, c(l_2',l_2,L_2)}{4\pi}$$

$$\times \begin{pmatrix} l_1' & l_1 & L_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & l_1 & L_1 \\ -m_1' & m_1 & M_1 \end{pmatrix} \begin{pmatrix} l_2' & l_2 & L_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2' & l_2 & L_2 \\ -m_2' & m_2 & M_2 \end{pmatrix} Y_{L_1M_1}(1)^* \, Y_{L_2-M_2}(2)$$

(A.8)

with $c(l',l,L) = \{(2l'+1)(2l+1)(2L+1)\}^{\frac{1}{2}}$

As mentioned above the angles θ_2, ϕ_2 are not independent variables, but the spherical harmonic $Y_{L_2-M_2}(\theta_2, \phi_2)$ can be written in terms of the independent variables by means of

$$Y_{L_2-M_2}(\theta_2,\phi_2) = \sum_n D^{L_2}_{-M_2,n}(\phi_1,\theta_1,\chi)^* \, Y_{L_2n}(\theta_{12},\phi_{12}) \qquad \text{(A.9)}$$

where $D^{L_2}_{-M_2,n}{}^*$ is a rotation matrix for a co-ordinate transformation in which the Z-axis is rotated into the $\hat{r}_1$ direction, and θ_{12},ϕ_{12} are the polar angles of $\hat{r}_2$ relative to $\hat{r}_1$ (see Fig. 3). Using also the relation

$$Y_{L_1M_1}(\theta_1,\phi_1)^* = \sqrt{\frac{2L_1+1}{4\pi}} \, D^{L_1}_{M_1,0}(\phi_1,\theta_1,\chi) \qquad \text{(A.10)}$$

and the orthogonality of the rotation matrices

$$\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} D^{L_1}_{M_1,M_1'}(\phi_1,\theta_1,\chi) \, D^{L_2}_{-M_2,n}(\phi_1,\theta_1,\chi)^* \sin\theta_1 \, d\theta_1 d\phi_1 d\chi$$

$$= \frac{8\pi^2}{2L_1+1} \, \delta_{M_1,-M_2} \, \delta_{M_1',n} \, \delta_{L_1,L_2} \qquad \text{(A.11)}$$

together with (A.9), we obtain the basic angular integral

$$\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} Y_{L_1M_1}(\theta_1,\phi_1)^* \, Y_{L_2-M_2}(\theta_2,\phi_2) \sin\theta_1 d\theta_1 d\phi_1 d\chi$$

$$= \frac{8\pi^2}{2L_1+1}\sqrt{\frac{2L_1+1}{4\pi}} \, \delta_{M_1,-M_2} \, \delta_{L_1,L_2} \, Y_{L_10}(\theta_{12},\theta_{12})$$

$$= 2\pi \, \delta_{M_1,-M_2} \, \delta_{L_1,L_1} \, P_{L_1}(\cos\theta_{12}) \qquad \text{(A.12)}$$

Thus the angular function (A.8) becomes, on integrating over θ_1,ϕ_1,χ

$$\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \begin{vmatrix} m_1' & m_2' \\ l_1' & l_1' \end{vmatrix} * \begin{vmatrix} m_1 & m_2 \\ l_1 & l_2 \end{vmatrix} \sin\theta_1 \, d\theta_1 \, d\phi_1 \, d\chi$$

$$= \frac{(-1)^{M+m_1'+m_2'}}{2} \sum_{L=L_{MIN}}^{L_{MAX}} c(l_1',l_1,L)\, c(l_2',l_2,L) \begin{pmatrix} l_1' & l_1 & L \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} l_1' & l_1 & L \\ -m_1' & m_1 & M \end{pmatrix} \begin{pmatrix} l_2' & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2' & l_2 & L \\ -m_2' & m_2 & -M \end{pmatrix} P_L(\cos\theta_{12}) \qquad \text{(A.13)}$$

with $L_{MIN} = \mathrm{Max}\ (|l_1'-l_1|, |l_2'-l_2|, |M|)$

$L_{MAX} = \mathrm{Min}\ (l_1'+l_1,\ l_2'+l_2)$

and $M = m_1' - m_1 = -m_2' + m_2$

Since $\cos\theta_{12} = \dfrac{r_1^2 + r_2^2 - r_{12}^2}{2r_1r_2}$, $P_L(\cos\theta_{12})$ is a function of r_1, r_2, and r_{12}, and is to be included in the integrand for the three remaining radial integrals in (A.6).

The radial integrals to be calculated are then of the form

$$I_L\ (a,b,c,\alpha,\beta) = \int_0^{\infty} r_1 dr_1 \int_0^{\infty} r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12}\, dr_{12}$$

$$\times\ r_1^a r_2^b r_{12}^c\, e^{-\alpha r_1 - \beta r_2}\, P_L(\cos\theta_{12}) \qquad \text{(A.14)}$$

A useful recursion relation exists which allows the calculation of $I_L\ (a,b,c,\alpha,\beta)$ for all L once I_0 and I_1 are known for a range of powers a,b and c. The recursion relation can be derived by considering matrix elements of the angular momentum operator $l_{2,z} = \frac{1}{i}\frac{\partial}{\partial\phi_2}$ of the form

$$L = \left\langle \begin{vmatrix} 1 & 0 \\ L & 0 \end{vmatrix},\ l_{2,z}\ F(a,b,c,\alpha,\beta) \begin{vmatrix} 0 & 1 \\ 0 & L \end{vmatrix} \right\rangle \qquad \text{(A.15)}$$

If $l_{2,z}$ operates to the left, then L=0. If $l_{2,z}$ operates to the right, then using (A.12)

$$L = \tfrac{1}{2}\left(F(a,b,c,\alpha,\beta)\ P_L(\cos\theta_{12})\right) + \left< \begin{vmatrix} 1 & 0 \\ L & 0 \end{vmatrix} , \begin{vmatrix} 0 & 1 \\ 0 & L \end{vmatrix} l_{2,z}\ F(a,b,c,\alpha,\beta) \right> = 0 \tag{A.16}$$

where the outer round brackets denote the triple radial integral (A.14) and the angle brackets denote the complete six-dimensional integral as before. Since

$$l_2\ F(a,b,c,\alpha,\beta) = c\ F(a+1,b+1,c-2)\ \frac{\hat{r}_1 \times \hat{r}_2}{i} \tag{A.17}$$

and

$$\frac{(\hat{r}_1 \times \hat{r}_2)}{i}_z = \frac{\sin\theta_1\ \sin\theta_2}{2}\ \{e^{i(\phi_2-\phi_1)} - e^{-i(\phi_2-\phi_1)}\} \tag{A.18}$$

equation (A.16) becomes

$$I_L(a,b,c,\alpha,\beta) = c\left< \begin{vmatrix} 1 & 0 \\ L & 0 \end{vmatrix}^* \sin\theta_1\ \sin\theta_2\ \{e^{i(\phi_2-\phi_1)} - e^{-i(\phi_2-\phi_1)}\} \begin{vmatrix} 0 & 1 \\ 0 & L \end{vmatrix} F(a+1,b+1,c-2) \right> \tag{A.19}$$

After re-expressing the above as a sum of products of two spherical harmonics and using (A.12) to perform the angular integrations, the recursion relation reduces to

$$I_L\ (a,b,c,\alpha,\beta) = \frac{c}{2L+1}\ \{I_{L+1}\ (a+1,b+1,c-2,\alpha,\beta) - I_{L-1}(a+1,b+1,c-2,\alpha,\beta)\} \tag{A.20}$$

or

$$I_{L+1}(a,b,c,\alpha,\beta) = \frac{(2L+1)}{c+2}\, I_L(a-1,b-1,c+2,\alpha,\beta) + I_{L-1}(a,b,c,\alpha,\beta) \qquad \text{(A.21)}$$

This is a recursion relation for integrals containing the Legendre polynomial $P_L(\cos\theta_{12})$ and is <u>not</u> equivalent to the well known recursion relation for the Legendre polynomials themselves. The plan of the calculation is to compute $I_0(a,b,c,\alpha,\beta)$ for sufficiently many values of a, b and c, and store the results in a table. Then, using

$\cos\theta_{12} = \dfrac{r_1^2 + r_2^2 - r_{12}^2}{2r_1r_2}$, I_1 is

$$I_1 = \tfrac{1}{2}\{I_0(a-1,b+1,c,\alpha,\beta) + I_0(a+1,b-1,c,\alpha,\beta) - I_0(a-1,b-1,c+2,\alpha,\beta)\} \qquad \text{(A.22)}$$

All other I_L can then be obtained from the recursion relation (A.21). The integral

$$I_0(a-1,b-1,c-1,\alpha\ \beta) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12}\, r_1^a r_2^b r_{12}^c\, e^{-\alpha r_1-\beta r_2}$$

is evaluated as follows. First, the range of integration over r_1 and r_2 is split into two parts depending on whether or not $r_1>r_2$ so that

$$\begin{aligned} I_0(a-1,b-1,c-1,\alpha,\beta) &= \int_0^\infty r_1^a\, e^{-\alpha r_1}\, dr_1 \int_{r_2}^\infty r_2^b\, e^{-\beta r_2}\, dr_2 \int_{r_2-r_1}^{r_1+r_2} r_{12}^c\, dr_{12} \\ &+ \int_0^\infty r_2^b\, e^{-\beta r_2}\, dr_2 \int_{r_1}^\infty r_1^a\, e^{-\alpha r_1}\, dr_1 \int_{r_2-r_1}^{r_1+r_2} r_{12}^c\, dr_{12} \end{aligned} \qquad \text{(A.23)}$$

The integrations over r_{12} yield

$$\int_{r_1-r_2}^{r_1+r_2} r_{12}^{\,c}\, dr_{12} = \frac{2}{c+1} \sum_{i=0}^{(c/2)} \binom{c+1}{2i+1} r_2^{\,c-2i}\, r_1^{\,2i+1} \tag{A.24}$$

and

$$\int_{r_2-r_1}^{r_1+r_2} r_{12}^{\,c}\, dr_{12} = \frac{2}{c+1} \sum_{i=0}^{(c/2)} \binom{c+1}{2i+1} r_1^{\,c-2i}\, r_2^{\,2i+1} \tag{A.25}$$

where $\binom{c+1}{2i+1}$ is a binomial coefficient and (c/2) denotes the greatest integer in c/2. The integration over r_1 and r_2 can then be performed with the help of the formula

$$\int r^n e^{-\alpha r}\, dr = - \sum_{j=0}^{n} \frac{r^j n!\, e^{-\alpha r}}{\alpha^{n-j+1} j!} \tag{A.26}$$

to obtain the final result

$I_0(a-1,b-1,c-1,\alpha,\beta)$

$$= \frac{2}{c+1} \sum_{i=0}^{(c/2)} \binom{c+1}{2i+1} \sum_{j=0}^{q} \frac{q!\,(p+j)!}{\beta^{q-j+1}\,(\alpha+\beta)^{p+j+1} j!} + \sum_{j=0}^{q'} \frac{q'!\,(p'+j)!}{\alpha^{q'-j+1}\,(\alpha+\beta)^{p'+j+1} j!} \tag{A.27}$$

with $p = a+2i+1$

$q = b+c-2i$

$p' = b+2i+1$

$q' = a+c-2i$

Notice that all contributions to (A.27) are of the same sign so that there is no possibility of numerical cancellation.

Collecting results and using (A.13) the integral M_i in (A.2) is

$$M_i = \frac{(-1)^{M+m_1'+m_2'}}{2} \sum_{L=L_{MIN}}^{L_{MAX}} c(l_1', l_1, L)\, c(l_2', l_2, L) \begin{pmatrix} l_1' & l_1 & L \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} l_1' & l_1 & L \\ -m_1' & m_1 & M \end{pmatrix} \begin{pmatrix} l_2' & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2' & l_2 & L \\ -m_2' & m_2 & -M \end{pmatrix} \qquad (A.28)$$

$$\times I_L(a,b,c,\alpha,\beta)$$

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