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RELATIVISTIC COMPUTATION OF SOME SPECTROSCOPIC CHARACTERISTICS OF MEDIUM AND HIGH Z-ATOMS

A Thesis Submitted to the College of Science of AL-Nahrain University in Partial Fulfilment of the Requirement for the Degree of Doctor of Philosophy in Physics

by

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بسم الله الرحمن الرحيم

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ABSTRACT

A systematic study of the non-relativistic Hartree-Fock method and its relativistic version, Dirac-Fock method for the average of configuration have been presented. In the non-relativistic case, a fully derivation of the Hartree-Fock equations were presented and relativistic corrections (mass-velocity, Darwin and spin-orbit terms) are treated as first-order perturbation. For the relativistic case, Dirac-Fock equations were derived, and Breit interaction operator is used as the relativistic correction for the interelectronic Coulomb interaction, and is treated as the first-order perturbation. Expressions for the matrix elements of the Breit interaction operator (magnetic and retardation terms) are given for the average of configuration. Numerical results of some atomic properties for the ground states of (Rb, Zr, Pd, Sn, Cs, Ba, Lu, Ir, Hg, Tl, Bi, Rn) atoms computed and compared with their corresponding experimental values. The relativistic effect on the orbital energies is important on the inner shells especially for the 1s and 2s shells and this effect becomes more pronounced as Z increases. The contribution of Breit interaction is about 2% of the relativistic shift (mass-velocity and Darwin correction). The Hartree-Fock calculations and relativistic correction gives reasonably good approximation for heavy atoms while Dirac-Fock calculation and Breit interaction gives high precision calculations.

CONTENTS

CHAPTER 1

1-1- INTRODUCTION

It has been noted that an accurate solution of Schrödinger's equation is possible only for the hydrogen atom and single-electron ions [1]. A majority of the elements in the periodic table are many-electron systems where the motion of every electron is coupled to the motion of all the other electrons as well as to the nucleus. To study such systems we have to rely on some approximation methods. One widely used approximation method is the Hartree-Fock method. It is based on the rather natural approximation that every electron moves in the potential created by the nucleus plus the average potential of all the other electrons. This assumption leads to the independent-particle model, which essentially reduces the many-electron problem to the problem of solving a number of coupled single-electron equations. The single-electron equations are solved in an iterative manner until a chosen level of self-consistent accuracy is achieved.

The Hartree-Fock approach is a method for obtaining approximate total wavefunctions for many-electron systems. It has been applied successfully to many areas of quantum mechanics including atomic, molecular, and solid-state systems [2].

It is well accepted that an accurate prediction of electronic properties of medium and heavy atoms cannot be achieved without the introduction of relativistic effects. To include these corrections the relativistic counterpart of Schrödinger's equation is considered which is the Dirac's equation, this is lead to Dirac-Fock method.

1-2- HISTORICAL PERSPECTIVES

In this section we try to trace some of the important developments that determined the directions taken by the field of the atomic structure theory.

Hartree published two important papers in 1928 [3,4]. In the first he described a numerical method for the solution of the radial equation with a non-coulomb central field; in the second he used these methods to find a field of force such that the distribution of charge given by the wavefunctions shall reproduce the field. He called this field the self-consistent field. The system of differential equations that he solved later became known as the Hartree equations or, as Hartree himself called them, “equation without exchange”.

Soon after, in 1930 Fock pointed out that the Hartree wavefunction was invalid, as it did not satisfy the Pauli exclusion principle that the wavefunction must be antisymmetric with respect to electron interchange. Fock also showed that a Hartree product could be made antisymmetric by appropriately adding and subtracting all possible permutations of the Hartree product, thereby forming the Hartree-Fock (HF) wavefunction [5]. Later, Slater showed that the resulting wavefunction is simply the determinant of a matrix, called a Slater determinant [6]. The idea of the configuration average was discussed early by Shortley [7] and has been treated in detail by Slater [8].

In 1935 attempts to set up relativistic self-consistent field calculations were initiated by Swirles [9]. She showed that Dirac’s equation could be able to carry through the relativistic version of Fock and Slater’s formulation of the Hartree-Fock equations for a closed shell configuration.

After this, nothing much was done until the introduction of computers in the 1950’s, with the exception of a relativistic Hartree calculation for cu^{+} by Willliams (1940) [10]. Similar calculations has been carried out by Mayers for Hg, this calculation required many hours of computer time [11]. After

this, Cohen (1960) published results for W, Pt, Hg and Hg^{++} in the same approximation [12].

Later, some relativistic self-consistent calculations were made by various authors, but most of these calculations either omitted the exchange term or made some approximations to avoid the numerical difficulties. For instance, Schonfelder computed for various atoms numerical wave functions without the exchange terms [13], and Liberman et al., calculated numerical wavefunctions for closed-shell configurations of some atoms by approximating the exchange term by Slater's method [14].

The problem was reformulated by Grant (1960, 1965) in terms of the algebra of tensor operators, and this has allowed the theory to be expressed in a simpler and more general form. He presented expressions for the relativistic Hartree-Fock equations for closed shell configurations, and also dealt with matrix elements of the magnetic part of the Breit operator [15,16]; the retardation part has since been treated by Kim in 1967 [17].

Desclaux [18] calculated highly accurate spinor energies, total energies, and other expectation values for closed shell atoms. He also published a program for calculation on multiconfiguration Dirac-Fock (MCDF) in 1975 [١٩]. In 1980 Grant et al., published their MCDF code [٢٠], the numerical methods they used are similar to those applied in Desclaux's code. Mrkus Reiher and Karsten Kind studied the effect of the inclusion of the frequency independent Breit interaction on Dirac-Fock total energies for He and Be-like ions [21]. C. Z. Dong et al., studied the M1 transitions of Ar^{13+} and Ar^{14+} using the multiconfiguration Dirac-Fock (MCDF) method [22].

Irimia and C. F. Fischer in 2004, performed multiconfiguration Hartree-Fock MCHF calculation with Breit-Pauli relativistic corrections to compute the energy levels and transition probabilities in Ar [23].

The purpose of this work is to study the various contributions to the energy for the relativistic and non-relativistic cases using Hartree-Fock method for some heavy atoms. In the non-relativistic case, the Schrödinger's Hamiltonian as non-perturbation and the one-electron relativistic corrections as a perturbation is used. In the relativistic case, Dirac-Hamiltonian as non-perturbation and the two-body Breit interaction correction from the quantum electrodynamics as a perturbation is used.

In chapter two, the non-relativistic many-body Hamiltonian, and the classification of the one and two body operators and the construction of the many-body wavefunction which built from central field wavefunctions are described. This followed by the derivation of the average energy of configuration and the Hartree-Fock equations.

In chapter three, the formulation of the relativistic Hamiltonian for many-electron system, and the derivation of the Dirac-Fock equations are discussed.

In chapter four, a full derivation of the matrix element of the frequency independent Breit interaction for both the magnetic and retardation parts is presented. A brief discussion on the numerical process to solve both the non-relativistic and relativistic Hartree-Fock equations is presented in chapter five. Finally, results and discussions for several selected atoms are presented in chapter six.

CHAPTER 2

THE HARTREE-FOCK THEORY

2-1- The Central Field Model

For an N-electron atom with a nuclear charge Z, the non-relativistic Hamiltonian may be written [24] (in atomic units)

$$H = \sum_{i=1}^{N} h_0(\vec{r}_i) + \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N}\frac{1}{r_{ij}} \qquad (2\text{-}1\text{-}1)$$

where $h_0(\vec{r})$ is the single-particle operator for the sum of the kinetic energy and the electron-nucleus interaction given by

$$h_0(\vec{r}) = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \qquad (2\text{-}1\text{-}2)$$

The term r_{ij}^{-1} represent the Coulomb repulsion among the electrons.

The Hamiltonian (2-1-1) is quite complex for any atom having more than a few electrons. As a further approximation it is then customary to assume that each electron moves independently of the other electrons in an average field caused by the nucleus and the electrons. This assumption leads to the independent-particle model, which provides an approximate description of the atom. The problem is considerably simplified if we assume that the average field is spherically symmetric. This is the well known central-field approximation [25]. The single-electron wavefunction $\phi_{nlm_l\mu}(\vec{r})$, can then be written as a product of a radial function $P_{nl}(r)$, a spherical harmonic $Y^{l}_{\mathrm{m_l}}(\theta,\varphi)$ and a spin function $\chi^{1/2}_{\mu}$ [25].

$$\phi_{nlm_l\mu}(\vec{r}) = \frac{1}{r} P_{nl}(r) Y^{l}_{m_l}(\theta,\varphi) \chi^{1/2}_{\mu} \tag{2-1-3}$$

where, n is the principal quantum number, l is the orbital angular momentum quantum number, m_l is the orbital magnetic quantum number, and $\mu = \pm 1/2$

A non-relativistic total atomic wavefunction (Atomic State Function ASF), Ψ is an approximate solution of the Schrödinger's equation

$$H\psi = E\psi \tag{2-1-4}$$

where ψ is the exact total wavefunction.

The total wavefunction for a bound state labeled Γ for an N electron atomic system is assumed to be expressed as a linear combination of configuration state functions CSF, $\Theta(\gamma LS)$ where γ represents the configuration and any other information required to uniquely identify a configuration state. Thus [26],

$$\Psi(\Gamma LS) = \sum_{r}^{n_c} c_r \Theta(\gamma_r LS) \tag{2-1-5}$$

where n_c is the number of CSFs included in the expansion and c_r are the configuration mixing coefficient for state Γ. Configuration state functions (CSF) themselves are formed by taking linear combinations of Slater determinants Φ, so as to obtain eigenfunctions of the total orbital angular momentum operators L^2, L_Z and total spin operators S^2, S_Z.

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(\vec{r}_1) & \phi_b(\vec{r}_1) & \cdots & \phi_N(\vec{r}_1) \\ \phi_a(\vec{r}_2) & \phi_b(\vec{r}_2) & \cdots & \phi_N(\vec{r}_2) \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \phi_a(\vec{r}_N) & \phi_b(\vec{r}_N) & \cdots & \phi_N(\vec{r}_N) \end{vmatrix} \tag{2-1-6}$$

where $a,b,...$ denote sets of four one-electron quantum numbers $(nlm_l\mu)$

2-2- The Average Energy of a Configuration

The energy of state Γ is given by

$$E_\Gamma = \left\langle \Psi\ (\Gamma LS) \middle| H \middle| \Psi\ (\Gamma LS) \right\rangle = \sum_{r,s} c_r^* H_{rs} c_s \tag{2-2-1}$$

where the Hamiltonian matrix element is given by

$$H_{rs} = \int_0^\infty \Theta^\dagger(\gamma_r\ LS)\, H\ \Theta\ (\gamma_s\ LS)\, d^3 r \tag{2-2-2}$$

(* denotes complex conjugate, † denote Hermitian conjugate)

The non-relativistic average energy of configuration represent the diagonal contribution to the Hamiltonian matrix, which can be written as [27]

$$E_{av} = \sum_r c_r^2 H_{rr} \tag{2-2-3}$$

The non-relativistic average energy of a configuration is defined as the center of gravity of all the states belonging to a given LS configuration, and given by [28]

$$E_{av} = \frac{\sum_r (2L_r + 1)(2S_r + 1)\, E(LS)_r}{\sum_r (2L_r + 1)(2S_r + 1)} \tag{2-2-4}$$

where L_r and S_r are respectively the orbital and the spin total angular momenta of a state $(LS)_r$, $E(LS)_r$ is the energy of a state $(LS)_r$ and the r summation extends over the number of states in the configuration.

From equations (2-2-3) and (2-2-4), we get

$$c_r = \sqrt{\frac{(2L_r + 1)(2S_r + 1)}{\sum_j (2L_j + 1)(2S_j + 1)}} \tag{2-2-5}$$

The Hamiltonian (2-1-1) includes one-electron operators of the type $h_0(\vec{r}_i)$, which act on the coordinates of one electron, and two electron operators of the kind r_{ij}^{-1}.

The matrix element of the one-electron operator $h_0(\vec{r}_i)$ [29]

$$\begin{aligned}\left\langle \Phi \left| \sum_{i=1}^{N} h_0(\vec{r}_i) \right| \Phi \right\rangle &= \sum_a \left\langle a \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \right| a \right\rangle \\ &= \sum_a I(a,a)\end{aligned} \tag{2-2-7}$$

where:

$$\begin{aligned}I(a,a) &= \left\langle n_a l_a m_{l_a} \mu_a \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \right| n_a l_a m_{l_a} \mu_a \right\rangle \\ &= \int_0^\infty P_{n_a l_a}(r) \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right] P_{n_a l_a}(r) dr\end{aligned} \tag{2-2-8}$$

The matrix element of the two-particle operator r_{ij}^{-1} [29]

$$\begin{aligned}\left\langle \Phi \left| \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} r_{ij}^{-1} \right| \Phi \right\rangle &= \frac{1}{2}\sum_{ab}\left(\left\langle ab \left| r_{12}^{-1} \right| ab \right\rangle - \left\langle ab \left| r_{12}^{-1} \right| ba \right\rangle \right) \\ &= \frac{1}{2}\sum_{ab}\left(g_{abab} - g_{abba} \right)\end{aligned} \tag{2-2-9}$$

In the above, subscripts i and j refer to individual electrons, while a and b stand for sets of one-electron quantum number.

g_{abab} and g_{abba} are called the direct and exchange matrix element of the Coulomb interaction r_{ij}^{-1} respectively, and is given by

$$\begin{aligned}g_{abcd} &= \left\langle ab \left| r_{12}^{-1} \right| cd \right\rangle \\ &= \int_0^\infty \int_0^\infty d^3 r_1 d^3 r_2 \phi_a^\dagger(\vec{r}_1) \phi_b^\dagger(\vec{r}_2) r_{12}^{-1} \phi_c(\vec{r}_1) \phi_d(\vec{r}_2)\end{aligned} \tag{2-2-10}$$

The evaluation of E_{av} amounts to averaging over all possible sets of values of the one-electron magnetic quantum numbers m_l and μ [30].

From equations (2-2-8) and (2-2-9),, the average energy of configuration is

$$E_{av} = \sum_a I(a,a) + \frac{1}{2}\sum_{ab}\left[\left(g_{abab}\right)_{av} - \left(g_{abba}\right)_{av}\right] \qquad (2\text{-}2\text{-}11)$$

Equation (2-2-11) can be rewritten as [30]

$$E_{av} = \sum_a q_a I(a,a) + \frac{1}{2}\sum_a q_a\left(q_a - 1\right)E_{aa} + \frac{1}{2}\sum_a\sum_{b\neq a} q_a q_b E_{ab} \qquad (2\text{-}2\text{-}12)$$

where a and b run over all nl shells rather than one-electron quantum number within a shell, and q is the occupation number of the shell.

and where

$$E_{aa} = \left(g_{abab}\right)_{av} - \left(g_{abba}\right)_{av} \qquad \text{for equivalent electrons} \quad a = b \qquad (2\text{-}2\text{-}13)$$

$$E_{ab} = \left(g_{abab}\right)_{av} - \left(g_{abba}\right)_{av} \qquad \text{for non - equivalent electrons} \quad a \neq b \qquad (2\text{-}2\text{-}14)$$

A general Coulomb matrix element g_{abcd} can be evaluated by using of the decomposition of r_{ij}^{-1} given [31]

$$\begin{aligned}\frac{1}{r_{12}} = \frac{1}{|\vec{r}_1 - \vec{r}_2|} &= \sum_{k=0}\frac{r_<^k}{r_>^{k+1}} C^k(1)\cdot C^k(2) \\ &= \sum_{k=0}\sum_{q=-k}^{k}(-1)^q \frac{r_<^k}{r_>^{k+1}} C_{-q}^k(1) C_q^k(2)\end{aligned} \qquad (2\text{-}2\text{-}15)$$

where $r_<$ is the lesser and $r_>$ the greater of the two distances r_1 and r_2 of the electrons from the nucleus, and where C^k is a tensor operator having components

$$C_q^k = \sqrt{\frac{4\pi}{2k+1}}\, Y_q^k(\theta,\varphi) \qquad (2\text{-}2\text{-}16)$$

With the aid of the above decomposition, equation (2-2-10) becomes

$$\begin{aligned}g_{abcd} = \sum_{k=0}\sum_{q=-k}^{k}(-1)^q R_k(abcd)\left\langle l_a m_{l_a}\middle| C_{-q}^k(1)\middle| l_c m_{l_c}\right\rangle \\ \times\left\langle l_b m_{l_b}\middle| C_q^k(2)\middle| l_d m_{l_d}\right\rangle \delta(\mu_a,\mu_c)\delta(\mu_b,\mu_d)\end{aligned} \qquad (2\text{-}2\text{-}17)$$

where $R_k(abcd)$ is called Slater integral given by

$$R_k(abcd) = \langle P_a P_b | \frac{r_<^k}{r_>^{k+1}} | P_c P_d \rangle$$
$$= \int_0^\infty \int_0^\infty P_a(r_1) P_c(r_1) \frac{r_<^k}{r_>^{k+1}} P_b(r_2) P_d(r_2) dr_1 dr_2 \quad (2\text{-}2\text{-}18)$$

By using Wigner-Eckart theorem [32]

$$\langle l_1 m_1 | C_q^k | l_2 m_2 \rangle = [(2l_1+1)]^{-1/2} C(l_1, k, l_2; m_{1_b}, q, m_2) \langle l_1 \| C^k \| l_2 \rangle \quad (2\text{-}2\text{-}19)$$

where , $C(l_1, k, l_2; m_1, q, m_2)$ is the Clebsch-Gordan coefficient,

and where $\langle l_1 \| C^k \| l_2 \rangle$ is the reduced matrix element, given by

$$\langle l_1 \| C^k \| l_2 \rangle = \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} [(2l_1+1)(2l_2+1)]^{1/2} \quad \text{if } l_1 + l_2 + k = even$$
$$= 0 \quad \text{if } l_1 + l_2 + k = odd \quad (2\text{-}2\text{-}20)$$

where $\begin{pmatrix} l_1 & k & l_2 \\ m_1 & q & m_2 \end{pmatrix}$ is 3-j symbol.

Equation (2-2-17) can be written in terms of the reduced matrix element

$$g_{abcd} = \sum_{k=0} \sum_{q=-k}^{k} (-1)^q R_k(abcd) C(l_a, k, l_c; m_{l_a}, -q, m_{l_c})$$
$$\times C(l_b, k, l_d; m_{l_b}, q, m_{l_d}) \langle l_a \| C^k(1) \| l_c \rangle \langle l_b \| C^k(2) \| l_d \rangle \quad (2\text{-}2\text{-}21)$$
$$\times [(2l_a+1)(2l_b+1)]^{-1/2} \delta(\mu_a, \mu_c) \delta(\mu_b, \mu_d)$$

From the above equation, the direct contribution

$$g_{abab} = \sum_{k=0} F_k(ab) C(l_a, k, l_a; m_{l_a}, 0, m_{l_a}) C(l_b, k, l_b; m_{l_b}, 0, m_{l_b})$$
$$\times \langle l_a \| C^k(1) \| l_a \rangle \langle l_b \| C^k(2) \| l_b \rangle [(2l_a+1)(2l_b+1)]^{-1/2} \quad (2\text{-}2\text{-}22)$$

where:

$$F_k(ab) = R_k(abab) = \int_0^\infty \int_0^\infty P_a(r_1) P_a(r_1) \frac{r_<^k}{r_>^{k+1}} P_b(r_2) P_b(r_2) dr_1 dr_2 \quad (2\text{-}2\text{-}23)$$

For the exchange contribution

$$g_{abba} = \sum_{k=0} G_k(ab) \left[C(l_a, k, l_b; m_{l_a}, m_{l_a} - m_{l_b}, m_{l_b}) \right]^2 \times \left[\langle l_a \| C^k \| l_b \rangle \right]^2 (2l_a + 1)^{-1} \delta(\mu_a, \mu_b) \quad (2\text{-}2\text{-}24)$$

where:

$$G_k(ab) = R_k(abba) = \int_0^\infty \int_0^\infty P_a(r_1) P_b(r_1) \frac{r_<^k}{r_>^{k+1}} P_b(r_2) P_a(r_2) dr_1 dr_2 \quad (2\text{-}2\text{-}25)$$

To carry out the averaging over all permissible values of the four magnetic quantum numbers, first, we sum over all permitted pairs of values of the two quantum numbers $m_{l_b} \mu_b$, and divide by the number of such pairs.

$$\sum_{m_{l_b} \mu_b} g_{abab} = \sum_{k=0} \sum_{m_{l_b} \mu_b} \sum C(l_b, k, l_b; m_{l_b}, 0, m_{l_b}) C(l_a, k, l_a; m_{l_a}, 0, m_{l_a}) \times F_k(ab) \langle l_a \| C^k(1) \| l_a \rangle \langle l_b \| C^k(2) \| l_b \rangle \left[(2l_a + 1)(2l_b + 1) \right]^{-1/2} \quad (2\text{-}2\text{-}26)$$

we make use of the identities [30]

$$\sum_{m_{l_b}} C(l_b, k, l_b; m_{l_b}, 0, m_{l_b}) = (2l_b + 1) \delta(k, 0) \quad (2\text{-}2\text{-}27)$$

and

$$C(l_a, 0, l_a; m_{l_a}, 0, m_{l_a}) = 1 \quad (2\text{-}2\text{-}28)$$

To obtain

$$\sum_{m_{l_b} \mu_b} g_{abab} = 2 F_0(ab) \langle l_a \| C^0(1) \| l_a \rangle \langle l_b \| C^0(2) \| l_b \rangle \left[\frac{(2l_b + 1)}{(2l_a + 1)} \right]^{1/2} \quad (2\text{-}2\text{-}29)$$

where the sum over μ_b just introduces a factor of two [25].

Similarly for the exchange term, we have [30]

$$\sum_{m_{l_b} \mu_b} g_{abba} = \sum_{k=0} G_k(ab) \langle l_a \| C^k(1) \| l_b \rangle^2 (2l_a + 1)^{-1} \quad (2\text{-}2\text{-}30)$$

Both equations (2-2-29) and (2-2-30) are independent of $m_{l_a}\mu_a$ and so there is no need to average over these quantum numbers. Therefore, from equations (2-2-29) and (2-2-30), equation (2-2-13) becomes

$$E_{aa}=\frac{1}{(4l_b+1)}\left[2F_0(aa)\left\langle l_a\middle\|C^0\middle\|l_a\right\rangle^2-\sum_{k=0}F_k(aa)\left\langle l_a\middle\|C^k\middle\|l_a\right\rangle^2(2l_a+1)^{-1}\right]$$

$$=F_0(aa)-\frac{(2l_a+1)}{(4l_a+1)}\sum_{k>0}\begin{pmatrix}l_a & k & l_a\\ 0 & 0 & 0\end{pmatrix}^2F_k(aa) \qquad (2-2-31)$$

where we have using equation (2-2-20), and $F_k(aa)=G_k(aa)$

Similarly, for non-equivalent electrons

$$E_{ab}=F_0(ab)-\frac{1}{2}\sum_k\begin{pmatrix}l_a & k & l_b\\ 0 & 0 & 0\end{pmatrix}^2G_k(ab) \qquad (2-2-32)$$

The expression for the average energy in non-relativistic case given in equation (2-2-12) becomes

$$E_{av}=\sum_a q_aI(a,a)$$

$$+\frac{1}{2}\sum_a q_a(q_a-1)\left[F_0(aa)-\frac{(2l_a+1)}{(4l_a+1)}\sum_{k>0}\begin{pmatrix}l_a & k & l_a\\ 0 & 0 & 0\end{pmatrix}^2F_k(aa)\right] \qquad (2-2-33)$$

$$+\frac{1}{2}\sum_a\sum_{b\neq a}q_aq_b\left[F_0(ab)-\frac{1}{2}\sum_k\begin{pmatrix}l_a & k & l_b\\ 0 & 0 & 0\end{pmatrix}^2G_k(ab)\right]$$

where the sum over k extends over all values permitted by the angular momentum selection rule $|l_1-l_2|\le k\le l_1+l_2$ with the constraint that the sum $l_1+l_2+k=even$

2-3- The Hartree-Fock equations

We invoke the Variational principle to determine the radial wave functions.

It is required that the average energy be stationary

$$\delta E_{av} = 0 \qquad (2\text{-}3\text{-}1)$$

for small changes in the radial part of the wave function subject to the orthonormalization constraint

$$\int_0^\infty P_{nl}(r)\, P_{n'l}(r) dr = \delta(n, n') \qquad (2\text{-}3\text{-}2)$$

Equation (2-3-1) with the condition (2-3-2) is equivalent to satisfying the equation [25]

$$\delta \left[E_{av} - \sum_a q_a \lambda_{aa} N_{aa} - \sum_{b \neq a} q_a q_b \delta(l_a, l_b) \lambda_{ab} N_{ab} \right] = 0 \qquad (2\text{-}3\text{-}3)$$

where N_{ab} represent the overlap integral given by equation (2-3-2), and the parameter λ_{ab} are the Lagrange multipliers , which they have the effect of preserving the orthonormality.

The variation in the function $P_a(r)$ is designate by $\delta P_a(r)$ and it is required $\delta P_a(0) = \delta P_a(\infty) = 0$.

From equation (2-2-32) the variation of E_{av} due to a variation of $P_a(r)$ only is

$$\delta E_{\mathrm{av}} = q_a \delta I(a,a) + \frac{1}{2} q_a (q_a - 1) \delta E_{aa} + \sum_{b \neq a} q_a q_b \delta E_{ab} \qquad (2\text{-}3\text{-}4)$$

or

$$\delta E_{av} = q_a \delta I(a,a) + \frac{1}{2} q_a (q_a - 1) \left[\delta F_0(aa) - \frac{(2l_a + 1)}{(4l_a + 1)} \sum_{k>0} \begin{pmatrix} l_a & k & l_a \\ 0 & 0 & 0 \end{pmatrix}^2 \right.$$

$$\left. \times \delta F_k(aa) \right] + \sum_{b \neq a} q_a q_b \left[\delta F_0(ab) - \frac{1}{2} \sum_k \begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0 \end{pmatrix}^2 \delta G_k(ab) \right] \qquad (2\text{-}3\text{-}5)$$

Combine the above equation with equation (2-3-3) to give

$$q_a \delta I(a,a) + \frac{1}{2} q_a (q_a - 1)\left[\delta F_0(aa) - \frac{(2l_a+1)}{(4l_a+1)} \sum_{k>0} \begin{pmatrix} l_a & k & l_a \\ 0 & 0 & 0 \end{pmatrix}^2 \delta F_k(aa) \right]$$

$$+ \sum_{b \neq a} q_a q_b \left[\delta F_0(ab) - \frac{1}{2} \sum_k \begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0 \end{pmatrix}^2 \delta G_k(ab) \right] \qquad (2-3-6)$$

$$- q_a \lambda_{aa} \delta N_{aa} - 2 \sum_{b \neq a} q_a q_b \delta(l_a, l_b) \lambda_{ab} \delta N_{ab} = 0$$

It follows from the above equation that the expression to be varied depend upon the integrals $I(a,a), F_k(ab), G_k(ab)$, and the overlap integral N_{ab}. We consider first the variation of these integrals separately. Using equation (2-2-8) we obtain

$$\delta I(a,a) = \int_0^\infty \delta P_a(r) \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l_a(l_a+1)}{2r^2} - \frac{Z}{r} \right] P_a(r) dr$$
$$+ \int_0^\infty P_a(r) \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l_a(l_a+1)}{2r^2} - \frac{Z}{r} \right] \delta P_a(r) dr \qquad (2-3-7)$$

integrating by parts and using the fact $P_a(r)$ and $\delta P_a(r)$ vanish at the origin and at infinity, one may have

$$\delta I(a,a) = 2\int_0^\infty \delta P_a(r) \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l_a(l_a+1)}{2r^2} - \frac{Z}{r} \right] P_a(r) dr \qquad (2-3-8)$$

In order to obtain the variation of $F_k(ab)$ and $G_k(ab)$ integrals it is convenient to introduce the Hartree function given by [25]

$$Y_k(ab, r_1) = r_1 \int_0^\infty dr_2 \frac{r_<^k}{r_>^{k+1}} P_a(r_2) P_b(r_2)$$
$$= \frac{1}{r_1^k} \int_0^{r_1} dr_2 r_2^k P_a(r_2) P_b(r_2) + r_1^{k+1} \int_{r_1}^\infty dr_2 \frac{1}{r_2^{k+1}} P_a(r_2) P_b(r_2) \qquad (2-3-9)$$

The $F_k(ab)$ and $G_k(ab)$ integrals in equations (22-2-23) and (2-2-25) becomes

$$F_k(ab) = \int_0^\infty dr_1 P_a^2(r_1) \frac{1}{r_1} Y_k(bb, r_1)$$
$$G_k(ab) = \int_0^\infty dr_1 P_a(r_1) P_b(r_1) \frac{1}{r_1} Y_k(ab, r_1) \qquad (2\text{-}3\text{-}10)$$

Therefore

$$\delta F_k(ab) = 2\int_0^\infty dr\, P_a(r) \delta P_a(r) \frac{1}{r} Y_k(bb, r) \qquad a \neq b \qquad (2\text{-}3\text{-}11)$$

$$\delta F_k(aa) = 4\int_0^\infty dr\, P_a(r) \delta P_a(r) \frac{1}{r} Y_k(aa, r) \qquad a = b \qquad (2\text{-}3\text{-}12)$$

combine the above two equation to obtain

$$\delta F_k(ab) = 2(1 + \delta_{ab}) \int_0^\infty dr\, P_a(r) \delta P_a(r) \frac{1}{r} Y_k(bb, r) \qquad (2\text{-}3\text{-}13)$$

similarly, the variations of the exchange integral and the overlap integral are

$$\delta G_k(ab) = 2(1 + \delta_{ab}) \int_0^\infty dr\, P_a(r) \delta P_b(r) \frac{1}{r} Y_k(ab, r) \qquad (2\text{-}3\text{-}14)$$

$$\delta N_{ab} = (1 + \delta_{ab}) \int_0^\infty dr \delta P_a(r) P_b(r) \qquad (2\text{-}3\text{-}15)$$

With the expression for the variations of the integrals given above, equation (2-3-6) becomes

$$\int_0^\infty \delta P_a(r)\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l_a(l_a+1)}{2r^2}-\frac{Z}{r}\right]P_a(r)dr$$
$$+(q_a-1)\left[\int_0^\infty dr\, P_a(r)\delta P_a(r)\frac{1}{r}Y_0(aa,r)\right.$$
$$\left.-\frac{(2l_a+1)}{(4l_a+1)}\sum_{k>0}\begin{pmatrix} l_a & k & l_a \\ 0 & 0 & 0\end{pmatrix}^2\int_0^\infty dr\, P_a(r)\delta P_a(r)\frac{1}{r}Y_k(aa,r)\right]$$
$$+\sum_{b\neq a}q_b\left[\int_0^\infty dr\, P_a(r)\delta P_a(r)\frac{1}{r}Y_0(bb,r)-\frac{1}{2}\sum_k\begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0\end{pmatrix}^2\right. \qquad (2-3-16)$$
$$\left.\times\int_0^\infty dr\,\delta P_a(r)\,P_b(r)\frac{1}{r}Y_k(ab,r)\right]$$
$$-\lambda_{aa}\int_0^\infty dr\, P_a(r)\delta P_a(r)-\sum_{b\neq a}q_b\,\delta(l_a,l_b)\lambda_{ab}\int_0^\infty dr\,\delta P_a(r)\,P_b(r)=0$$

This integral will vanish for arbitrary $\delta P_a(r)$, only if the radial functions satisfy the equation [25]

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l_a(l_a+1)}{2r^2}-\frac{Z}{r}\right]P_a(r)$$
$$+(q_a-1)\frac{1}{r}\left[Y_0(aa,r)-\frac{(2l_a+1)}{(4l_a+1)}\sum_{k>0}\begin{pmatrix} l_a & k & l_a \\ 0 & 0 & 0\end{pmatrix}^2 Y_k(aa,r)\right]P_a(r)$$
$$+\sum_{b\neq a}q_b\left[P_a(r)\frac{1}{r}Y_0(bb,r)-\frac{1}{2}\sum_k\begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0\end{pmatrix}^2 P_b(r)\frac{1}{r}Y_k(ab,r)\right] \qquad (2-3-17)$$
$$-\lambda_{aa}P_a(r)-\sum_{b\neq a}q_b\,\delta(l_a,l_b)\lambda_{ab}P_b(r)=0$$

In this equation λ_{aa} serves as a single-electron eigenvalue. If we denote $\varepsilon_a=\lambda_{aa}$ and $\varepsilon_{ab}=\lambda_{ab}$

$$Y_a(r) = Z - (q_a - 1)\left[Y_0(aa,r) - \frac{(2l_a+1)}{(4l_a+1)} \times \sum_{k>0} \begin{pmatrix} l_a & k & l_a \\ 0 & 0 & 0 \end{pmatrix}^2 Y_k(aa,r) \right] - \sum_{b\neq a} q_b Y_0(bb,r) \qquad (2\text{-}3\text{-}18)$$

and

$$X_a(r) = \sum_{b\neq a} q_b \left[\sum_{k=0} \begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{1}{r} Y_k(ab,r) + 2\,\delta(l_a,l_b)\varepsilon_{ab} \right] P_b(r) \qquad (2\text{-}3\text{-}19)$$

equation (2-3-17) becomes

$$\frac{d^2 P_a}{dr^2} - \frac{l_a(l_a+1)\,P_a}{r^2} + 2\left[\varepsilon_a + \frac{Y_a(r)}{r} \right] P_a(r) = -X_a(r) \qquad (2\text{-}3\text{-}20)$$

This is the Hartree-Fock equation for the radial part of the orbitals in the subshell a. There is one HF equation (2-3-20) for each occupied subshell a.

2-4- Koopman's Theorem

The value of ε_a has a direct physical significance. To see this, we multiply all terms of equation (2-3-20) from the left by $P_a(r)$ and integrating, and using equations (2-2-8), (2-3-10), (2-3-18) and (2-3-19) this gives

$$\varepsilon_a = I(a,a) + (q_a - 1)\left[F_0(aa) - \frac{(2l_a+1)}{(4l_a+1)} \sum_{k>0} \begin{pmatrix} l_a & k & l_a \\ 0 & 0 & 0 \end{pmatrix}^2 F_k(aa) \right] + \sum_{b\neq a} q_b \left[F_0(ab) - \frac{1}{2} \sum_k \begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0 \end{pmatrix}^2 G_k(ab) \right] \qquad (2\text{-}4\text{-}1)$$

using equations (2-2-31) and (2-2-32), then

$$\varepsilon_a = I(a,a) + (q_a - 1)E_{aa} + \sum_{b\neq a} q_b E_{ab} \qquad (2\text{-}4\text{-}2)$$

This quantity is the energy associated with an electron in subshell a according to (2-2-12).

The Hartree-Fock energy eigenvalue ε_c is related to the energy required to remove an electron from the subshell c. The energy of an ion is

$$E_{ion} = \sum_a I(a,a) - I(c,c) + \frac{1}{2}\sum_{ab}\left(g_{abab} - g_{abba}\right) - \sum_a \left(g_{acac} - g_{acca}\right) \qquad (2\text{-}4\text{-}3)$$

$$E_{ion} - E_{atom} = -I(c,c) - \sum_a \left(g_{acac} - g_{acca}\right) = -\varepsilon_c \qquad (2\text{-}4\text{-}4)$$

Thus the removal energy, calculated with Hartree-Fock wave function for the atom, is the negative of the corresponding Hartree-Fock eigenvalue. This result is called Koopman's theorem [33].

2-5- Off- Diagonal Energy Parameters

The off-diagonal energy parameters enter into the Hartree-Fock equations through an orthogonality constraint. We can a obtain relation to determine these parameters, by multiplying equation (2-3-20) by P_b, and integrating over r from zero to infinity, we get

$$\varepsilon_{ab} = I(a,b) + \int_0^\infty \frac{1}{r}\left[Z - Y_a(r)\right] P_a P_b \, dr - \frac{1}{2}\int_0^\infty \eta_a(r)\, P_b \, dr \qquad (2\text{-}5\text{-}1)$$

where

$$I(a,b) = \int_0^\infty P_{n_a l_a}\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l_a(l_a+1)}{r^2} - \frac{Z}{r}\right] P_{n_b l_a}\, dr \qquad (2\text{-}5\text{-}2)$$

and

$$\eta_a(r) = \sum_{b\neq a} q_b \left[\sum_{k=0} \begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{1}{r} Y_k(ab,r)\right] P_b(r) \qquad (2\text{-}5\text{-}3)$$

2-6- Relativistic Corrections

There exists two approaches to include relativistic effects. One way is to treat the relativistc interactions as perturbations to the nonrelativistic Hamiltonian. This is done in the Pauli approximation, where relativistc effects are treated to order α^2 (where α is the fine structure constant).

A more accurate way of treating the relativistc interactions is to approximate the Hamiltonian by a sum of single-particle Dirac Hamiltonians $h_D(\vec{r})$ and the Coulomb interaction between the electrons, r_{12}^{-1}, as can be seen in the next chapter.

For the first approach, we starting from Dirac Hamiltonian for a particle moving in a central field *V* [34]

$$h_D(\vec{r}) = c\vec{\alpha}\cdot\vec{p} + \beta c^2 + V \qquad (2\text{-}6\text{-}1)$$

Where $\vec{p}$ is the momentum operator, c is the speed of light; in atomic units, c=137.0359895. The quantities $\vec{\alpha}$ and β are (4×4) Dirac matrices:

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix},\ \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \qquad (2\text{-}6\text{-}2)$$

Where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is (2×2) Pauli spin matrices, which are given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (2\text{-}6\text{-}3)$$

, I and 0 the (2×2) unit and zero matrices, respectively.

If $\phi(\vec{r})$ is an eigenfunction of the one-electron Dirac Hamiltonian $h_D(\vec{r})$ with eigenvalue ε, then

$$\phi(\vec{r}) = \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} \qquad (2\text{-}6\text{-}4)$$

$$\varepsilon' = \varepsilon - c^2 \qquad (2\text{-}6\text{-}5)$$

where ϕ_1 and ϕ_2 represent the large and small components of the wave function respectively.

The wave equation then becomes

$$\begin{aligned} -c(\vec{\sigma}\cdot\vec{p})\phi_2 + (\varepsilon' - V)\phi_1 = 0 \\ -c(\vec{\sigma}\cdot\vec{p})\phi_1 + (\varepsilon' - V + 2c^2)\phi_2 = 0 \end{aligned} \qquad (2\text{-}6\text{-}6)$$

eliminating ϕ_2 by substitute the second of the above equations into the first, gives:

$$\varepsilon'\phi_1 = \frac{1}{2}(\vec{\sigma}\cdot\vec{p})\left(1+\frac{\varepsilon'-V}{2c^2}\right)^{-1}(\vec{\sigma}\cdot\vec{p})\phi_1 + V\phi_1 \qquad (2\text{-}6\text{-}7)$$

expanded to the order of $1/c^2$ to obtain

$$\varepsilon'\phi_1 = \frac{p^2}{2}\phi_1 - \frac{1}{4c^2}\left[(\vec{\sigma}\cdot\vec{p})\varepsilon'(\vec{\sigma}\cdot\vec{p}) - (\vec{\sigma}\cdot\vec{p})V(\vec{\sigma}\cdot\vec{p})\right]\phi_1 + V\phi_1 \qquad (2\text{-}6\text{-}8)$$

using [32] $\vec{p}V = V\vec{p} - i\vec{\nabla}V$, then equation (2-6-8) becomes

$$\varepsilon'\phi_1 = \frac{p^2}{2}\phi_1 - \frac{1}{4c^2}\left[p^2\varepsilon' - Vp^2 + i(\vec{\sigma}\cdot\vec{\nabla}V)(\vec{\sigma}\cdot\vec{p})\right]\phi_1 + V\phi_1 \qquad (2\text{-}6\text{-}9)$$

with the help of $(\vec{\sigma}\cdot\vec{\nabla}V)(\vec{\sigma}\cdot\vec{p}) = \vec{\nabla}V.\vec{p} + i\vec{\sigma}.(\vec{\nabla}V\times\vec{p})$ equation (2-6-9) becomes

$$\varepsilon'\phi_1 = \frac{p^2}{2}\phi_1 - \frac{\varepsilon'-V}{4c^2}p^2\phi_1 - \frac{1}{4c^2}\vec{\nabla}V.\vec{\nabla}\phi_1 + \frac{1}{4c^2}\vec{\sigma}\cdot(\vec{\nabla}V\times\vec{p})\phi_1 + V\phi_1 \qquad (2\text{-}6\text{-}10)$$

since V is spherically symmetric, then

$$\vec{\nabla}V = \frac{1}{r}\frac{dV}{dr}\vec{r} \quad ; \quad \vec{\nabla}V.\vec{\nabla} = \frac{dV}{dr}\frac{\partial}{\partial \mathrm{r}}$$

equation (2-6-10) becomes

$$\varepsilon'\phi_1 = \frac{p^2}{2}\phi_1 + V\phi_1 - \frac{(\varepsilon'-V)^2}{2c^2}\phi_1 - \frac{1}{4c^2}\frac{dV}{dr}\frac{\partial}{\partial r}\phi_1 + \frac{1}{2c^2}\frac{1}{r}\frac{dV}{dr}(\vec{s}.\vec{l})\phi_1 \qquad (2\text{-}6\text{-}11)$$

where $\vec{s} = \frac{1}{2}\vec{\sigma}$; $l = \vec{r}\times\vec{p}$ and $\varepsilon' - V = \frac{p^2}{2}$

The first and second terms on the right side of equation (2-6-11) give the non-relativistic Schrödinger equation. The third term is called the mass-velocity term because it arises from the relativistic variation of mass with velocity [35]. The forth term is called the Darwin term which represents a relativistic correction to the potential energy [30]. The last term is the spin orbit term which represents the magnetic interaction energy between the electron's spin magnetic moment and the magnetic field due to the electron orbital motion [30].

Incorporating these relativistic effects within the format of the non-relativistic approach.

For the spin-orbit term, the matrix element is

$$\left\langle \mathbf{\Phi} \left| \frac{1}{2c^2} \sum_{i=1}^{N} \frac{1}{r_i} \frac{dV_i}{dr_i} \left(\vec{s}(i).\vec{l}(i) \right) \right| \mathbf{\Phi} \right\rangle \qquad (2\text{-}6\text{-}12)$$

Equation (2-6-12) involves summation over possible values of μ_a, therefore, for any specific value of $n_a l_a m_a$, there will be one–electron matrix elements with μ_a equal to both $+1/2$ and $-1/2$. Therefore these two matrix elements will be equal in magnitude but opposite in sign; thus the spin-orbit contribution to E_{av} is zero [30].

For mass-velocity term

$$\begin{aligned} E_m &= \left\langle \mathbf{\Phi} \left| \frac{1}{2c^2} \sum_{i=1}^{N} \left(\varepsilon_i' - V_i \right)^2 \right| \mathbf{\Phi} \right\rangle \\ &= \frac{1}{2c^2} \sum_a \int_0^\infty P_a \left(\varepsilon_a' - V_a \right)^2 P_a \, dr \end{aligned} \qquad (2\text{-}6\text{-}13)$$

and for the Darwin term

$$\begin{aligned} E_D &= \left\langle \mathbf{\Phi} \left| \frac{1}{4c^2} \sum_{i=1}^{N} \frac{dV_i}{dr} \frac{\partial}{\partial r} \right| \mathbf{\Phi} \right\rangle \\ &= \frac{1}{4c^2} \sum_a \int_0^\infty P_a \frac{dV_a}{dr} r \frac{d}{dr} (r^{-1} P_a) dr \end{aligned} \qquad (2\text{-}6\text{-}14)$$

where

$$V_a = (q_a - 1)\left[\frac{1}{r}Y_0(aa,r) - \frac{(2l_a+1)}{(4l_a+1)}\sum_{k>0}\begin{pmatrix} l_a & k & l_a \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{1}{r}Y_k(aa,r)\right] \quad (2\text{-}6\text{-}15)$$
$$+ \sum_{b\neq a} q_b\left[\frac{1}{r}Y_0(bb,r)\right] - \frac{Z}{r}$$

From equation (2-6-13) and (2-6-14), the relativistic shift due to mass-velocity and Darwin term is:

$$\text{Re}\,\textit{lativistic shift} = E_m + E_D \quad (2\text{-}6\text{-}16)$$

CHAPTER 3

DIRAC-FOCK THEORY

3-1- Dirac-Fock Equations

Pauli approximation becomes less satisfactory for high atomic numbers where the use of perturbation theory starts to break down [3٦]. Therefore, a theory in which the one-body relativistic correction are treated in non-perturbative fashion must be used. This is achieved by using Dirac's equation. All relativistic single-particle effects, namely the mass correction, the Darwin term and the spin-own-orbit interaction are automatically included via the Dirac Hamiltonian (2-6-1).

The Hartree-Fock is extended to include relativistic effect. Starting with a relativistic many-body Hamiltonian [3٧]

$$H = \sum_{i=1}^{N} h_D(\vec{r}_i) + \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N}\frac{1}{r_{ij}} \qquad (3\text{-}1\text{-}1)$$

This is known as the Dirac-Coulomb Hamiltonian.

Where $h_D(\vec{r})$ is the single-particle Dirac Hamiltonian for an electron moving in nuclear Coulomb potential $\frac{Z}{r}$ and is given in equation (2-6-1)

$$h_D(\vec{r}) = c\vec{\alpha}\cdot\vec{p} + (\beta - 1)c^2 - \frac{Z}{r} \qquad (3\text{-}1\text{-}2)$$

Where, the rest-mass energy term from the Dirac Hamiltonian has been subtracted in order to choose the zero of energy equal to the electron rest mass [3٨].

The one-electron Dirac wave function $\phi(\vec{r})$ satisfies the single-particle Dirac equation

$$h_D\phi(\vec{r}) = \varepsilon\phi(\vec{r}) \tag{3-1-3}$$

The one-electron, bound-state solution to the Dirac equation (3-1-3) having the form [39]

$$\phi_{n\kappa m}(\vec{r}) = \frac{1}{r}\begin{pmatrix} P_{n\kappa}(r)\Omega_{\kappa m}(\theta,\varphi) \\ iQ_{n\kappa}(r)\Omega_{-\kappa m}(\theta,\varphi) \end{pmatrix} \tag{3-1-4}$$

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components of the one-electron radial wavefunctions respectively, and satisfy the orthonormality condition [40]

$$\int_0^\infty \left[P_{n\kappa}(r)P_{n'\kappa}(r) + Q_{n\kappa}(r)Q_{n'\kappa}(r)\right]dr = \delta(\mathrm{n},\mathrm{n}') \tag{3-1-5}$$

where $\delta(\mathrm{n},\mathrm{n}')$ is the Kronecker delta.

The angular function $\Omega_{\kappa m}(\theta,\varphi)$ is the spherical spinor, which is defined by the equation [41]

$$\Omega_{\kappa m}(\theta,\varphi) = \sum_{\mu} C(l,1/2,j;m-\mu,\mu,m)Y^{l}_{m-\mu}(\theta,\varphi)\chi^{1/2}_{\mu} \tag{3-1-6}$$

Here n is the principal quantum number, and κ is the Dirac quantum number which is related to the total angular momentum quantum number j and the orbital angular momenta quantum numbers l and $\bar{l}$ of large and small components, respectively by [17]

$$\begin{aligned} j &= |\kappa| - \frac{1}{2} \\ l &= \left|\kappa + \frac{1}{2}\right| - \frac{1}{2} \\ \bar{l} &= \left|-\kappa + \frac{1}{2}\right| - \frac{1}{2} \end{aligned} \tag{3-1-7}$$

The Dirac spinors which is defined by equation (3-1-4) are used to build the configuration state functions (CSF) $\Theta\ (\gamma\ JM)$ by taking linear combination of Slater determinants, so as to obtain eigenfunctions of the total angular momentum operators J^2 and J_Z [٤٢]

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(\vec{r}_1) & \phi_b(\vec{r}_1) & \cdot\ \cdot\ \cdot & \phi_N(\vec{r}_1) \\ \phi_a(\vec{r}_2) & \phi_b(\vec{r}_2) & \cdot\ \cdot\ \cdot & \phi_N(\vec{r}_2) \\ \cdot & \cdot & \cdot\ \cdot\ \cdot & \cdot \\ \cdot & \cdot & \cdot\ \cdot\ \cdot & \cdot \\ \cdot & \cdot & \cdot\ \cdot\ \cdot & \cdot \\ \phi_a(\vec{r}_N) & \phi_b(\vec{r}_N) & \cdot\ \cdot\ \cdot & \phi_N(\vec{r}_N) \end{vmatrix} \qquad (3\text{-}1\text{-}8)$$

where the subscripts $a,b,...$ denote the set of the wave function $n\kappa m$.

An atomic state function (ASF) $\Psi\ (\Gamma JM)$ can now be formed from $\Theta\ (\gamma\ JM)$ for state Γ with total angular momentum JM in the following way [43,44]:

$$\Psi\ (\Gamma JM) = \sum_r^{n_c} c_r\ \Theta\ (\gamma_r\ JM) \qquad (3\text{-}1\text{-}9)$$

where n_c is the number of CSFs included in the expansion and c_r are the configuration mixing coefficient for state Γ such that $\sum_r^{n_c} c_r^2 = 1$.

The total relativistic atomic energy is

$$\begin{aligned} E_\Gamma &= \left\langle \Psi\ (\Gamma JM) \middle| H \middle| \Psi\ (\Gamma JM) \right\rangle \\ &= \sum_{r,s} c_r^*\, H_{rs}\, c_s \end{aligned} \qquad (3\text{-}1\text{-}10)$$

where the Hamiltonian matrix element is given by

$$H_{rs} = \int \Theta^\dagger(\gamma_r\ JM)\, H\ \Theta\ (\gamma_s\ JM)\, d^3r \qquad (3\text{-}1\text{-}11)$$

The relativistic average energy of configuration represents the diagonal contribution to the Hamiltonian matrix which can be written as [42]

$$E_{av} = \sum_{r}^{n_c} c_r^2 \, H_{rr} \qquad (3\text{-}1\text{-}12)$$

As in the non-relativistic case, the relativistic average energy of configuration is defined as the center of gravity of all the J -levels belonging to a given relativistic (jj)-configuration, and is given by [28]

$$E_{av} = \frac{\sum_{r} (2J_r + 1) E\ (J_r)}{\sum_{r} (2J_r + 1)} \qquad (3\text{-}1\text{-}13)$$

where $E\ (J_r)$ is the energy of the level J_r and the r summation extends over the total number of J -levels in the relativistic (jj)-configuration.

From equations (3-1-12) and (3-1-13), we get

$$c_r = \sqrt{\frac{(2J_r + 1)}{\sum_{r} (2J_r + 1)}} \qquad (3\text{-}1\text{-}14)$$

In relativistic case each nonrelativistic configuration split up into several relativistic (jj)-subconfiguration, and therefore, at this point it is useful to introduce the concept of extended average energy (EAL), which has the property that exactly reduces to the nonrelativistic average energy. The EAL is defined as the sum of the relativistic subconfiguration average energy defined in equation (3-1-13), sum that includes all the relativistic (jj)-subconfigurations arising from a single nonrelativistic configuration. In the sum, each of the relativistic (jj)-subconfiguration is weighted by its degeneracy [45].

$$E_{EAL} = \frac{\sum_{r} w_r \left(E_{av}\right)_r}{\sum_{s}^{n_L} \left(2J_s + 1\right)} \qquad (3\text{-}1\text{-}15)$$

with

$$w_r = \sum_i (2J_i + 1)$$

Where the summation over s is run over all the values of the J -levels in all relativistic (jj)-subconfigurations and the summation over i is run over the values of the J -levels in the given subconfiguration r.

The relativistic average of energy is defined by [46]

$$E_{av} = \sum_a I(a,a) + \frac{1}{2}\sum_{ab}\left[\left(\left\langle ab\left|\frac{1}{r_{12}}\right|ab\right\rangle\right)_{av} - \left(\left\langle ab\left|\frac{1}{r_{12}}\right|ba\right\rangle\right)_{av}\right] \tag{3-1-16}$$

$$= \sum_a I(a,a) + \frac{1}{2}\sum_{ab}\left[\left(g_{abab}\right)_{av} - \left(g_{abba}\right)_{av}\right]$$

Where the averaging over all possible sets of values of magnetic quantum numbers m_a and m_b.

Here the Coulomb matrix elements g_{abcd} are to be evaluated using Dirac single-particle wave function (3-1-4) rather than non-relativistic single-particle wave function.

Where $I(a,a)$ is the one-electron energy integral for the Dirac Hamiltonian (3-1-2), given by

$$I(a,a) = \left\langle n_a \kappa_a m_a \left| h_D \right| n_a \kappa_a m_a \right\rangle \tag{3-1-7}$$

$$= \int_0^\infty dr\left\{cQ_a\left(\frac{dP_a}{dr} + \frac{\kappa_a}{r}P_a\right) - cP_a\left(\frac{dQ_a}{dr} - \frac{\kappa_a}{r}Q_a\right) - \frac{Z}{r}\left(P_a^2 + Q_a^2\right) - 2c^2Q_a^2\right\}$$

where we have used [29]

$$\vec{\sigma}.\vec{P}f(r)\,\Omega_{\kappa m}(\theta,\varphi) = i\left[\frac{df}{dr} + \frac{\kappa+1}{r}f(r)\right]\Omega_{-\kappa m}(\theta,\varphi) \tag{3-1-18}$$

and where g_{abab} and g_{abba} are the direct and exchange matrix element of the Coulomb operator respectively, and is given by

$$g_{abcd} = \int_0^\infty \int_0^\infty d^3 r_1 d^3 r_2 \phi_a^\dagger(\vec{r}_1)\phi_b^\dagger(\vec{r}_2)\frac{1}{r_{12}}(1,2)\phi_c(\vec{r}_1)\phi_d(\vec{r}_2) \qquad (3\text{-}1\text{-}19)$$

The expression for the average energy given in equation (3-1-16) can be rewritten as

$$E_{av} = \sum_a q_a I(a,a) + \frac{1}{2}\sum_{\mathrm{a}} q_a\left(q_a - 1\right)E_{aa}^C + \frac{1}{2}\sum_a \sum_{\mathrm{b}\neq\mathrm{a}} q_a q_b E_{ab}^C \qquad (3\text{-}1\text{-}20)$$

where

$$\begin{aligned} E_{aa}^C &= \left(g_{abab}\right)_{av} - \left(g_{abba}\right)_{av} \qquad \text{with} \quad a = b \\ E_{ab}^C &= \left(g_{abab}\right)_{av} - \left(g_{abba}\right)_{av} \qquad \text{with} \quad a \neq b \end{aligned} \qquad (3\text{-}1\text{-}21)$$

and where q is the occupation number of the subshell.

A general Coulomb matrix element g_{abcd} can be decomposed by using equation (2-2-15)

$$\frac{1}{r_{12}} = \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{k=0} \frac{r_<^k}{r_>^{k+1}} C^k(1)\cdot C^k(2) \qquad (3\text{-}1\text{-}22)$$

and using equation (3-1-4) in the form

$$\phi(\vec{r}) = \begin{pmatrix} u(\vec{r}) \\ v(\vec{r}) \end{pmatrix} \qquad (3\text{-}1\text{-}23)$$

Where u and v are large and small component of the electron wavefunction respectively.

Equation (3-1-19) becomes

$$\begin{aligned} g_{abcd} = &\left\langle u_a u_b \middle| \frac{1}{r_{12}} \middle| u_c u_d \right\rangle + \left\langle u_a v_b \middle| \frac{1}{r_{12}} \middle| u_c v_d \right\rangle \\ &+ \left\langle v_a u_b \middle| \frac{1}{r_{12}} \middle| v_c u_d \right\rangle + \left\langle v_a v_b \middle| \frac{1}{r_{12}} \middle| v_c v_d \right\rangle \end{aligned} \qquad (3\text{-}1\text{-}24)$$

Treating the first term of the above equation, by using equations (3-1-22) and (3-1-4)

$$\langle u_a u_b|\frac{1}{r_{12}}|u_c u_d\rangle = \sum_{k=0}\langle P_a P_b|\frac{r_<^k}{r_>^{k+1}}|P_c P_d\rangle \times\langle \Omega_a\Omega_b|C^k(1)\cdot C^k(2)|\Omega_c\Omega_d\rangle \quad (3\text{-}1\text{-}25)$$

Using the definition of the spherical spinor (3-1-6), then the above equation becomes

$$\langle u_a u_b|\frac{1}{r_{12}}|u_c u_d\rangle \quad (3\text{-}1\text{-}26)$$

$$= \sum_{k=0}\langle P_a P_b|\frac{r_<^k}{r_>^{k+1}}|P_c P_d\rangle\left\langle Y^{l_a}_{m_a-\mu_a}Y^{l_b}_{m_b-\mu_b}\middle|C^k(1).C^k(2)\middle|Y^{l_c}_{m_c-\mu_c}Y^{l_d}_{m_d-\mu_d}\right\rangle$$

$$\times\sum_{\mu_a\mu_c} C(l_a,1/2,j_a;m_a-\mu_a,\mu_a,m_a)C(l_c,1/2,j_c;m_c-\mu_c,\mu_c,m_c)\delta(\mu_a,\mu_c)$$

$$\times\sum_{\mu_b\mu_d} C(l_b,1/2,j_b;m_b-\mu_b,\mu_b,m_b)C(l_d,1/2,j_d;m_d-\mu_d,\mu_d,m_d)\delta(\mu_b,\mu_d)$$

The matrix element of the scalar product of the spherical tensor operators can be decomposed by applying Wigner-Eckart theorem to give [46]

$$\left\langle Y^{l_a}_{m_a-\mu_a}Y^{l_b}_{m_b-\mu_b}\middle|C^k(1).C^k(2)\middle|Y^{l_c}_{m_c-\mu_c}Y^{l_d}_{m_d-\mu_d}\right\rangle$$

$$= (-1)^{l_a+l_b-m_a-m_b+\mu_a+\mu_b}\frac{\langle l_a\|C^k(1)\|l_c\rangle}{\sqrt{2k+1}}\frac{\langle l_b\|C^k(2)\|l_d\rangle}{\sqrt{2k+1}} \quad (3\text{-}1\text{-}27)$$

$$\times C(l_a,k,l_c;m_a-\mu_a,m_c-m_a+\mu_a-\mu_c,m_c-\mu_c)$$

$$\times C(l_b,k,l_d;m_b-\mu_b,m_d-m_b+\mu_b-\mu_d,m_d-\mu_d)$$

with

$$\langle l_1\|C^k\|l_2\rangle = C(l_1kl_2;000)\left[\frac{(2l_1+1)(2l_2+1)}{(2k+1)}\right]^{1/2} \text{ if } l_1+l_2+k=even \quad (3\text{-}1\text{-}28)$$

$$= 0 \qquad \text{if } l_1+l_2+k=odd$$

Equation (3-1-26) becomes

$$\langle u_a u_b|\frac{1}{r_{12}}|u_c u_d\rangle=\sum_{k=0}\langle P_a P_b|\frac{r_<^k}{r_>^{k+1}}|P_c P_d\rangle$$
$$\times\sum_{\mu_a}(-1)^{l_a-m_a+\mu_a}C(l_a,1/2,j_a;m_a-\mu_a,\mu_a,m_a)$$
$$\times C(l_c,1/2,j_c;m_c-\mu_a,\mu_a,m_c)\frac{\langle l_a\|C^k(1)\|l_c\rangle}{\sqrt{2k+1}}$$
$$\times C(l_a,k,l_c;m_a-\mu_a,m_c-m_a,m_c-\mu_a) \qquad (3\text{-}1\text{-}29)$$
$$\times\sum_{\mu_b}(-1)^{l_b-m_b+\mu_b}C(l_b,1/2,j_b;m_b-\mu_b,\mu_b,m_b)$$
$$\times C(l_d,1/2,j_d;m_d-\mu_b,\mu_b,m_d)\frac{\langle l_b\|C^k(2)\|l_d\rangle}{\sqrt{2k+1}}$$
$$\times C(l_b,k,l_d;m_b-\mu_b,m_d-m_b,m_d-\mu_b)$$

Now introducing a coefficient

$$d^k(jm,j'm')=\frac{\langle l\|C^k\|l'\rangle}{\sqrt{2k+1}}\sum_{\mu}(-1)^{l-m+\mu}C(l,1/2,j;m-\mu,\mu,m)$$
$$\times C(l',1/2,j';m'-\mu,\mu,m') \qquad (3\text{-}1\text{-}30)$$
$$\times C(l,k,l';m-\mu,m-m',m'-\mu)$$

Equation (3-1-29) becomes

$$\langle u_a u_b|\frac{1}{r_{12}}|u_c u_d\rangle=\sum_{k=0}\langle P_a P_b|\frac{r_<^k}{r_>^{k+1}}|P_c P_d\rangle \qquad (3\text{-}1\text{-}31)$$
$$\times d^k(j_a m_a,j_c m_c)d^k(j_b m_b,j_d m_d)$$

From [46], it is find that

$$d^k(jm,j'm')=(-1)^{m+1/2}\frac{[(2j+1)(2j'+1)]^{1/2}}{(2k+1)}$$
$$\times C(j,k,j';\frac{1}{2}0\frac{1}{2})C(j,k,j';m,m'-m,m') \qquad (3\text{-}1\text{-}32)$$

Similarly for the rest terms of equation (3-1-24)

$$\langle v_a u_b|\frac{1}{r_{12}}|v_c u_d\rangle = \sum_{k=0}\langle Q_a P_b|\frac{r_<^k}{r_>^{k+1}}|Q_c P_d\rangle \times d^k(j_a m_a, j_c m_c) d^k(j_b m_b, j_d m_d) \quad (3\text{-}1\text{-}33)$$

$$\langle u_a v_b|\frac{1}{r_{12}}|u_c v_d\rangle = \sum_{k=0}\langle P_a Q_b|\frac{r_<^k}{r_>^{k+1}}|P_c Q_d\rangle \times d^k(j_a m_a, j_c m_c) d^k(j_b m_b, j_d m_d) \quad (3\text{-}1\text{-}34)$$

$$\langle v_a v_b|\frac{1}{r_{12}}|v_c v_d\rangle = \sum_{k=0}\langle Q_a Q_b|\frac{r_<^k}{r_>^{k+1}}|Q_c Q_d\rangle \times d^k(j_a m_a, j_c m_c) d^k(j_b m_b, j_d m_d) \quad (3\text{-}1\text{-}35)$$

Combine equations (3-1-31), (3-1-33), (3-1-34) and (3-1-35) into equation (3-1-24), then we have

$$g_{abcd} = \sum_{k=0}^{\infty} d^k(j_a m_a, j_c m_c) d^k(j_b m_b, j_d m_d) R_k(abcd) \quad (3\text{-}1\text{-}36)$$

Where $R_k(abcd)$ is the relativistic Slater integral defined by

$$\begin{aligned} R_k(abcd) &= \int_0^{\infty} dr_1 \left[P_a(r_1) P_c(r_1) + Q_a(r_1) Q_c(r_1)\right] \\ &\times \int_0^{\infty} dr_2 \frac{r_<^k}{r_>^{k+1}} \left[P_b(r_2) P_d(r_2) + Q_b(r_2) Q_d(r_2)\right] \\ &= \int_0^{\infty} \frac{1}{r_1} Y_k(bd, r_1) \left[P_a(r_1) P_c(r_1) + Q_a(r_1) Q_c(r_1)\right] dr_1 \end{aligned} \quad (3\text{-}1\text{-}37)$$

where

$$Y_k(bd, r_1) = r_1 \int_0^{\infty} dr_2 \frac{r_<^k}{r_>^{k+1}} \left[P_b(r_2) P_d(r_2) + Q_b(r_2) Q_d(r_2)\right] \quad (3\text{-}1\text{-}38)$$

The summation over k in equation (3-1-36) is limited by rules on d^k coefficients which can be derived from the triangular condition of the Clebsch-Gordan coefficients of equation (3-1-32) and from equation (3-1-30), respectively

$$\max\left(|j_a - j_c|,|j_b - j_d|\right) \le k \le \min\left(j_a + j_c, j_b + j_d\right) \tag{3-1-39}$$

$$\begin{aligned} l_a + l_c + k &= even \\ l_b + l_d + k &= even \end{aligned} \tag{3-1-40}$$

From equation (3-1-36), the direct part

$$\begin{aligned} g_{abab} &= \sum_{k=0}^{\infty} d^k(j_a m_a, j_a m_a) d^k(j_b m_b, j_b m_b) F_k(ab) \\ &= \sum_{k=0}^{\infty} a^k(j_a m_a, j_b m_b) F_k(ab) \end{aligned} \tag{3-1-41}$$

Where, we have used

$$\begin{aligned} a^k(j_a m_a, j_b m_b) &= d^k(j_a m_a, j_a m_a) d^k(j_b m_b, j_b m_b) \\ &= (-1)^{m_a + m_b + 1} \frac{\left[(2j_a + 1)(2j_b + 1)\right]}{(2k+1)^2} C(j_a, k, j_a; \tfrac{1}{2} 0 \tfrac{1}{2}) C(j_a, k, j_a; m_a, 0, m_a) \\ &\times C(j_b, k, j_b; \tfrac{1}{2} 0 \tfrac{1}{2}) C(j_b, k, j_b; m_b, 0, m_b) \end{aligned} \tag{3-1-42}$$

and

$$F_k(ab) = R_k(abab)$$

Using equation (3-1-39) and (3-1-40), the permitted values of k are:

$$k = 0,2,4,....,\min\left((2j_a - 1),(2j_b - 1)\right) \tag{3-1-43}$$

For the exchange contribution, we obtain

$$\begin{aligned} g_{abba} &= \sum_k \left[d^k(j_a m_a, j_b m_b)\right]^2 G_k(ab) \\ &= b^k(j_a m_a, j_b m_b) G_k(ab) \end{aligned} \tag{3-1-44}$$

Where we have used

$$b^k(j_a m_a, j_b m_b) = \left[d^k(j_a m_a, j_b m_b)\right]^2 \tag{3-1-45}$$

$$= \frac{\left[(2j_a + 1)(2j_b + 1)\right]}{(2k+1)^2} C(j_a, k, j_b; \tfrac{1}{2} 0 \tfrac{1}{2})^2 C(j_a, k, j_b; m_a, m_b - m_a, m_b)^2$$

and

$$G_k(ab) = R_k(abba)$$

The range of k for the exchange integral is limited by the following conditions:

$$\left| j_a - j_b \right| \le k \le j_a + j_b \qquad (3\text{-}1\text{-}46)$$

and

$$l_a + l_b + k = even \qquad (3\text{-}1\text{-}47)$$

To perform the averaging, the sum over the magnetic quantum numbers m_a and m_b in equation (3-1-41) is carried out first, we have

$$\sum_{m_b} g_{abab} = \sum_{m_b} \sum_{k=0} a^k(j_a m_a, j_b m_b) F_k(ab) \qquad (3\text{-}1\text{-}48)$$

using the identity [35]

$$\sum_{m_b} a^k(j_a m_a, j_b m_b) = (2j_b + 1)\delta_{k0} \qquad (3\text{-}1\text{-}49)$$

to obtain

$$\sum_{m_b} g_{abab} = (2j_b + 1) F_0(ab) \qquad (3\text{-}1\text{-}50)$$

Similarly, for the exchange term in equation (3-1-44)

$$\sum_{m_b} g_{abba} = \frac{1}{2}(2j_b + 1) \sum_{k=0} \Gamma_{j_a k\ j_b} G_k(ab) \qquad (3\text{-}1\text{-}51)$$

where we have used [46]

$$\sum_{m_b} b^k(j_a m_a, j_b m_b) = \frac{1}{2}(2j_b + 1)\Gamma_{j_a k\ j_b} \qquad (3\text{-}1\text{-}52)$$

with

$$\Gamma_{j_a k\ j_b} = 2 \begin{pmatrix} j_a & k & j_b \\ 1/2 & 0 & -1/2 \end{pmatrix}^2 \qquad (3\text{-}1\text{-}53)$$

From equations (3-1-50) and (3-1-51), the quantities E^C_{aa} and E^C_{ab} given in equation (3-1-21) become

$$E^C_{aa} = \left(g_{abab}\right)_{av} - \left(g_{abba}\right)_{av} \qquad \text{with } a = b$$

$$= \frac{1}{2j_a}\left[(2j_a+1)F_0(aa) - \frac{1}{2}(2j_a+1)\sum_{k=0}\Gamma_{j_a k\ j_a}F_k(aa)\right] \qquad (3\text{-}1\text{-}54)$$

$$= F_0(aa) - \frac{1}{2}\frac{(2j_a+1)}{2j_a}\sum_{k>0}\Gamma_{j_a k\ j_a}F_k(aa)$$

$$E^C_{ab} = \left(g_{abab}\right)_{av} - \left(g_{abba}\right)_{av} \qquad \text{with } a \neq b$$

$$= F_0(ab) - \frac{1}{2}\sum_{k=0}\Gamma_{j_a k\ j_b}G_k(ab) \qquad (3\text{-}1\text{-}55)$$

Substitute equations (3-1-54) and (3-1-55) into equation (3-1-20), then we get

$$E_{av} = \sum_a q_a I(a,a) + \frac{1}{2}\sum_{\mathrm{a}} q_a\left(q_a - 1\right)F_0(aa)$$

$$-\frac{1}{2}\sum_{\mathrm{a}}\frac{q_a\left(q_a-1\right)}{2j_a}\left[\frac{1}{2}(2j_a+1)\sum_{k>0}\Gamma_{j_a k\ j_a}F_k(aa)\right] \qquad (3\text{-}1\text{-}56)$$

$$+\frac{1}{2}\sum_a\sum_{\mathrm{b}\neq\mathrm{a}} q_a q_b\left[F_0(ab) - \frac{1}{2}\sum_{k=0}\Gamma_{j_a k\ j_b}G_k(ab)\right]$$

where $I(a,a)$ is given in equation (3-1-17).

Again, as in the non-relativistic case, we require that E_{av} be stationary with respect to variations in the radial functions $P_{n_a\kappa_a}$ and $Q_{n_a\kappa_a}$. This requirement is combined with the orthonormalization condition (3-1-5)

$$N_{n_a\kappa_a,n_b\kappa_a} = \int_0^\infty\left[P_{n_a\kappa_a}P_{n_b\kappa_a} + Q_{n_a\kappa_a}Q_{n_b\kappa_a}\right]dr = \delta(n_a,n_b) \qquad (3\text{-}1\text{-}57)$$

Introducing Lagrange multipliers $\lambda_{n_a\kappa_a,n_b\kappa_a}$ the variational condition is [29]

$$\delta\left\{E_{av} - \sum_a q_a\lambda_{aa}N_{n_a\kappa_a,n_a\kappa_a} - \sum_{b\neq a}\delta(\kappa_a,\kappa_b)q_a q_b\lambda_{ab}N_{n_a\kappa_a,n_b\kappa_a}\right\} = 0 \quad (3\text{-}1\text{-}58)$$

The variations $\delta P_{n_a\kappa_a}$ and $\delta Q_{n_a\kappa_a}$ are required to vanish at the origin and infinity.

Using the abbreviation $P_{n_a\kappa_a} = P_a$

We consider first the variations of the integral I_a in equation (3-1-17), we get

$$\delta I(a,a) = 2c\int_0^\infty dr\Big[\big(P'_a\,\delta Q_a - Q'_a\,\delta P_a\big) + \frac{\kappa_a}{r}\big(P_a\,\delta Q_a + Q_a\,\delta P_a\big) - \frac{1}{c}\frac{Z}{r}\big(P_a\,\delta P_a + Q_a\,\delta Q_a\big) - 2c\,Q_a\,\delta Q_a\Big] \tag{3-1-59}$$

where we have used

$$P'_a = \frac{d}{dr}P_{\mathrm{a}} \quad , \qquad Q'_a = \frac{d}{dr}Q_{\mathrm{a}}$$

From equation (3-1-20), the following variation in the average energy due to variation of $P_a(r)$ and $Q_a(r)$ is obtained, while the remaining orbitals are held constant

$$\delta E_{av} = q_a\,\delta I(a,a) + \frac{1}{2}q_a\big(q_a - 1\big)\delta E^c_{aa} + \sum_{\mathrm{b}\neq\mathrm{a}} q_a\,q_b\,\delta E^{\mathrm{c}}_{ab} \tag{3-1-60}$$

The variation of the $F_k(ab)$ integral with respect to variation of the radial function $P_a(r)$ and $Q_a(r)$ is:

for non-equivalent electrons $a \neq b$

$$\delta F_k(ab) = 2\int_0^\infty \Big[P_a(r)\delta P_a(r) + Q_a(r)\delta Q_a(r)\Big]\frac{1}{r}Y_k(bb,r)dr \tag{3-1-61}$$

and for equivalent electrons $a = b$

$$\delta F_k(aa) = 4\int_0^\infty \Big[P_a(r)\delta P_a(r) + Q_a(r)\,Q_a(r)\Big]\frac{1}{r}Y_k(aa,r)dr \tag{3-1-62}$$

In general,

$$\delta F_k(ab) = 2(1+\delta_{ab})\int_0^\infty \Big[P_a(r)\delta P_a(r) + Q_a(r)\delta Q_a(r)\Big]\frac{1}{r}Y_k(bb,r)dr \tag{3-1-63}$$

Similarly, the variation of the exchange integral $G_k(ab)$

$$\delta G_k(ab) = 2(1+\delta_{ab})\int_0^\infty \left[\delta P_a(r)\, P_b(r) + \delta Q_a(r)\, Q_b(r)\right]\frac{1}{r} Y_k(ab,r)dr \quad (3\text{-}1\text{-}64)$$

With the expressions for the variations of the integrals given in (3-1-63) and (3-1-64), we obtain

$$\begin{aligned}\delta E^C_{aa} = 4\int_0^\infty &\left[P_a(r)\delta P_a(r) + Q_a(r)\delta Q_a(r)\right] \\ &\times\frac{1}{r}\left[Y_0(aa,r) - \frac{(2j_a+1)}{2j_a}\sum_{k>0}\Gamma_{j_a k\, j_a}\frac{1}{2}Y_k(aa,r)\right]dr\end{aligned} \quad (3\text{-}1\text{-}65)$$

and

$$\begin{aligned}\delta E^C_{ab} = 2\int_0^\infty &\left[P_a\delta P_a + Q_a\delta Q_a\right]\frac{1}{r}Y_0(bb,r)dr \\ &-\sum_{k=0}\Gamma_{j_a k\ j_b}\int_0^\infty\left[\delta P_a P_b + \delta Q_a Q_b\right]\frac{1}{r}Y_k(ab,r)dr\end{aligned} \quad (3\text{-}1\text{-}66)$$

From equations (3-1-59), (3-1-65) and (3-1-66), equation (3-1-60) becomes

$$\begin{aligned}&\delta E_{av} = \\ &2c\,q_a\int_0^\infty dr\left\{\left(P'_a\delta Q_a - Q'_a\delta P_a\right) + \frac{\kappa_a}{r}\left(P_a\delta Q_a + Q_a\delta P_a\right)\right. \\ &\left.-\frac{1}{c}\frac{Z}{r}\left(P_a\delta P_a + Q_a\delta Q_a\right) - 2c\,Q_a\delta Q_a\right\} + 2\,q_a\left(q_a-1\right)\int_0^\infty\left[P_a\delta P_a + Q_a\delta Q_a\right] \\ &\times\frac{1}{r}\left[Y_0(aa,r) - \frac{(2j_a+1)}{2j_a}\sum_{k>0}\Gamma_{j_a k\, j_a}\frac{1}{2}Y_k(aa,r)\right]dr \\ &+2\sum_{b\neq a} q_a q_b\int_0^\infty\left[P_a\delta P_a + Q_a\delta Q_a\right]\frac{1}{r}Y_0(bb,r)dr \\ &-\sum_{b\neq a} q_a q_b\sum_{k=0}\Gamma_{j_a k\, j_b}\int_0^\infty\left[\delta P_a P_b + \delta Q_a Q_b\right]\frac{1}{r}Y_k(ab,r)dr\end{aligned} \quad (3\text{-}1\text{-}67)$$

substitute the above equation into equation (3-1-58), and dividing by $2q_a c$, we get

$$\int_0^\infty dr\Big[\Big(P_a'\delta Q_a-\delta P_a Q_a'\Big)+\frac{\kappa_a}{r}\big(P_a\delta Q_a+Q_a\delta P_a\big)$$

$$-2cQ_a\delta Q_a\Big]-\frac{1}{c}\int_0^\infty\frac{dr}{r}\Big[Z-(q_a-1)Y_0(aa,r)-\sum_{b\neq a}q_bY_0(bb,r)$$

$$+\frac{1}{2}\frac{(q_a-1)(2j_a+1)}{2j_a}\sum_{k>0}\Gamma_{j_ak\,j_a}Y_k(aa,r)\Big]\big(P_a\delta P_a+Q_a\delta Q_a\big)$$

$$-\frac{1}{2c}\sum_{b\neq a}q_b\sum_{k=0}\Gamma_{j_ak\,j_b}\int_0^\infty\frac{dr}{r}Y_k(ab,r)\big(\delta P_aP_b+\delta Q_aQ_b\big)$$

$$-\frac{1}{c}\lambda_{aa}\int_0^\infty\big(P_a\delta P_a+Q_a\delta Q_a\big)dr$$

$$-\frac{1}{c}\sum_{b\neq a}\delta(\kappa_a,\kappa_b)q_b\lambda_{ab}\int_0^\infty\big(\delta P_aP_b+\delta Q_aQ_b\big)dr=0 \qquad (3\text{-}1\text{-}68)$$

Introduce the function

$$Y_a(r)=Z-(q_a-1)Y_0(aa,r)$$

$$-\sum_{b\neq a}q_bY_0(bb,r)+\frac{1}{2}\frac{(q_a-1)(2j_a+1)}{2j_a}\sum_{k>0}\Gamma_{j_ak\,j_a}Y_k(aa,r) \qquad (3\text{-}1\text{-}69)$$

equation (3-1-68) becomes

$$\int_0^\infty dr\Big[\Big(P_a'\delta Q_a-\delta P_aQ_a'\Big)+\frac{\kappa_a}{r}\big(P_a\delta Q_a+Q_a\delta P_a\big)$$

$$-2cQ_a\delta Q_a\Big]-\frac{1}{c}\int_0^\infty\frac{dr}{r}Y_a(r)\big(P_a\delta P_a+Q_a\delta Q_a\big)$$

$$-\frac{1}{2c}\sum_{b\neq a}q_b\sum_{k=0}\Gamma_{j_ak\,j_b}\int_0^\infty\frac{dr}{r}Y_k(ab,r)\big(\delta P_aP_b+\delta Q_aQ_b\big) \qquad (3\text{-}1\text{-}70)$$

$$-\frac{1}{c}\lambda_{aa}\int_0^\infty\big(P_a\delta P_a+Q_a\delta Q_a\big)dr$$

$$-\frac{1}{c}\sum_{b\neq a}\delta(\kappa_a,\kappa_b)q_b\lambda_{ab}\int_0^\infty\big(\delta P_aP_b+\delta Q_aQ_b\big)dr=0$$

The coefficient of δQ_a and $-\delta P_a$

$$P'_a + \frac{\kappa_a}{r} P_a - \left[2c + \frac{1}{c}\left(\varepsilon_a + \frac{Y_a(r)}{r} \right) \right] Q_a = X^P_a(r) \qquad \text{(3-1-71a)}$$

$$Q'_a - \frac{\kappa_a}{r} Q_a + \frac{1}{c}\left(\varepsilon_a + \frac{Y_a(r)}{r} \right) P_a = - X^Q_a(r) \qquad \text{(3-1-71b)}$$

where we denote

$\varepsilon_a = \lambda_{aa}$, $\varepsilon_{ab} = \lambda_{ab}$

and

$$X^P_a(r) = \frac{1}{c} \sum_{b \neq a} q_b \left[\frac{1}{2} \sum_{k=0} \Gamma_{j_a k j_b} \frac{Y_k(ab,r)}{r} + \delta(\kappa_a, \kappa_b) \varepsilon_{ab} \right] Q_b \qquad \text{(3-1-72)}$$

$$X^Q_a(r) = \frac{1}{c} \sum_{b \neq a} q_b \left[\frac{1}{2} \sum_{k=0} \Gamma_{j_a k j_b} \frac{Y_k(ab,r)}{r} + \delta(\kappa_a, \kappa_b) \varepsilon_{ab} \right] P_b \qquad \text{(3-1-73)}$$

equations (3-1-71) are called Dirac-Fock equations.

3-2- The Relativistic Koopman's Theorem

We multiply equation (3-1-71a) by cQ_a and equation (3-1-71b) by $-cP_a$ and using (3-1-72) and (3-1-73), yield

$$c P'_a Q_a + c \frac{\kappa_a}{r} P_a Q_a - 2c Q_a^2 - \frac{Y_a(r)}{r} Q_a^2 - \frac{1}{2} \sum_{b \neq a} q_b \sum_{k=0} \Gamma_{j_a k j_b} \frac{Y_k(ab,r)}{r} Q_a Q_b$$

$$= \varepsilon_a Q_a^2 + \sum_{b \neq a} \delta(\kappa_a, \kappa_b) q_b Q_a Q_b \varepsilon_{ab} \qquad \text{(3 - 2 - 1)}$$

$$- c P_a Q'_a + c \frac{\kappa_a}{r} P_a Q_a - \frac{Y_a(r)}{r} P_a^2 - \frac{1}{2} \sum_{b \neq a} q_b \sum_{k=0} \Gamma_{j_a k j_b} \frac{Y_k(ab,r)}{r} P_a P_b$$

$$= \varepsilon_a P_a^2 + \sum_{b \neq a} \delta(\kappa_a, \kappa_b) q_b P_a P_b \varepsilon_{ab} \qquad \text{(3 - 2 - 2)}$$

adding, and integrating over r from zero to infinity, we get

$$\varepsilon_a = c\int_0^\infty dr\left[(P_a' Q_a + \frac{\kappa_a}{r} P_a Q_a) - (P_a Q_a' - \frac{\kappa_a}{r} P_a Q_a) - 2c Q_a^2\right] \qquad (3-2-3)$$
$$-\int_0^\infty \frac{Y_a(r)}{r}(P_a^2 + Q_a^2)dr - \frac{1}{2}\sum_{b\neq a} q_b \sum_{k=0} \Gamma_{j_a k j_b} \int_0^\infty \frac{Y_k(ab,r)}{r}(P_a P_b + Q_a Q_p)dr$$

by using equation (3-1-69)

$$\varepsilon_a = I(a,a) + (q_a - 1)\left[F_0(aa) - \frac{1}{2}\sum_{b\neq a}\frac{(2j_a+1)}{2j_a}\sum_{k>0}\Gamma_{j_a k j_a} F_k(aa)\right] \qquad (3-2-4)$$
$$+\sum_{b\neq a} q_b\left[F_0(ab) - \frac{1}{2}\sum_{k=0}\Gamma_{j_a k j_b} G_k(ab)\right]$$

and finally from equation (3-1-21), yield

$$\varepsilon_a = I(a,a) + (q_a - 1)E_{aa}^c + \sum_{b\neq a} q_b E_{ab}^c \qquad (3-2-5)$$

This quantity is the energy associated with an electron in subshell according to (3-1-20), which is equal to the relativistic configuration-average binding energy of an electron in the subshell a [29].

The Dirac-Fock energy eigenvalue ε_c is related to the energy required to remove an electron from the subshell c. The energy of an ion is:

$$E_{ion} = \sum_a I(a,a) - I(c,c) + \frac{1}{2}\sum_{ab}(g_{abab} - g_{abba}) - \sum_a (g_{acac} - g_{acca}) \qquad (3-2-6)$$

$$E_{ion} - E_{atom} = -I(c,c) - \sum_a (g_{acac} - g_{acca}) = -\varepsilon_c \qquad (3-2-7)$$

Thus, the removal energy, calculated using Dirac-Fock wave function for the atom, is the negative of the corresponding Dirac-Fock eigenvalue. This result is called Koopman's theorem [29].

3-3- Off- Diagonal Energy Parameters

As in the nonrelativistic case, we can obtain relation to determine the off-diagonal energy parameters, by multiplying equation (3-1-71a) by Q_b and equation (3-1-71b) by P_b, subtract and integrating over r from zero to infinity, we get

$$\frac{\varepsilon_{ab}}{q_b} = I(a,b) + \int_0^\infty \left[\frac{1}{r}(Z - Y_a(r))(P_a P_b + Q_a Q_b) - c(\xi_a^P Q_b + \xi_a^Q P_b) \right] dr \quad (3-3-1)$$

where

$$\xi_a^P(r) = \frac{1}{c} \sum_{b \neq a} q_b \left[\frac{1}{2} \sum_{k=0} \Gamma_{j_a k j_b} \frac{Y_k(ab,r)}{r} \right] Q_b \quad (3-3-2)$$

$$\xi_a^Q(r) = \frac{1}{c} \sum_{b \neq a} q_b \left[\frac{1}{2} \sum_{k=0} \Gamma_{j_a k j_b} \frac{Y_k(ab,r)}{r} \right] P_b \quad (3-3-3)$$

and

$$I(a,b) = c \int_0^\infty dr \left[Q_b (P_a' + \frac{\kappa_a}{r} P_a) - P_b (Q_a' - \frac{\kappa_a}{r} Q_a) - 2c Q_a Q_b \right] - \int_0^\infty \frac{Z}{r} (P_a P_b + Q_a Q_b) dr \quad (3-3-4)$$

CHAPTER 4

BREIT INTERACTION

The relativistic Hamiltonian which we have used so far has been constructed in a simple manner; we have taken the non-relativistic form, and replaced the terms corresponding to the single-particle interactions by their relativistic equivalents, leaving the two-particle interaction terms unchanged. A correct relativistic treatment of the many-electron problem is much more complicated than this; the main effect neglected is contained in the Breit interaction. The correction to the Coulomb repulsion between two electrons due to the exchange of a virtual photon is referred to as the Breit interaction [47].

The Breit interaction is given by [48,49]

$$B_\omega(i,j) = -\frac{\vec{\alpha}(i)\cdot\vec{\alpha}(j)}{r_{ij}}\cos(\omega r_{ij}) + \left(\vec{\alpha}(i)\cdot\vec{\nabla}(i)\right)\left(\vec{\alpha}(j)\cdot\vec{\nabla}(j)\right)\frac{\cos(\omega r_{ij})-1}{\omega^2 r_{ij}} \tag{4-1}$$

where ω is the frequency of the virtual photon exchanged between the interacting electrons.

The Breit operator may be written in its long wavelength limit (independent frequency) [٥٠,٥١,٥٢]

$$B_0(i,j) = -\left[\frac{\vec{\alpha}(i)\cdot\vec{\alpha}(j)}{r_{ij}} + \frac{1}{2}\left(\vec{\alpha}(i)\cdot\vec{\nabla}(i)\right)\left(\vec{\alpha}(j)\cdot\vec{\nabla}(j)\right)r_{ij}\right] \tag{4-2}$$

where the Taylor series expansion of the cosine is used

where the magnetic (Gaunt) term

$$g^{M}(i,j)=\frac{\vec{\alpha}(i)\cdot\vec{\alpha}(j)}{r_{ij}} \tag{4-3}$$

and the retardation term

$$g^{R}(i,j)=\frac{1}{2}\left(\vec{\alpha}(i)\cdot\vec{\nabla}(i)\right)\left(\vec{\alpha}(j)\cdot\vec{\nabla}(j)\right)r_{ij} \tag{4-4}$$

We deal first with the magnetic term.

Using the definition of the $\vec{\alpha}$-Dirac matrix in equation (2-6-2), then equation (4-3) becomes

$$g^{M}(1,2)=\begin{pmatrix}0 & \vec{\sigma}(1)\\ \vec{\sigma}(1) & 0\end{pmatrix}.\begin{pmatrix}0 & \vec{\sigma}(2)\\ \vec{\sigma}(2) & 0\end{pmatrix}\frac{1}{r_{12}} \tag{4-5}$$

The energy correction due to the magnetic term is:

$$\begin{aligned}E^{M}&=\left\langle\Phi\left|\frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N}g^{M}(i,j)\right|\Phi\right\rangle\\&=\frac{1}{2}\sum_{ab}\left(\langle ab|\,g^{M}(1,2)\,|ab\rangle-\langle ab|\,g^{M}(1,2)\,|ba\rangle\right)\\&=\frac{1}{2}\sum_{ab}\left(g^{M}_{abab}-g^{M}_{abba}\right)\end{aligned} \tag{4-6}$$

Where g^{M}_{abab} and g^{M}_{abba} are the direct and exchange matrix element of the magnetic term respectively, which, in general, can be written as:

$$g^{M}_{abcd}=\int_{0}^{\infty}\int_{0}^{\infty}\phi^{\dagger}_{a}(\vec{r}_1)\phi^{\dagger}_{b}(\vec{r}_2)\,g^{M}(1,2)\,\phi_{c}(\vec{r}_1)\phi_{d}(\vec{r}_2)\,d\vec{r}_1\,d\vec{r}_2 \tag{4-7}$$

Where $\phi(\vec{r})$ is given by equation (3-1-4).

A general matrix element of the magnetic term can be evaluated by inserting equations (3-1-23) and (4-5) into equation (4-7).

$$\begin{aligned}g^{M}_{abcd}=&\langle u_a u_b|M|v_c v_d\rangle+\langle u_a v_b|M|v_c u_d\rangle\\&+\langle v_a u_b|M|u_c v_d\rangle+\langle v_a v_b|M|u_c u_d\rangle\end{aligned} \tag{4-8}$$

where

$$M=\left(\vec{\sigma}(1).\vec{\sigma}(2)\right)\frac{1}{r_{12}} \tag{4-9}$$

Using equation (3-1-22) to expand the M -operator in the form

$$M = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \left(C^k(1).C^k(2)\right)\left(\vec{\sigma}(1)\cdot\vec{\sigma}(2)\right) \tag{4-10}$$

Dealing with the first term in equation (4-8)

From equation (3-1-4) and (4-10), the first term becomes

$$\begin{aligned}\langle u_a u_b|M|v_c v_d\rangle = -\sum_k \langle P_a P_b|\frac{r_<^k}{r_>^{k+1}}|Q_c Q_d\rangle \\ \times\langle \Omega_a \Omega_b|\left(C^k(1).C^k(2)\right)\left(\vec{\sigma}(1)\cdot\vec{\sigma}(2)\right)|\Omega_{-c}\Omega_{-d}\rangle\end{aligned} \tag{4-11}$$

Using equation (3-1-6), then equation (4-11) becomes

$$\begin{aligned}&\langle u_a u_b|M|v_c v_d\rangle = -\sum_k \langle P_a P_b|\frac{r_<^k}{r_>^{k+1}}|Q_c Q_d\rangle \\ &\times \sum_{\mu_a\mu_c} C(l_a,1/2,j_a;m_a-\mu_a,\mu_a,m_a)C(\bar{l}_c,1/2,j_c;m_c-\mu_c,\mu_c,m_c) \\ &\times \sum_{\mu_b\mu_d} C(l_b,1/2,j_b;m_b-\mu_b,\mu_b,m_b)C(\bar{l}_d,1/2,j_d;m_d-\mu_d,\mu_d,m_d) \\ &\times\left\langle Y^{l_a}_{m_a-\mu_a} Y^{l_b}_{m_b-\mu_b}\middle| C^k(1).C^k(2)\middle| Y^{\bar{l}_c}_{m_c-\mu_c} Y^{\bar{l}_d}_{m_d-\mu_d}\right\rangle\left\langle \chi^{1/2}_{\mu_a}\chi^{1/2}_{\mu_b}\middle|\vec{\sigma}(1)\cdot\vec{\sigma}(2)\middle|\chi^{1/2}_{\mu_c}\chi^{1/2}_{\mu_d}\right\rangle\end{aligned} \tag{4 - 12}$$

Using Wigner-Eckart theorem, then the matrix element of the scalar product of the tensor operators becomes [1٧]

$$\begin{aligned}&\langle l_a, m_a-\mu_a; l_b, m_b-\mu_b|C^k(1).C^k(2)|\bar{l}_c, m_c-\mu_c; \bar{l}_d, m_d-\mu_d\rangle \\ &= (-1)^{l_a-m_a+\mu_a+l_b-m_b+\mu_b}\frac{\langle l_a\|C^k(1)\|\bar{l}_c\rangle}{\sqrt{2k+1}}\frac{\langle l_b\|C^k(2)\|\bar{l}_d\rangle}{\sqrt{2k+1}} \\ &\times C(l_a,k,\bar{l}_c;m_a-\mu_a,\mu_a-m_a-\mu_c+m_c,m_c-\mu_c) \\ &\times C(l_b,k,\bar{l}_d;m_b-\mu_b,\mu_b-m_b+m_d-\mu_d,m_d-\mu_d)\end{aligned} \tag{4-13}$$

With

$$\begin{aligned}\langle l_1\|C^k\|l_2\rangle &= C(l_1 k l_2;000)\left[\frac{(2l_1+1)(2l_2+1)}{(2k+1)}\right]^{1/2} \quad \text{if } l_1+l_2+k=even \\ &= 0 \qquad\qquad\qquad\qquad\qquad\qquad\quad \text{if } l_1+l_2+k=odd\end{aligned} \tag{4-14}$$

and

$$\left\langle \chi^{1/2}_{\mu_a}\chi^{1/2}_{\mu_b}\middle|\vec{\sigma}(1)\cdot\vec{\sigma}(2)\middle|\chi^{1/2}_{\mu_c}\chi^{1/2}_{\mu_d}\right\rangle = 2(-1)^{1-\mu_a-\mu_b}\delta(\mu_a+\mu_b,\mu_c+\mu_d) \times C(\tfrac{1}{2}1\tfrac{1}{2};\mu_a,\mu_c-\mu_a,\mu_c)\,C(\tfrac{1}{2}1\tfrac{1}{2};\mu_b,\mu_d-\mu_b,\mu_d) \tag{4-15}$$

Therefore equation (4-12) can be written as:

$$\begin{aligned}
&\langle u_a u_b|M|v_c v_d\rangle = -2\sum_k \left\langle P_a P_b\middle|\frac{r_<^k}{r_>^{k+1}}\middle|Q_c Q_d\right\rangle \\
&\times \sum_{\mu_a\mu_c}\sum_{\mu_b\mu_d} C(l_a,1/2,j_a;m_a-\mu_a,\mu_a,m_a)C(\bar{l}_c,1/2,j_c;m_c-\mu_c,\mu_c,m_c) \\
&\times C(\tfrac{1}{2}1\tfrac{1}{2};\mu_a,\mu_c-\mu_a,\mu_c)C(\tfrac{1}{2}1\tfrac{1}{2};\mu_b,\mu_d-\mu_b,\mu_d)(-1)^{l_a-m_a+1/2}(-1)^{l_b-m_b+1/2} \\
&\times C(l_a,k,\bar{l}_c;m_a-\mu_a,\mu_a-m_a-\mu_c+m_c,m_c-\mu_c)\frac{\langle l_a\|C^k(1)\|\bar{l}_c\rangle}{\sqrt{2k+1}} \qquad (4\text{-}16)\\
&\times C(l_b,1/2,j_b;m_b-\mu_b,\mu_b,m_b)C(\bar{l}_d,1/2,j_d;m_d-\mu_d,\mu_d,m_d) \\
&\times C(l_b,k,\bar{l}_d;m_b-\mu_b,\mu_b-m_b+m_d-\mu_d,m_d-\mu_d)\frac{\langle l_b\|C^k(2)\|\bar{l}_d\rangle}{\sqrt{2k+1}}
\end{aligned}$$

The summations over $\mu_a\mu_c$ and $\mu_b\mu_d$ in the above equation can be performed by using the formula [1٧]

$$\begin{aligned}
&\sum_{\mu\mu'}(-1)^{l-m+1/2}C(l,1/2,j;m-\mu,\mu,m)C(l',1/2,j';m'-\mu',\mu',m') \\
&\times C(l,k,l';m-\mu,m'-m+\mu-\mu',m'-\mu')C(\tfrac{1}{2}1\tfrac{1}{2};\mu,\mu'-\mu,\mu') \qquad (4\text{-}17)\\
&= \sum_J C(jJj',m,m'-m,m')\left[3(2j+1)(2j'+1)(2k+1)\right]^{1/2}\begin{Bmatrix} l & 1/2 & j \\ l' & 1/2 & j' \\ k & 1 & J \end{Bmatrix}
\end{aligned}$$

Where $\begin{Bmatrix} l & 1/2 & j \\ l' & 1/2 & j' \\ k & 1 & J \end{Bmatrix}$ is the 9-j symbol.

Equation (4-16) becomes

$$\langle u_a u_b|M|v_c v_d\rangle = -2\sum_{kJ}\langle P_a P_b|\frac{r_<^k}{r_>^{k+1}}|Q_c Q_d\rangle$$
$$\times C(j_a\, J\, j_c, m_a, m_c - m_a, m_c)\, e_J^k(j_a l_a, j_c \bar{l}_c) \qquad (4\text{-}18)$$
$$\times C(j_b\, J\, j_d, m_b, m_d - m_b, m_d)\, e_J^k(j_b l_b, j_d, \bar{l}_d)$$

Where

$$e_J^k(jl, j'l') = [3(2j+1)(2j'+1)]^{1/2}\langle l\|C^k\|l'\rangle \begin{Bmatrix} l & 1/2 & j \\ l' & 1/2 & j' \\ k & 1 & J \end{Bmatrix} \qquad (4\text{-}19)$$

The integer J takes only the values $k-1$, k, $k+1$ to satisfy the triangular conditions of the 9-j symbols, and the allowed values of k are determined from those of the Clebsch-Gordan coefficients in equation (4-14)

$$|l - l'| \le k \le l + l'$$
and (4-20)
$$l + k + l' = even$$

The rest of the terms in equation (4-8), may now be deduced from equation (4-18)

$$\langle u_a v_b|M|v_c u_d\rangle = 2\sum_{kJ}\langle P_a Q_b|\frac{r_<^k}{r_>^{k+1}}|Q_c P_d\rangle$$
$$\times C(j_a\, J\, j_c, m_a, m_c - m_a, m_c)\, e_J^k(j_a l_a, j_c \bar{l}_c) \qquad (4\text{-}21)$$
$$\times C(j_b\, J\, j_d, m_b, m_d - m_b, m_d)\, e_J^k(j_b \bar{l}_b, j_d, l_d)$$

$$\langle v_a u_b|M|u_c v_d\rangle = 2\sum_{kJ}\langle Q_a P_b|\frac{r_<^k}{r_>^{k+1}}|P_c Q_d\rangle$$
$$\times C(j_a\, J\, j_c, m_a, m_c - m_a, m_c)\, e_J^k(j_a \bar{l}_a, j_c, l_c) \qquad (4\text{-}22)$$
$$\times C(j_b\, J\, j_d, m_b, m_d - m_b, m_d)\, e_J^k(j_b l_b, j_d \bar{l}_d)$$

$$\langle v_a v_b|M|u_c u_d\rangle = -2\sum_{kJ}\left\langle Q_a Q_b\left|\frac{r_<^k}{r_>^{k+1}}\right|P_c P_d\right\rangle$$

$$\times C(j_a J\, j_c, m_a, m_c - m_a, m_c)\, e_J^k(j_a \bar{l}_a, j_c, l_c) \qquad (4\text{-}23)$$

$$\times C(j_b J\, j_d, m_b, m_d - m_b, m_d)\, e_J^k(j_b \bar{l}_b, j_d, l_d)$$

Therefore, equation (4-8) becomes

$$g_{abcd}^M = 2\sum_{kJ} C(j_a J\, j_c, m_a, m_c - m_a, m_c) C(j_b J\, j_d, m_b, m_d - m_b, m_d)$$

$$\times\Bigg\{-\left\langle P_a P_b\left|\frac{r_<^k}{r_>^{k+1}}\right|Q_c Q_d\right\rangle e_J^k(j_a l_a, j_c \bar{l}_c)\, e_J^k(j_b l_b, j_d, \bar{l}_d)$$

$$+\left\langle P_a Q_b\left|\frac{r_<^k}{r_>^{k+1}}\right|Q_c P_d\right\rangle e_J^k(j_a l_a, j_c \bar{l}_c)\, e_J^k(j_b \bar{l}_b, j_d, l_d) \qquad (4\text{-}24)$$

$$+\left\langle Q_a P_b\left|\frac{r_<^k}{r_>^{k+1}}\right|P_c Q_d\right\rangle e_J^k(j_a \bar{l}_a, j_c, l_c)\, e_J^k(j_b l_b, j_d \bar{l}_d)$$

$$-\left\langle Q_a Q_b\left|\frac{r_<^k}{r_>^{k+1}}\right|P_c P_d\right\rangle e_J^k(j_a \bar{l}_a, j_c, l_c)\, e_J^k(j_b \bar{l}_b, j_d l_d)\Bigg\}$$

For the direct part of the magnetic interaction, we put a=c, b=d in equation (4-24), then we get

$$g_{abab}^M = \sum_k f^k(j_a m_a, j_b m_b)\, F_k^M(a,b) \qquad (4\text{-}25)$$

Where

$$f^k(j_a m_a, j_b m_b) = 2\sum_J C(j_a J\, j_a; m_a, 0, m_a)\, C(j_b J\, j_b; m_b, 0, m_b)$$

$$\times\Big\{-e_J^k(j_a l_a; j_a \bar{l}_a)\, e_J^k(j_b l_b; j_b \bar{l}_b) + e_J^k(j_a l_a; j_a \bar{l}_a)\, e_J^k(j_b \bar{l}_b; j_b l_b) \qquad (4\text{-}26)$$

$$+e_J^k(j_a \bar{l}_a; j_a l_a)\, e_J^k(j_b l_b; j_b \bar{l}_b) - e_J^k(j_a \bar{l}_a; j_a l_a)\, e_J^k(j_b \bar{l}_b; j_b l_b)\Big\}$$

and

$$F_k^M(a,b) = \int_0^\infty\int_0^\infty P_a(r_1) Q_a(r_1) \frac{r_<^k}{r_>^{k+1}} P_b(r_2) Q_b(r_2)\, d r_1\, d r_2 \qquad (4\text{-}27)$$

From the symmetry relation [27]

$$e_J^k(j_b l_b; j_a \bar{l}_a) = (-1)^{1+k+J} e_J^k(j_a \bar{l}_a; j_b l_b) \tag{4-28}$$

It is noticed that $f^k(j_a m_a, j_b m_b)$ vanishes unless $k + J$ is even. From equation (4-20), $l + \bar{l} + k$ must be even and since $l + \bar{l}$ is odd [١٧], k must be odd. Hence $J = k$ and we have

$$\begin{aligned} f^k(j_a m_a, j_b m_b) = -8C(j_a k\, j_a; m_a, 0, m_a)\, C(j_b k\, j_b; m_b, 0, m_b) \\ \times e_k^k(j_a l_a; j_a \bar{l}_a) e_k^k(j_b l_b; j_b \bar{l}_b) \end{aligned} \tag{4-29}$$

For the exchange part

$$\begin{aligned} g_{abba}^M = 2\sum_{kJ} (-1)^{1+k+J} \left[C(j_a J\, j_b, m_a, m_b - m_a, m_b)\right]^2 \\ \times \Big\{ G_k^M(ab, ab)\left[e_J^k(j_a l_a, j_b \bar{l}_b)\right]^2 + G_k^M(ba, ba)\left[e_J^k(j_a \bar{l}_a, j_b l_b)\right]^2 \\ - 2 G_k^M(ab, ba)\, e_J^k(j_a \bar{l}_a, j_b l_b)\, e_J^k(j_a l_a, j_b \bar{l}_b) \Big\} \end{aligned} \tag{4-30}$$

Where

$$G_k^M(ab, cd) = \int_0^\infty \int_0^\infty P_a(r_1) Q_b(r_1) \frac{r_<^k}{r_>^{k+1}} P_c(r_2) Q_d(r_2) d r_1 d r_2 \tag{4-31}$$

From equation (4-6), the configuration average energy correction due to the magnetic term is:

$$E_{av}^M = \frac{1}{2} \sum_{\mathrm{a}} q_a (q_a - 1) E_{aa}^M + \frac{1}{2} \sum_a \sum_{\mathrm{b} \neq \mathrm{a}} q_a q_b E_{ab}^M \tag{4-32}$$

Where

$$E_{aa}^M = \left(g_{abab}^M\right)_{av} - \left(g_{abba}^M\right)_{av} \qquad \text{with} \quad a = b \tag{4-33}$$

$$E_{ab}^M = \left(g_{abab}^M\right)_{av} - \left(g_{abba}^M\right)_{av} \qquad \text{with} \quad a \neq b \tag{4-34}$$

Where the averaging over m_a and m_b

From [٤٦], we obtain

$$\sum_{m_b} f^k(j_a m_a, j_b m_b) = 0 \tag{4-35}$$

and hence

$$\sum_{m_b} g^M_{abab} = 0 \tag{4-36}$$

The averaging over the exchange part is:

$$\begin{aligned}\sum_{m_b} g^M_{abba} = 2\sum_{kJ}(-1)^{1+k+J}\Big\{ & G^M_k(ab,ab)\left[e^k_J(j_a l_a, j_b \bar{l}_b)\right]^2 \\ & + G^M_k(ba,ba)\left[e^k_J(j_a \bar{l}_a, j_b l_b)\right]^2 \\ & - 2G^M_k(ab,ba)\, e^k_J(j_a \bar{l}_a, j_b l_b)\, e^k_J(j_a l_a, j_b \bar{l}_b)\Big\}\end{aligned} \tag{4-37}$$

Where, from [١7]

$$\sum_{m_b}\left[C(j_a J\ j_b, m_a, m_b - m_a, m_b)\right]^2 = 1 \tag{4-38}$$

From equations (4-36) and (4-37), equations (4-33) and (4-34) becomes

$$\begin{aligned}E^M_{aa} = \frac{1}{j_a}\sum_{kJ}(-1)^{1+k+J} F^M_k(a,a)\Big\{ & 2(-1)^{1+k+J}\left[e^k_J(j_a l_a, j_a \bar{l}_a)\right]^2 \\ & - \left[e^k_J(j_a l_a, j_a \bar{l}_a)\right]^2 - \left[e^k_J(j_a l_a, j_a \bar{l}_a)\right]^2\Big\}\end{aligned} \tag{4-39}$$

Where, equation (4-28) is used, and the fact that

$$F^M_k(a,a) = G^M_k(aa,aa) \tag{4-40}$$

Equation (4-39) will not vanish only if $k + J$ is even. From equation (4-20), $l + \bar{l} + k$ must be even and since $l + \bar{l}$ is odd [1٧], k must be odd. Hence $J = k$ and we have

$$E^M_{aa} = \frac{4}{j_a}\sum_{k(odd)}\left[e^k_k(j_a l_a, j_a \bar{l}_a)\right]^2 F^M_k(a,a) \tag{4-41}$$

and

$$\begin{aligned}E^M_{ab} = -\frac{2}{2j_b+1}\sum_{kJ}(-1)^{1+k+J}\Big\{ & G^M_k(ab,ab)\left[e^k_J(j_a l_a, j_b \bar{l}_b)\right]^2 \\ & + G^M_k(ba,ba)\left[e^k_J(j_a \bar{l}_a, j_b l_b)\right]^2 - 2G^M_k(ab,ba)\, e^k_J(j_a \bar{l}_a, j_b l_b)\, e^k_J(j_a l_a, j_b \bar{l}_b)\Big\}\end{aligned} \tag{4 - 42}$$

From equation (4-32), (4-41) and (4-42) the configuration average energy correction due to the magnetic term is:

$$E_{av}^{M} = 2\sum_{\mathrm{a}} q_a\left(q_a - 1\right)\frac{1}{j_a}\sum_{k(odd)}\left[e_k^k(j_a l_a, j_a \bar{l}_a)\right]^2 F_k^{M}(a,a)$$

$$-\sum_{a}\sum_{\mathrm{b}\neq\mathrm{a}} q_a q_b \frac{1}{2j_b+1}\sum_{kJ}(-1)^{1+k+J}\left\{G_k^M(ab,ab)\left[e_J^k(j_a l_a, j_b \bar{l}_b)\right]^2\right. \qquad (4-43)$$

$$\left. + G_k^M(ba,ba)\left[e_J^k(j_a \bar{l}_a, j_b l_b)\right]^2 - 2G_k^M(ab,ba)\, e_J^k(j_a \bar{l}_a, j_b l_b)\, e_J^k(j_a l_a, j_b \bar{l}_b)\right\}$$

Dealing now with the retardation term.

The retardation operator can be simplified by using the definition of the α-Dirac matrix in equation (2-6-2), then equation (4-4) becomes

$$g^R(i,j) = \frac{1}{2}\begin{pmatrix} 0 & \left(\vec{\sigma}(i)\cdot\vec{\nabla}(i)\right) \\ \left(\vec{\sigma}(i)\cdot\vec{\nabla}(i)\right) & 0 \end{pmatrix}\cdot\begin{pmatrix} 0 & \left(\vec{\sigma}(j)\cdot\vec{\nabla}(j)\right) \\ \left(\vec{\sigma}(j)\cdot\vec{\nabla}(j)\right) & 0 \end{pmatrix} r_{ij} \qquad (4-44)$$

The energy correction due to the retardation term is:

$$E^R = \left\langle \Phi \left| \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} g^R(i,j) \right| \Phi \right\rangle$$

$$= \frac{1}{2}\sum_{ab}\left(\langle ab| g^R(1,2)|ab\rangle - \langle ab| g^R(1,2)|ba\rangle\right) \qquad (4-45)$$

$$= \frac{1}{2}\sum_{ab}\left(g^R_{abab} - g^R_{abba}\right)$$

Where g^R_{abab} and g^R_{abba} are the direct and exchange matrix element of the retardation term respectively, which, in general, can be written as:

$$g^R_{abcd} = \int_0^\infty\int_0^\infty \phi_a^\dagger(\vec{r}_1)\phi_b^\dagger(\vec{r}_2)\, g^R(1,2)\,\phi_c(\vec{r}_1)\phi_d(\vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2 \qquad (4-46)$$

Where $\phi(\vec{r})$ is given by equation (3-1-4).

A general matrix element of the retardation term can be evaluated by inserting equations (3-1-14) and (4-44) into equation (4-46), and we have

$$g^{R}_{abcd} = \langle u_a u_b | R | v_c v_d \rangle + \langle u_a v_b | R | v_c u_d \rangle + \langle v_a u_b | R | u_c v_d \rangle + \langle v_a v_b | R | u_c u_d \rangle \quad (4\text{-}47)$$

Where

$$R = \frac{1}{2}\left(\vec{\sigma}(1)\cdot\vec{\nabla}(1)\right)\left(\vec{\sigma}(2)\cdot\vec{\nabla}(2)\right) r_{12} \quad (4\text{-}48)$$

The interelectronic distance r_{12} may be expanded as [٥٣]

$$r_{12} = \sum_k W_k(1,2)\, C^k(1)\cdot C^k(2) \quad (4\text{-}49)$$

Where

$$W_k(1,2) = \frac{r_<^k}{r_>^{k+1}}\left[\frac{r_<^2}{(2k+3)} - \frac{r_>^2}{(2k-1)}\right] \quad (4\text{-}50)$$

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

Equation (4-48), becomes

$$R = \frac{1}{2}\sum_k \left(\vec{\sigma}(1)\cdot\vec{\nabla}(1)\right)\left(\vec{\sigma}(2)\cdot\vec{\nabla}(2)\right)\left(C^k(1)\cdot C^k(2)\right) W_k(1,2) \quad (4\text{-}51)$$

Performing the scalar product between the tensor operators, we obtain

$$R = \frac{1}{2}\sum_k \sum_{pmq} (-1)^{p+m+q} \times \left(\sigma_{-p}(1)\nabla_p(1)\right)\left(\sigma_{-m}(2)\nabla_m(2)\right)\left(C^k_{-q}(1)\, C^k_q(2)\right) W_k(1,2) \quad (4\text{-}52)$$

From [١٧], we get

$$C^k_q(i)\nabla_p(i) = \sum_\omega \frac{1}{\sqrt{2k+1}} C(k1\omega;000) C(k1\omega; q, p, q+p)\, C^\omega_{p+q}(i)\, \partial_\omega(i) \quad (4\text{-}53)$$

Where

$$\partial_\omega(i) = \frac{\partial}{\partial r_i} - \frac{k}{r_i} \quad \text{if } \omega = k+1$$
$$= \frac{\partial}{\partial r_i} + \frac{k+1}{r_i} \quad \text{if } \omega = k-1 \quad (4\text{-}54)$$
$$= 0 \quad \text{otherwise}$$

Therefore, equation (4-52) becomes

$$R=\frac{1}{2}\sum_{k\lambda\omega pmq}\sum(-1)^{p+m+q}\frac{1}{(2k+1)}\partial_{\lambda}(1)\partial_{\omega}(2)W_k(1,2)$$
$$\times C(k1\lambda;000)C(k1\lambda;-q,p,p-q)\sigma_{-p}(1)C^{\lambda}_{p-q}(1) \qquad (4\text{-}55)$$
$$\times C(k1\omega;000)C(k1\omega;q,m,q+m)\sigma_{-m}(2)C^{\omega}_{q+m}(2)$$

In this context the differentiations apply to the $W_k(1,2)$ and not to the wave function on which g^R operates.

Dealing with the first term in equation (4-47)

From equation (4-55), we obtain

$$\langle u_a u_b|R|v_c v_d\rangle=-\frac{1}{2}\sum_{k\lambda\omega pmq}\sum(-1)^{p+m+q}(2k+1)^{-1}$$
$$\times C(k1\lambda;000)C(k1\lambda;-q,p,p-q)C(k1\omega;000)C(k1\omega;q,m,q+m) \qquad (4\text{-}56)$$
$$\times\langle P_a P_b|\partial_{\lambda}(1)\partial_{\omega}(2)W_k(1,2)|Q_c Q_d\rangle$$
$$\times\langle\kappa_a m_a|\sigma_{-p}(1)C^{\lambda}_{p-q}(1)|-\kappa_c m_c\rangle\langle\kappa_b m_b|\sigma_{-m}(2)C^{\omega}_{m+q}(2)|-\kappa_d m_d\rangle$$

Where

$$\langle\kappa_a m_a|\sigma_p C^{\lambda}_q|\kappa_b m_b\rangle=\int_0^{\infty}\Omega^{\dagger}_a\sigma_p C^{\lambda}_q\Omega_b\sin\theta d\theta d\varphi \qquad (4\text{-}57)$$

Using equation (3-1-6), then equation (4-56) becomes

$$\langle u_a u_b|R|v_c v_d\rangle=-\frac{1}{2}\sum_{k\lambda\omega pmq}\sum_{\mu_a\mu_c}\sum_{\mu_b\mu_d}(-1)^{p+m+q}(2k+1)^{-1}$$
$$\times C(k1\lambda;-q,p,p-q)C(l_a,1/2,j_a;m_a-\mu_a,\mu_a,m_a)$$
$$\times C(\bar{l}_c,1/2,j_c;m_c-\mu_c,\mu_c,m_c)C(k1\lambda;000)$$
$$\times\langle l_a,m_a-\mu_a|C^{\lambda}_{p-q}(1)|\bar{l}_c,m_c-\mu_c\rangle\langle 1/2,\mu_a|\sigma_{-p}(1)|1/2,\mu_c\rangle \qquad (4\text{-}58)$$
$$\times C(k1\omega;q,m,q+m)C(l_b,1/2,j_b;m_b-\mu_b,\mu_b,m_b)$$
$$\times C(\bar{l}_d,1/2,j_d;m_d-\mu_d,\mu_d,m_d)C(k1\omega;000)$$
$$\times\langle l_b,m_b-\mu_b|C^{\omega}_{m+q}(2)|\bar{l}_d,m_d-\mu_d\rangle\langle 1/2,\mu_b|\sigma_m(2)|1/2,\mu_d\rangle$$
$$\times\langle P_a P_b|\partial_{\lambda}(1)\partial_{\omega}(2)W_k(1,2)|Q_c Q_d\rangle$$

Using Wigner-Eckart theorem, then the above equation becomes

$$\langle u_a u_b | R | v_c v_d \rangle = -\frac{1}{2} \sum_{k\lambda\omega} \sum_{pmq} \sum_{\mu_a \mu_c} \sum_{\mu_b \mu_d} (-1)^{p+m+q} (2k+1)^{-1}$$

$$\times C(k1\lambda;000) C(k1\omega;000) \frac{\langle l_a \| C^{\lambda}(1) \| \bar{l}_c \rangle}{\sqrt{2\lambda+1}} \frac{\langle l_b \| C^{\omega}(2) \| \bar{l}_d \rangle}{\sqrt{2\omega+1}}$$

$$\times C(l_a, 1/2, j_a; m_a - \mu_a, \mu_a, m_a) C(\bar{l}_c, 1/2, j_c; m_c - \mu_c, \mu_c, m_c)$$

$$\times C(k1\lambda; -q, p, p-q) C(1/2, 1, 1/2; \mu_a, -p, \mu_c)$$

$$\times C(l_a, \lambda, \bar{l}_c; m_a - \mu_a, p-q, m_c - \mu_c) \qquad (4-59)$$

$$\times C(l_b, 1/2, j_b; m_b - \mu_b, \mu_b, m_b) C(\bar{l}_d, 1/2, j_d; m_d - \mu_d, \mu_d, m_d)$$

$$\times C(k1\omega; q, m, q+m) C(1/2, 1, 1/2; \mu_b, -m, \mu_d)$$

$$\times C(l_b \omega, \bar{l}_d; m_b - \mu_b, m+q, m_d - \mu_d)$$

$$\times \frac{\langle 1/2 \| \sigma(1) \| 1/2 \rangle}{\sqrt{3}} \frac{\langle 1/2 \| \sigma(2) \| 1/2 \rangle}{\sqrt{3}} \langle P_a P_b | \partial_{\lambda}(1) \partial_{\omega}(2) W_k(1,2) | Q_c Q_d \rangle$$

Where

$$\langle l_1 \| C^k \| l_2 \rangle = C(l_1 k l_2; 000) \left[\frac{(2l_1+1)(2l_2+1)}{(2k+1)} \right]^{1/2} \quad \text{if } l_1 + l_2 + k = even \qquad (4\text{-}60)$$

$$= 0 \qquad \text{if } l_1 + l_2 + k = odd$$

and

$$\langle 1/2 \| \sigma \| 1/2 \rangle = \sqrt{6} \qquad (4\text{-}61)$$

Because the triangular conditions of the Clebsch-Gordan coefficients in equation (4-59), the summation over p, q and m may be carried out, and their values are limited to

$$p = \mu_a - \mu_c$$
$$m = \mu_b - \mu_d \qquad (4\text{-}62)$$
$$q = m_a - m_c = m_d - m_b$$

Therefore, equation (4-59) can be written as:

$$\langle u_a u_b|R|v_c v_d\rangle = -\sum_{k\lambda\omega}\sum_{\mu_a\mu_c}\sum_{\mu_b\mu_d}(2k+1)^{-1}(-1)^{\mu_a-\mu_c+\mu_b-\mu_d+m_a-m_c}$$
$$\times C(k1\lambda;000)C(k1\omega;000)\frac{\langle l_a\|C^{\lambda}(1)\|\bar{l}_c\rangle}{\sqrt{2\lambda+1}}\frac{\langle l_b\|C^{\omega}(2)\|\bar{l}_d\rangle}{\sqrt{2\omega+1}}$$
$$\times C(l_a,1/2,j_a;m_a-\mu_a,\mu_a,m_a)C(\bar{l}_c,1/2,j_c;m_c-\mu_c,\mu_c,m_c)$$
$$\times C(k1\lambda;m_c-m_a,\mu_a-\mu_c,\mu_a-\mu_c+m_c-m_a)$$
$$\times C(l_a,\lambda,\bar{l}_c;m_a-\mu_a,\mu_a-\mu_c+m_c-m_a,m_c-\mu_c) \qquad (4-63)$$
$$C(1/2,1,1/2;\mu_a,\mu_c-\mu_a,\mu_c)\delta(m_a+m_b,m_c+m_d)$$
$$\times C(l_b,1/2,j_b;m_b-\mu_b,\mu_b,m_b)C(\bar{l}_d,1/2,j_d;m_d-\mu_d,\mu_d,m_d)$$
$$C(k1\omega;m_d-m_b,\mu_b-\mu_d,m_d-m_b+\mu_b-\mu_d)$$
$$\times C(l_b\omega,\bar{l}_d;m_b-\mu_b,m_d-m_b+\mu_b-\mu_d,m_d-\mu_d)$$
$$\times C(1/2,1,1/2;\mu_b,\mu_d-\mu_b,\mu_d)\langle P_a P_b|\partial_{\lambda}(1)\partial_{\omega}(2)W_k(1,2)|Q_c Q_d\rangle$$

The summations over μ_a and μ_c in the above equation can be performed by using the formula [1٧]

$$\sum_{\mu_a\mu_c}(-1)^{\mu_a-\mu_c+m_a}C(l_a,1/2,j_a;m_a-\mu_a,\mu_a,m_a)$$
$$\times C(k1\lambda;m_c-m_a,\mu_a-\mu_c,\mu_a-\mu_c+m_c-m_a)$$
$$\times C(l_a,\lambda,\bar{l}_c;m_a-\mu_a,\mu_a-\mu_c+m_c-m_a,m_c-\mu_c) \qquad (4-64)$$
$$\times C(1/2,1,1/2;\mu_a,\mu_c-\mu_a,\mu_c)C(\bar{l}_c,1/2,j_c;m_c-\mu_c,\mu_c,m_c)$$
$$=\left[3(2j_a+1)(2j_c+1)(2\lambda+1)\right]^{1/2}C(j_a\,k\,j_c;m_a,m_c-m_a,m_c)\begin{Bmatrix} l_a & 1/2 & j_a \\ \bar{l}_c & 1/2 & j_c \\ k & 1 & \lambda \end{Bmatrix}$$

A similar relation also holds for the sum over μ_b and μ_d. With these results, equation (4-63) becomes

$$\langle u_a u_b | R | v_c v_d \rangle = -\sum_{k\lambda\omega} (2k+1)^{-1} C(k1\lambda;000) C(k1\omega;000)$$
$$\times C(j_a, k, j_c; m_a, m_c - m_a, m_c) e_\lambda^k (j_a l_a, j_c \bar{l}_c)$$
$$\times C(j_b k, j_d; m_b, m_d - m_b, m_d) e_\omega^k (j_b l_b, j_d \bar{l}_d) \qquad (4\text{-}65)$$
$$\times \langle P_a P_b | \partial_\lambda(1) \partial_\omega(2) W_k(1,2) | Q_c Q_d \rangle$$

Where, we have used the definition of the e-coefficient given in equation (4-19)

The rest of the matrix element of the retardation term, equation (4-47), may be now deduced from equation (4-65). The general expression for the matrix element of the retardation term is:

$$g^R_{abcd} = -\sum_{k\lambda\omega} (2k+1)^{-1} C(k1\lambda;000) C(k1\omega;000) \qquad (4\text{ - }66)$$
$$\times C(j_a, k, j_c; m_a, m_c - m_a, m_c) C(j_b k, j_d; m_b, m_d - m_b, m_d)$$
$$\times \{ e_\lambda^k (j_a l_a, j_c \bar{l}_c) e_\omega^k (j_b l_b, j_d \bar{l}_d) \langle P_a P_b | \partial_\lambda(1) \partial_\omega(2) W_k(1,2) | Q_c Q_d \rangle$$
$$- e_\lambda^k (j_a l_a, j_c \bar{l}_c) e_\omega^k (j_b \bar{l}_b, j_d l_d) \langle P_a Q_b | \partial_\lambda(1) \partial_\omega(2) W_k(1,2) | Q_c P_d \rangle$$
$$- e_\lambda^k (j_a \bar{l}_a, j_c l_c) e_\omega^k (j_b l_b, j_d \bar{l}_d) \langle Q_a P_b | \partial_\lambda(1) \partial_\omega(2) W_k(1,2) | P_c Q_d \rangle$$
$$+ e_\lambda^k (j_a \bar{l}_a, j_c l_c) e_\omega^k (j_b \bar{l}_b, j_d l_d) \langle Q_a Q_b | \partial_\lambda(1) \partial_\omega(2) W_k(1,2) | P_c P_d \rangle \}$$

The allowed values of λ and ω in the above equation are limited to $k \pm 1$. The values of k are restricted by the triangular condition of the 9-j symbol and the Clebsch Gordan coefficient embedded in the e-coefficients

$$|l - l'| \le k \le l + l'$$
and (4-67)
$$l + k + l' = even$$

From equation (3-3-66) the direct part of the retardation term is:

$$
\begin{aligned}
g^{R}_{abab} &= -\sum_{k\lambda\omega}(2k+1)^{-1} F^{R}_{\lambda\omega k}(a,b) \\
&\times C(k1\lambda;000)C(j_a,k,j_a;m_a,0,m_a)C(k1\omega;000)C(j_b k,j_b;m_b,0,m_b) \\
&\times\{e^{k}_{\lambda}(j_a l_a,j_a\bar{l}_a)e^{k}_{\omega}(j_b l_b,j_b\bar{l}_b)-e^{k}_{\lambda}(j_a l_a,j_a\bar{l}_a)e^{k}_{\omega}(j_b\bar{l}_b,j_b l_b) \\
&-e^{k}_{\lambda}(j_a\bar{l}_a,j_a l_a)e^{k}_{\omega}(j_b l_b,j_b\bar{l}_b)+e^{k}_{\lambda}(j_a\bar{l}_a,j_a l_a)e^{k}_{\omega}(j_b\bar{l}_b,j_b l_b)\}
\end{aligned}
\tag{4-68}
$$

Where

$$
\begin{aligned}
&F^{R}_{\lambda\omega k}(a,b) \\
&=\int_0^\infty\int_0^\infty P_a(r_1)Q_a(r_1)\left[\partial_\lambda(1)\partial_\omega(2)W_k(1,2)\right]P_b(r_2)Q_b(r_2)dr_1dr_2
\end{aligned}
\tag{4-69}
$$

Using the symmetry relation in equation (4-28), then equation (4-68) becomes

$$
\begin{aligned}
g^{R}_{abab} &= -\sum_{k\lambda\omega}(2k+1)^{-1} F^{R}_{\lambda\omega k}(a,b)C(k1\lambda;000)C(j_a,k,j_a;m_a,0,m_a) \\
&\times C(k1\omega;000)C(j_b k,j_b;m_b,0,m_b)\{e^{k}_{\lambda}(j_a l_a,j_a\bar{l}_a)e^{k}_{\omega}(j_b l_b,j_b\bar{l}_b) \\
&-(-1)^{\omega+k+1}e^{k}_{\lambda}(j_a l_a,j_a\bar{l}_a)e^{k}_{\omega}(j_b l_b,j_b\bar{l}_b) \\
&-e^{k}_{\lambda}(j_a\bar{l}_a,j_a l_a)e^{k}_{\omega}(j_b l_b,j_b\bar{l}_b) \\
&+(-1)^{\omega+k+1}e^{k}_{\lambda}(j_a\bar{l}_a,j_a l_a)e^{k}_{\omega}(j_b l_b,j_b\bar{l}_b)\}
\end{aligned}
\tag{4-70}
$$

From the triangular condition of the Clebsch-Gordan coefficient of the above equation, we obtain

$$\omega + k + 1 = even \tag{4-71}$$

It follows that the direct matrix element of the retardation term vanishes identically.

$$g^{R}_{abab} = 0 \tag{4-72}$$

For the exchange part of the retardation term is:

$$
\begin{aligned}
g^R_{abba} = \sum_{k\lambda\omega} (2k+1)^{-1} C(k1\lambda;000) C(k1\omega;000) \left[C(j_a, k, j_b; m_a, m_b - m_a, m_b) \right]^2 \\
\times \Big\{ & e^k_\lambda(j_a l_a, j_b \bar{l}_b) e^k_\omega(j_b \bar{l}_b, j_a l_a) G^R_{\lambda\omega k}(\mathrm{ab,ab}) \\
& + e^k_\lambda(j_a \bar{l}_a, j_b l_b) e^k_\omega(j_b l_b, j_a \bar{l}_a) G^R_{\lambda\omega k}(\mathrm{ba,ba}) \\
& - \Big[e^k_\lambda(j_a l_a, j_b \bar{l}_b) e^k_\omega(j_b l_b, j_a \bar{l}_a) \\
& + e^k_\lambda(j_a \bar{l}_a, j_b l_b) e^k_\omega(j_b \bar{l}_b, j_a l_a) \Big] G^R_{\lambda\omega k}(\mathrm{ab,ba}) \Big\}
\end{aligned}
\tag{4-73}
$$

Where

$$
\begin{aligned}
& G^R_{\lambda\omega k}(ab, cd) \\
& = \int_0^\infty \int_0^\infty P_a(r_1) P_c(r_2) \left[\partial_\lambda(1) \partial_\omega(2) W_k(1,2) \right] Q_b(r_1) Q_d(r_2) d r_1 d r_2
\end{aligned}
\tag{4-74}
$$

Kim [1٧] has remarked that this is a consequence of the fact that $\phi^\dagger_a(\vec{r}_1)\phi_a(\vec{r}_1)$ and $\phi^\dagger_b(\vec{r}_2)\phi_b(\vec{r}_2)$ necessarily represent static charge distributions so that their Coulomb repulsion cannot be retarded. On the other hand, the exchange matrix elements involve an interaction between charge distributions $\phi^\dagger_a(\vec{r}_1)\phi_b(\vec{r}_1)$ and $\phi^\dagger_b(\vec{r}_2)\phi_a(\vec{r}_2)$ which are necessarily non-stationary in time, unless, of course a=b.

When we carry out the differentiation of $W_k(1,2)$ in the above radial matrix element, we find that

$$
\begin{aligned}
G^R_{(k+1)(k-1)k}(ab, cd) = & -(2k+1) \int_0^\infty P_a(r_1) Q_b(r_1) \\
& \times \left[\int_0^{r_1} P_c(r_2) \left(\frac{r_2^{k+1}}{r_1^{k+2}} - \frac{r_2^{k-1}}{r_1^k} \right) Q_d(r_2) d r_2 \right] d r_1
\end{aligned}
\tag{4-75}
$$

$$
\begin{aligned}
G^R_{(k-1)(k+1)k}(ab, cd) = & -(2k+1) \int_0^\infty P_a(r_1) Q_b(r_1) \\
& \times \left[\int_{r_1}^\infty P_c(r_2) \left(\frac{r_1^{k+1}}{r_2^{k+2}} - \frac{r_1^{k-1}}{r_2^k} \right) Q_d(r_2) d r_2 \right] d r_1
\end{aligned}
\tag{4-76}
$$

and

$$G^R_{vvk}(ab,cd) = -2\frac{(2k+1)}{(2v+1)} G^R_k(ab,cd) \qquad \text{if} \quad v = k \pm 1 \tag{4-77}$$

Where

$$G^R_k(ab,cd) = \int_0^\infty \int_0^\infty P_a(r_1)\, P_c(r_2) \frac{r_<^k}{r_>^{k+1}} Q_b(r_1) Q_d(r_2) d\, r_1 d\, r_2 \tag{4-78}$$

The summation over λ and ω can be carried out, by substituting $k \pm 1$ in equation (4-73), then we obtain

$$\begin{aligned}
g^R_{abba} &= \sum_k (2k+1)^{-1} \left[C(j_a, k, j_b; m_a, m_b - m_a, m_b)\right]^2 \\
&\times \Big\{ \left(C(k1(k-1);000)\right)^2 \Big[\left(e^k_{k-1}(j_a l_a, j_b \bar{l}_b)\right)^2 G^R_{(k-1)(k-1)k}(\text{ab,ab}) \\
&+ \left(e^k_{k-1}(j_a \bar{l}_a, j_b l_b)\right)^2 G^R_{(k-1)(k-1)k}(\text{ba,ba}) \\
&- 2 e^k_{k-1}(j_a l_a, j_b \bar{l}_b) e^k_{k-1}(j_a \bar{l}_a, j_b l_b) G^R_{(k-1)(k-1)k}(\text{ab,ba}) \Big] \\
&+ \left(C(k1(k+1);000)\right)^2 \Big[\left(e^k_{k+1}(j_a l_a, j_b \bar{l}_b)\right)^2 G^R_{(k+1)(k+1)k}(\text{ab,ab}) \\
&+ \left(e^k_{k+1}(j_a \bar{l}_a, j_b l_b)\right)^2 G^R_{(k+1)(k+1)k}(\text{ba,ba}) \\
&- 2 e^k_{k+1}(j_a l_a, j_b \bar{l}_b) e^k_{k+1}(j_a \bar{l}_a, j_b l_b) G^R_{(k+1)(k+1)k}(\text{ab,ba}) \Big] \\
&+ C(k1(k-1);000) C(k1(k+1);000) \Big[e^k_{k-1}(j_a l_a, j_b \bar{l}_b) e^k_{k+1}(j_a l_a, j_b \bar{l}_b) \\
&\times \left(G^R_{(k-1)(k+1)k}(\text{ab,ab}) + G^R_{(k+1)(k-1)k}(\text{ab,ab})\right) + e^k_{k-1}(j_a \bar{l}_a, j_b l_b) e^k_{k+1}(j_a \bar{l}_a, j_b l_b; k) \\
&\times \left(G^R_{(k-1)(k+1)k}(\text{ba,ba}) + G^R_{(k+1)(k-1)k}(\text{ba,ba})\right) - \left(e^k_{k-1}(j_a l_a, j_b \bar{l}_b) e^k_{k+1}(j_a \bar{l}_a, j_b l_b) \right. \\
&\left. + e^k_{k-1}(j_a \bar{l}_a, j_b l_b) e^k_{k+1}(j_a l_a, j_b \bar{l}_b)\right) \left(G^R_{(k-1)(k+1)k}(\text{ab,ba}) + G^R_{(k+1)(k+1)k}(\text{ab,ba})\right) \Big] \Big\}
\end{aligned} \tag{4 - 79}$$

using equations (4-75) and (4-76), we get

$$\begin{aligned}
&G^R_{(k-1)(k+1)k}(\text{ab,cd}) + G^R_{(k+1)(k-1)k}(\text{ab,cd}) \\
&= (2\text{k}+1)\left[G^R_{(k-1)}(\text{ab,cd}) - G^R_{(k+1)}(\text{ab,cd})\right]
\end{aligned} \tag{4-80}$$

using the above relation with equation (4-77), equation (4-79) becomes

$$
\begin{aligned}
g^{R}_{abba} = & -2\sum_{k}\left[C(j_a,k,j_b;m_a,m_b-m_a,m_b)\right]^2 \\
& \times\left\{\frac{\left(C(k1(k-1);000)\right)^2}{(2k-1)}\left[\left(e^{k}_{k-1}(j_a l_a, j_b \bar{l}_b)\right)^2 G^{R}_{(k-1)}(\mathrm{ab,ab})\right.\right. \\
& +\left(e^{k}_{k-1}(j_a \bar{l}_a, j_b l_b)\right)^2 G^{R}_{(k-1)}(\mathrm{ba,ba}) \\
& \left.-2e^{k}_{k-1}(j_a l_a, j_b \bar{l}_b)e^{k}_{k-1}(j_a \bar{l}_a, j_b l_b)G^{R}_{(k-1)}(\mathrm{ab,ba})\right] \\
& +\frac{\left(C(k1(k+1);000)\right)^2}{(2k+3)}\left[\left(e^{k}_{k+1}(j_a l_a, j_b \bar{l}_b)\right)^2 G^{R}_{(k+1)}(\mathrm{ab,ab})\right. \\
& +\left(e^{k}_{k+1}(j_a \bar{l}_a, j_b l_b)\right)^2 G^{R}_{(k+1)}(\mathrm{ba,ba}) \\
& \left.-2e^{k}_{k+1}(j_a l_a, j_b \bar{l}_b)e^{k}_{k+1}(j_a \bar{l}_a, j_b l_b)G^{R}_{(k+1)}(\mathrm{ab,ba})\right] \\
& -C(k1(k-1);000)C(k1(k+1);000)\left[e^{k}_{k-1}(j_a l_a, j_b \bar{l}_b)e^{k}_{k+1}(j_a l_a, j_b \bar{l}_b)\right. \\
& \times\left(G^{R}_{(k-1)}(\mathrm{ab,ab})-G^{R}_{(k+1)}(\mathrm{ab,ab})\right)+e^{k}_{k-1}(j_a \bar{l}_a, j_b l_b)e^{k}_{k+1}(j_a \bar{l}_a, j_b l_b) \\
& \times\left(G^{R}_{(k-1)}(\mathrm{ba,ba})-G^{R}_{(k+1)}(\mathrm{ba,ba})\right)-\left(e^{k}_{k-1}(j_a l_a, j_b \bar{l}_b)e^{k}_{k+1}(j_a \bar{l}_a, j_b l_b)\right. \\
& \left.\left.\left.+e^{k}_{k-1}(j_a \bar{l}_a, j_b l_b)e^{k}_{k+1}(j_a l_a, j_b \bar{l}_b)\right)\left(G^{R}_{(k-1)}(\mathrm{ab,ba})-G^{R}_{(k+1)}(\mathrm{ab,ba})\right)\right\}
\end{aligned}
\qquad (4-81)
$$

performing the sum over m_b, the above equation becomes

$$
\begin{aligned}
\sum_{m_b} g^{R}_{abba} = & -2\sum_{k}\left\{\frac{\left(C(k1(k-1);000)\right)^2}{(2k-1)}\left[\left(e^{k}_{k-1}(j_a l_a, j_b \bar{l}_b;k)\right)^2 G^{R}_{(k-1)}(\mathrm{ab,ab})\right.\right. \\
& +\left(e^{k}_{k-1}(j_a \bar{l}_a, j_b l_b)\right)^2 G^{R}_{(k-1)}(\mathrm{ba,ba}) \\
& \left.-2e^{k}_{k-1}(j_a l_a, j_b \bar{l}_b)e^{k}_{k-1}(j_a \bar{l}_a, j_b l_b)G^{R}_{(k-1)}(\mathrm{ab,ba})\right] \\
& +\frac{\left(C(k1(k+1);000)\right)^2}{(2k+3)}\left[\left(e^{k}_{k+1}(j_a l_a, j_b \bar{l}_b)\right)^2 G^{R}_{(k+1)}(\mathrm{ab,ab})\right. \\
& +\left(e^{k}_{k+1}(j_a \bar{l}_a, j_b l_b)\right)^2 G^{R}_{(k+1)}(\mathrm{ba,ba}) \\
& \left.-2e^{k}_{k+1}(j_a l_a, j_b \bar{l}_b)e^{k}_{k+1}(j_a \bar{l}_a, j_b l_b)G^{R}_{(k+1)}(\mathrm{ab,ba})\right] \\
& -C(k1(k-1);000)C(k1(k+1);000)\left[e^{k}_{k-1}(j_a l_a, j_b \bar{l}_b)e^{k}_{k+1}(j_a l_a, j_b \bar{l}_b)\right. \\
& \times\left(G^{R}_{(k-1)}(\mathrm{ab,ab})-G^{R}_{(k+1)}(\mathrm{ab,ab})\right)+e^{k}_{k-1}(j_a \bar{l}_a, j_b l_b)e^{k}_{k+1}(j_a \bar{l}_a, j_b l_b) \\
& \times\left(G^{R}_{(k-1)}(\mathrm{ba,ba})-G^{R}_{(k+1)}(\mathrm{ba,ba})\right)-\left(e^{k}_{k-1}(j_a l_a, j_b \bar{l}_b)e^{k}_{k+1}(j_a \bar{l}_a, j_b l_b)\right. \\
& \left.\left.\left.+e^{k}_{k-1}(j_a \bar{l}_a, j_b l_b)e^{k}_{k+1}(j_a l_a, j_b \bar{l}_b)\right)\left(G^{R}_{(k-1)}(\mathrm{ab,ba})-G^{R}_{(k+1)}(\mathrm{ab,ba})\right)\right\}
\end{aligned}
\qquad (4-82)
$$

The configuration average energy correction due to the retardation term is:

$$E^R_{av} = \frac{1}{2}\sum_{\mathrm{a}} q_a\left(q_a - 1\right)E^R_{aa} + \frac{1}{2}\sum_{a}\sum_{\mathrm{b}\neq\mathrm{a}} q_a\, q_b\, E^R_{ab} \qquad (4\text{-}83)$$

Where

$$E^R_{aa} = \left(g^R_{abab}\right)_{av} - \left(g^R_{abba}\right)_{av} \quad \text{with} \quad a = b \qquad (4\text{-}84)$$

$$E^R_{ab} = \left(g^R_{abab}\right)_{av} - \left(g^R_{abba}\right)_{av} \quad \text{with} \quad a \neq b \qquad (4\text{-}85)$$

Where the averaging over m_a and m_b

From equations (4-82), (4-84) and (4-85) we get

$$E^R_{aa} = 0$$

and

$$\begin{aligned}
E^R_{ab} = {} & \frac{2}{(2\,j_b+1)}\sum_k \Bigg\{ \frac{\left(C(k1(k-1);000)\right)^2}{(2k-1)} \\
& \times \Big[\left(e^k_{k-1}(j_a l_a, j_b \bar{l}_b)\right)^2 G^R_{(k-1)}(\mathrm{ab},\mathrm{ab}) + \left(e^k_{k-1}(j_a \bar{l}_a, j_b l_b)\right)^2 G^R_{(k-1)}(\mathrm{ba},\mathrm{ba}) \\
& - 2e^k_{k-1}(j_a l_a, j_b \bar{l}_b)\, e^k_{k-1}(j_a \bar{l}_a, j_b l_b)\, G^R_{(k-1)}(\mathrm{ab},\mathrm{ba}) \Big] \\
& + \frac{\left(C(k1(k+1);000)\right)^2}{(2k+3)} \Big[\left(e^k_{k+1}(j_a l_a, j_b \bar{l}_b)\right)^2 G^R_{(k+1)}(\mathrm{ab},\mathrm{ab}) \\
& + \left(e^k_{k+1}(j_a \bar{l}_a, j_b l_b)\right)^2 G^R_{(k+1)}(\mathrm{ba},\mathrm{ba}) \\
& - 2e^k_{k+1}(j_a l_a, j_b \bar{l}_b)\, e^k_{k+1}(j_a \bar{l}_a, j_b l_b)\, G^R_{(k+1)}(\mathrm{ab},\mathrm{ba}) \Big] \\
& - C(k1(k-1);000)\, C(k1(k+1);000) \Big[e^k_{k-1}(j_a l_a, j_b \bar{l}_b)\, e^k_{k+1}(j_a l_a, j_b \bar{l}_b) \\
& \times \left(G^R_{(k-1)}(\mathrm{ab},\mathrm{ab}) - G^R_{(k+1)}(\mathrm{ab},\mathrm{ab})\right) + e^k_{k-1}(j_a \bar{l}_a, j_b l_b)\, e^k_{k+1}(j_a \bar{l}_a, j_b l_b) \\
& \times \left(G^R_{(k-1)}(\mathrm{ba},\mathrm{ba}) - G^R_{(k+1)}(\mathrm{ba},\mathrm{ba})\right) - \left(e^k_{k-1}(j_a l_a, j_b \bar{l}_b)\, e^k_{k+1}(j_a \bar{l}_a, j_b l_b)\right. \\
& \left. + e^k_{k-1}(j_a \bar{l}_a, j_b l_b)\, e^k_{k+1}(j_a l_a, j_b \bar{l}_b)\right)\left(G^R_{(k-1)}(\mathrm{ab},\mathrm{ba}) - G^R_{(k+1)}(\mathrm{ab},\mathrm{ba})\right) \Big\}
\end{aligned} \qquad (4\text{-}86)$$

From equation (4-83) and (4-86) the configuration average energy due to retardation term

$$E_{av}^{R}=\sum_{a}\sum_{b\neq a}q_a q_b\frac{1}{(2j_b+1)}\sum_{k}\Bigg\{\frac{\left(C(k1(k-1);000)\right)^2}{(2k-1)}$$
$$\times\Big[\left(e_{k-1}^{k}(j_a l_a,j_b\bar{l}_b)\right)^2 G_{(k-1)}^{R}(\mathrm{ab,ab})$$
$$+\left(e_{k-1}^{k}(j_a\bar{l}_a,j_b l_b)\right)^2 G_{(k-1)}^{R}(\mathrm{ba,ba})$$
$$-2e_{k-1}^{k}(j_a l_a,j_b\bar{l}_b)e_{k-1}^{k}(j_a\bar{l}_a,j_b l_b)G_{(k-1)}^{R}(\mathrm{ab,ba})\Big]$$
$$+\frac{\left(C(k1(k+1);000)\right)^2}{(2k+3)}\Big[\left(e_{k+1}^{k}(j_a l_a,j_b\bar{l}_b)\right)^2 G_{(k+1)}^{R}(\mathrm{ab,ab}) \qquad (4\text{-}87)$$
$$+\left(e_{k+1}^{k}(j_a\bar{l}_a,j_b l_b)\right)^2 G_{(k+1)}^{R}(\mathrm{ba,ba})$$
$$-2e_{k+1}^{k}(j_a l_a,j_b\bar{l}_b)e_{k+1}^{k}(j_a\bar{l}_a,j_b l_b)G_{(k+1)}^{R}(\mathrm{ab,ba})\Big]$$
$$-C(k1(k-1);000)C(k1(k+1);000)\Big[e_{k-1}^{k}(j_a l_a,j_b\bar{l}_b)e_{k+1}^{k}(j_a l_a,j_b\bar{l}_b)$$
$$\times\left(G_{(k-1)}^{R}(\mathrm{ab,ab})-G_{(k+1)}^{R}(\mathrm{ab,ab})\right)+e_{k-1}^{k}(j_a\bar{l}_a,j_b l_b)e_{k+1}^{k}(j_a\bar{l}_a,j_b l_b)$$
$$\times\left(G_{(k-1)}^{R}(\mathrm{ba,ba})-G_{(k+1)}^{R}(\mathrm{ba,ba})\right)-\left(e_{k-1}^{k}(j_a l_a,j_b\bar{l}_b)e_{k+1}^{k}(j_a\bar{l}_a,j_b l_b)\right.$$
$$\left.+e_{k-1}^{k}(j_a\bar{l}_a,j_b l_b)e_{k+1}^{k}(j_a l_a,j_b\bar{l}_b)\right)\left(G_{(k-1)}^{R}(\mathrm{ab,ba})-G_{(k+1)}^{R}(\mathrm{ab,ba})\right)\Big\}$$

CHAPTER 5

NUMERICAL SOLUTION OF THE HARTREE-FOCK EQUATIONS

In this chapter we try to present a brief description of the general scheme for the solution of the non-relativistic Hartree-Fock equations which lead to a system of second order differential equations, and then proceed with solution of the relativistic Hartree-Fock (Dirac-Fock) equation which lead to a system of pairs of first order differential equation.

5-1- Solution of the Non-relativistic Hartree-Fock Equations

Our object now is to obtain solutions of equations (2-3-20) by straightforward iterative scheme. From estimates of all the functions $P_a(r)$, we tabulate the functions $X_a(r)$ and $Y_a(r)$ for some particular choice a. The solution of the radial differential equations (2-3-20) then gives new estimate of the function $P_a(r)$. The process is then repeated with each function until the whole system is self-consistent to within the prescribed tolerance.

There are, therefore, three processes :

a- Tabulation of $X_a(r)$ and $Y_a(r)$:

From equations (2-3-18) and (2-3-19), it is clear that $Y_a(r)$ and $X_a(r)$ depend completely on the function $Y_k(ab,r)$, and because this type of function occur frequently in Hartree-Fock calculations, it is desirable to determine them with maximum efficiency.

The $Y_k(ab,r)$ function given by equation (2-3-9) can be rewritten as:

$$Y_k(ab,r) = r\int_0^{\infty} ds\, U_k(r,s)\, P_a(s)\, P_b(s) \tag{5-1-1}$$

where

$$\begin{aligned} U_k(r,s) &= \frac{s^k}{r^{k+1}} \qquad \text{if} \quad r \geq s \\ &= \frac{r^k}{s^{k+1}} \qquad \text{if} \quad r < s \end{aligned} \tag{5-1-2}$$

introducing the function

$$Z_k(ab,r) = r\int_0^{r} ds\, U_k(r,s)\, P_a(s)\, P_b(s) = \int_0^{r} ds \left(\frac{s}{r}\right)^k P_a(s)\, P_b(s) \tag{5-1-3}$$

Equations (5-1-1) and (5-1-3) can be regarded as solutions of a pair of differential equations [54]

$$\frac{d\,Z_k}{dr} + \frac{k}{r} Z_k = P_a(r)\, P_b(r) \tag{5-1-4}$$

$$\frac{d\,Y_k}{dr} - \frac{k+1}{r} Y_k = -\frac{2k+1}{r} Z_k \tag{5-1-5}$$

with the boundary conditions

$$\begin{aligned} Z_k &= 0 \qquad \text{at} \quad r = 0 \\ Y_k &\to Z_k \quad \text{as} \quad r \to \infty \end{aligned} \tag{5-1-6}$$

Because the bound orbitals exhibit a rapid variation near the origin and an exponential decay at large values of r it is more efficient to make the change of variable [2]:

$$t = \ln r \tag{5-1-7}$$

with grid points

$$\left.\begin{array}{l} t_i = t_0 + (i-1)h \\ \textit{or} \\ r_i = r_0 \exp\ (i\text{-}1)h \end{array}\right\},\ i = 1,\ 2,....,M \tag{5-1-8}$$

where h is the step size.

with this transformation, equations (5-1-4) and (5-1-5) become

$$\frac{dZ_k}{dt} + kZ_k = e^t P_a P_b \tag{5-1-9}$$

$$\frac{dY_k}{dt} - (k+1)Y_k = -(2k+1)Z_k \tag{5-1-10}$$

both of which are of the form

$$\frac{df}{dt} + af = \phi(t) \tag{5-1-11}$$

where a is constant and $\phi(t)$ is known tabulated function. Step by step integration of this equation in the direction of increasing (decreasing) t is stable for a positive (negative), so that we can integrate Z_k equation outwards from the initial value $Z_k(ab,t_1)$, and then Y_k equation inwards from some sufficiently large value $t=t_m$ with $Y_k(ab,t_m) = Z_k(ab,t_m)$.

Equation (5-1-11) is equivalent to the relation [55]

$$f(t_{i+1}) = e^{-ah} f(t_i) + \int_{t_i}^{t_{i+1}} e^{a(x-t_{i+1})} \phi(x) dx \tag{5-1-12}$$

The integral is approximated by Adams method [56]

$$\int_{t_i}^{t_{i+1}} F(x)dx = \frac{h}{24}\{-F(t_{i-1}) + 13F(t_i) + 13F(t_{i+1}) - F(t_{i+2})\} \tag{5-1-13}$$

equation (5-1-12) becomes

$$\begin{aligned} f(t_{i+1}) = e^{-ah} f(t_i) + \frac{h}{24}\{&-e^{-2ah}\phi(t_{i-1}) \\ &+ 13e^{-ah}\phi(t_i) + 13\phi(t_{i+1}) - e^{-ah}\phi(t_{i+2})\} \end{aligned} \tag{5-1-14}$$

The initial value needed to start the integration for Z_k can be obtained from[2]

$$\begin{aligned} Z_k(ab,t_1) = &\frac{1}{l_a + l_b + k + 3} e^{2t_1} P_a P_b \\ &\times \left\{1 + \frac{Z e^{t_1}}{(l_a + l_b + k + 4)}\left[\frac{1}{(l_a+1)} + \frac{1}{(l_b+1)}\right]\right\} \end{aligned} \tag{5-1-15}$$

b- Solution of the radial differential equation for $P_a(r)$:

Now, we ought to solve the equations

$$\frac{d^2 P_a}{dr^2} - \frac{l_a(l_a+1)P_a}{r^2} + 2\left[\varepsilon_a + \frac{Y_a(r)}{r}\right]P_a(r) = -X_a(r) \qquad (5\text{-}1\text{-}16)$$

where $Y_a(r)$ and $X_a(r)$ are regarded as given tabulated functions, as well as the ε_{ab} parameter from equation (2-5-1). The boundary conditions are

$P_a(0) = 0$ and $P_a(r) \to 0$ as $r \to \infty$

The change of variable $t = \ln r$ gives rise to a second order differential equation of the form

$$\frac{d^2 \overline{P}_a}{dt^2} - \left[(l_a + 1/2)^2 - 2(\varepsilon_a r^2 + r Y_a)\right]\overline{P}_a = -r^{3/2} X_a \qquad (5\text{-}1\text{-}17)$$

where $\overline{P}_a = \frac{P_a}{\sqrt{r}}$

equation (5-17), has the form:

$$\frac{d^2 F}{dt^2} + \phi(t)F = W(t) \qquad (5\text{-}1\text{-}18)$$

Using Numerov,s method, which takes the form [55]

$$\left[1 + \frac{1}{12}h^2\phi(t_{i+1})\right]F(t_{i+1}) = \left[2 - \frac{5}{6}h^2\phi(t_i)\right]F(t_i) - \left[1 + \frac{1}{12}h^2\phi(t_{i-1})\right]F(t_{i-1}) + \frac{h^2}{12}\left[W(t_{i+1}) + 10\,W(t_i) + W(t_{i-1})\right] \qquad (5\text{-}1\text{-}19)$$

The possible instability in the region where $\phi(t) < 0$ ought to be avoided. Therefore it is required an outward integration for small r, and inward integration for large r [55].

Starting values of the outward integration are obtained from a series expansion [2]

$$P(r) = A r^{l+1}\left(1 - \frac{Z}{l+1}r + \alpha r^2 + O(r^3)\right) \qquad (5\text{-}1\text{-}20)$$

$$Y_a(r) = y_0 r + O(r^3) \tag{5-1-21}$$

$$\eta_a(r) = r^{l+1}\left\{x_0 + x_1 r + O(r^2)\right\} \tag{5-1-22}$$

where $\alpha = \dfrac{\left\{Z^2 + (l+1)\left[(\varepsilon_a/2) + (y_0 + x_0\right]\right\}}{(2l+3)(l+1)}$

and where A, y_0, x_0 and x_1 are constants.

Numerov's method is then used step by step to the point t_j where the term $\phi(t)$ becomes negative. The inward integration is treated as a boundary value problem[57].

we have thus obtained solutions of the equation (5-1-19) of the form

$$\begin{aligned} &F_i^{(0)} \quad \text{for} \quad i \le j \\ &F_i^{(1)} \quad \text{for} \quad i > j \end{aligned} \tag{5-1-23}$$

which match at the point j, that is $F_j^{(0)} = F_j^{(1)}$, however, the two solutions will not agree, and must adjust the original estimates (A, ε_a and ε_{ab}) to satisfy the normalization and orthogonality until they give the same value at the matching point.

c- Self consistency

The solution $P_a^{n+1}(r)$ can now be compared with the estimate $P_a^n(r)$ used in computing $Y_a(r)$ and $X_a(r)$. The new estimate is derived from the combination [2]

$$(1 - c_a)\, P_a^{n+1}(r) + c_a\, P_a^n(r) \tag{5-1-24}$$

where c_a is a constant.

Initial estimates are chosen to be hydrogenic orbitals with effective nuclear charge $Z^* = (Z - \sigma)$, where σ is the screening parameter.

5-2- Solution of the Relativistic Hartree-Fock Equations

The general scheme for the solution of the system of pairs of first-order differential equations is very similar to the non-relativistic case described above. The tabulation of the functions $Y_a(r)$, $X_a^P(r)$ and $X_a^Q(r)$ involves the same numerical problems as in the non-relativistic calculations, and is carried out in the same way. The only important difference in the computational procedure is in the actual solution of equations (3-1-71):

$$P'_a + \frac{\kappa_a}{r} P_a - \left[2c + \frac{1}{c}\left(\varepsilon_a + \frac{Y_a(r)}{r} \right) \right] Q_a = X_a^P(r) \qquad \text{(5-2-1a)}$$

$$Q'_a - \frac{\kappa_a}{r} Q_a + \frac{1}{c}\left(\varepsilon_a + \frac{Y_a(r)}{r} \right) P_a = - X_a^Q(r) \qquad \text{(5-2-1b)}$$

Now, we consider the solution of the above pair of differential equations.
For the same reasons as in the non-relativistic case it is convenient to make the change of variable

$$t = \ln r \qquad \text{(5-2-2)}$$

making this transformation, and omit the suffix a, equations (5-2-1) become

$$P' + \kappa P - \left[2c + \frac{1}{c}\left(\varepsilon r + Y(r) \right) \right] Q = r X^P(r) \qquad \text{(5-2-3a)}$$

$$Q' - \kappa Q + \frac{1}{c}\left(\varepsilon r + Y(r) \right) P = r X^Q(r) \qquad \text{(5-2-3b)}$$

Using the predictor-corrector method [58] to solve the system of two first order coupled differential equations

Predictor :

$$p(t_{i+1}) = y(t_i) + \frac{h}{720}\left[1901 y'(t_i) - 2774 y'(t_{i-1}) + 2616 y'(t_{i-2}) - 1274 y'(t_{i-3}) + 251 y'(t_{i-4}) \right] \qquad \text{(5-2-4)}$$

Corrector :

$$C(t_{i+1}) = y(t_i) + \frac{h}{720}\left[251p'(t_{i+1}) + 646y'(t_i) - 264y'(t_{i-1}) + 106y'(t_{i-2}) - 19y'(t_{i-3})\right] \quad (5\text{-}2\text{-}5)$$

Final value :

$$y(t_{i+1}) = \frac{1}{502}\left[475C(t_{i+1}) + 27p(t_{i+1})\right] \quad (5\text{-}2\text{-}6)$$

where y stands for either the large P or small Q radial wavefunction, y' and p' denotes the derivatives with respect to the tabulation variable.

As in the non relativistic case, the solution involves both an inward and outward integration for stability purposes. Starting values of the outward integration are obtained from a series expansion [46]

$$\begin{aligned} P\ (r) &= Ar^{\lambda}\left(p_0 + p_1 r + O(r^2)\right) \\ Q\ (r) &= Ar^{\lambda}\left(q_0 + q_1 r + O(r^2)\right) \end{aligned} \quad (5\text{-}2\text{-}7)$$

where $\lambda = \left[\kappa^2 - \alpha^2 Z^2\right]^{1/2}$ and where the coefficients $p_0, p_1, q_0, q_1,$ etc., can be expressed in terms of the unknown value of A.

To begin the inward integration, we use the asymptotic form [58]

$$\begin{aligned} P\ (r) &= p\exp(-\mu r) \\ Q\ (r) &= q\exp(-\mu r) \end{aligned} \quad (5\text{-}2\text{-}8)$$

where

$$\mu = \left(\varepsilon - \frac{\varepsilon^2}{4c^2}\right)^{1/2} \quad \text{and} \quad \mu\, p = \left(2c - \frac{\varepsilon}{2c}\right)^{1/2} q$$

As a result of this process, we shall have two values of $Q\ (t_j)$ which, in general, will not agree unless the values of A, ε_a and ε_{ab} are correctly chosen during the matching process.

CHAPTER 6

RESULTS AND DISCUSSION

After the iterative process has converged, the Hartree-Fock (non-relativistic and relativistic) wavefunctions can be used to compute the subshell energies for both calculations by using equations (2-4-1) and (3-2-4) respectively and compared with the corresponding experimental values [59,60]. Also the expectation values of the orbital mean radii r^n for both non-relativistic and relativistic cases, computed by using

$$\left\langle r^n \right\rangle_{i;j}^{l} = \int_0^\infty \left[P_i P_j \right] r^n \, dr \tag{6-1}$$

$$\left\langle r^n \right\rangle_{i;j}^{l} = \int_0^\infty \left[P_i P_j + Q_i Q_j \right] r^n \, dr \qquad \text{if } l = 0$$

$$\left\langle r^n \right\rangle_{i;j}^{l} = \int_0^\infty \left[P_i Q_j + P_j Q_i \right] r^n \, dr \qquad \text{if } l \neq 0 \tag{6-2}$$

The non-relativistic and relativistic average energy of configuration given by equations (2-2-3٣) and (3-1-56) respectively, the configuration average energy correction due to magnetic and retardation terms of the Breit interaction from equations (4-43) and (4-87) can be computed.

These properties were calculated using

These properties were tabulated for selected neutral ground state atoms ranging from Rb to Rn. The calculations were performed by using the programs [General Hartree-Fock Program modified by C. F. Fischer] and [GRASP: is an acronym for the General-purpose Relativistic Atomic Structure Package developed by Ian Grant and co-workers].

Where, in the tables below , we have used $2p^* = 2p_{1/2}$, etc.

These atoms were classified according to their outermost shell, where the atoms (${}_{37}Rb$, ${}_{55}Cs$, ${}_{56}Ba$ and ${}_{80}Hg$) represent the case in which the s-shell is the outermost shell, for open and closed shells. Each of these atoms had single relativistic configuration. For the atoms (${}_{40}Zr$, ${}_{46}Pd$, ${}_{71}Lu$ and ${}_{77}Ir$), in which the d-shell is the outermost shell, the non-relativistic configuration is split up into two relativistic sub-configurations for the ${}_{71}Lu$ atom, three relativistic sub-configuration for ${}_{40}Zr$ atom, four relativistic sub-configurations for the ${}_{77}Ir$ atom, and single relativistic configuration for ${}_{46}Pd$ atom. For the atoms (${}_{50}Sn$, ${}_{81}Tl$, ${}_{83}Bi$ and ${}_{86}Rn$), This case represent in which the p-shell is the outermost shell, the non-relativistic configuration is split up into two relativistic sub-configurations for ${}_{81}Tl$ atom, single relativistic configuration for the ${}^{86}Rn$ atom, and three relativistic sub-configurations for the ${}_{50}Sn$ and ${}^{83}Bi$ atoms.

The tables above display the following features:

- Along the considered range of atoms, the Dirac-Fock calculations gives higher binding energies for the s-subshells than the Hartree-Fock calculations whereas the binding energies of the Dirac-Fock calculations for the d and f-subshells are smaller than that for Hartree-Fock calculations. Furthermore, the data shows that the relativistic and non-relativistic binding energies for the p-subshells are approximately identical especially for the lower Z-atoms.
- The values of $\langle r \rangle$ and $\langle r^2 \rangle$ predicted from the Hartree-Fock calculations may be larger than those predicted from the corresponding Dirac-Fock calculations. Also, a contraction of all subshells, becoming more marked as Z increases. Whereas, the values of $\langle 1/r \rangle$ predicted from Hartree-Fock calculations are smaller than those predicted from

Dirac-Fock calculations. Also, an expansion of the values of $\langle 1/r \rangle$ as Z increases.

- The relativistic result indicates clearly that the energy for the 5s electron is larger than that for the 4f electron, and this result decreases as Z increases as shown for Rn-atom were the situation is reversed.
- The average energy of configuration predicted from Dirac-Fock calculations is about 1.4% to 8% larger than those predicted from the Hartree-Fock calculations.
- The effect of the Breit interaction is not large, since it is seen that the Slater integrals concerned contain two of the small components $Q(r)$ as factors, and are, therefore, considerably smaller than that associated with the Coulomb interaction. The energy shift due to retardation part of the Breit interaction is about 10% of the energy shift due to the magnetic part throughout the considered range, and that the magnetic and retardation contributions are of opposite signs.
- The contribution of the relativistic effect due to mass-velocity term and Darwin term increasing the average energy of configuration predicted from Hartree-Fock calculation from 1% to 6% throughout the considered range.

6-1- Rubidium $_{37}Rb$

subshell	HF energy/a.u.	DHF energy/a.u.	Exp. energy/a.u.
1s	551.4573165	562.1446122873	558.8125
2s	75.04932265	77.50271454893	75.6
2p*		70.01638909688	68.52
2p	67.90620685	67.76410350875	66.3
3s	12.1331814	12.56013187422	11.84
3p*		9.818275532751	9.095
3p	9.48767595	9.464863829160	8.768
3d*		4.675845534557	4.110
3d	4.73226905	4.615814521106	4.05
4s	1.52354505	1.566303618300	1.077
4p*		0.8323037367485	0.54
4p	0.8100679	0.7962684443181	0.51
5s	0.13786685	0.1400454031414	0.1535

Table (6-1a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Rb*.

subshell	r(a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.04128	0.04027724	36.49597	37.88202	0.00228	0.002185
2s	0.18174	0.17705799	8.16149	8.530965	0.03888	0.037032
2p*		0.15231097		8.466035		0.028477
2p	0.15693	0.15634115	8.11329	8.158655	0.03007	0.02.987
3s	0.51811	0.50724032	2.74124	2.834400	0.30767	0.295249
3p*		0.50946568		2.715626		0.302960
3p	0.52076	0.51924552	2.62914	2.644874	0.31606	0.314517
3d*		0.52078207		2.401879		0.330826
3d	0.52134	0.52444179	2.39426	2.382972	0.33104	0.335363
4s	1.49921	1.4727529	0.87631	0.897332	2.55722	2.469672
4p*		1.7034948		0.769573		3.355036
4p	1.73495	1.7391492	0.75206	0.751660	3.47783	3.498241
5s	5.63186	5.5449411	0.21776	0.221908	36.1790	35.10924

Table (6-1-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Rb*.

HF/a.u.	Relativistic shift /a.u.	Total energy/a.u.
-2938.357453	-38.95749849	-2977.31495191

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-2979.832904	1.73597290	-0.16756788	-2978.264499

Table (6-1-c): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Rb*.

6-2- Zirconium $_{40}Zr$

subshell	HF energy/a.u.	DHF energy/a.u.	Exp. energy/a.u.
1s	650.711731	665.5491068874	661.676
2s	91.3847302	94.85119059383	93.0
2p*		86.50523607257	84.80
2p	83.4855444	83.32781985570	81.70
3s	16.0617975	16.70048789095	15.82
3p*		13.53564676378	12.65
3p	13.02650895	13.00951336481	12.15
3d*		7.454652491938	6.70
3d	7.52249905	7.359449571294	6.61
4s	2.4247528	2.512844449940	1.8
4p*		1.547748498484	}1.05
4p	1.4925095	1.477990672895	
4d*		0.2931393197296	
4d	0.31093785	0.2893931784083	0.25
5s	0.2086036	0.2153173625709	

Table (6-2-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Zr*.

subshell	r(a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.03814	0.03705297	39.49003	41.26185	0.00195	0.001851
2s	0.16696	0.16190180	8.89079	9.368531	0.03280	0.030970
2p*		0.13873339		9.306589		0.023627
2p	0.14372	0.14305894	8.84879	8.909105	0.02519	0.024997
3s	0.46656	0.45525703	3.05475	3.177189	0.24910	0.237511
3p*		0.45283467		3.064105		0.238825
3p	0.46444	0.46270301	2.94986	2.971786	0.25075	0.249149
3d*		0.44909719		2.754855		0.243277
3d	0.45010	0.45254411	2.74215	2.730461	0.24398	0.246878
4s	1.24517	1.2195720	1.06774	1.098426	1.75334	1.683124
4p*		1.3555066		0.978190		2.105134
4p	1.38482	1.3847391	0.95141	0.953747	2.19585	2.197372
4d*		2.1751453		0.612351		5.781382
4d	2.13621	2.1949795	0.62119	0.606373	5.55422	5.886855
5s	4.07776	3.9790241	0.30767	0.316827	19.0470	18.15065

Table (6-2-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Zr*.

HF/a.u.	Relativistic shift /a.u.	Total energy/a.u.
-3538.968663	-54.40456948	-3593.3732329

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-3597.113789	2.27528260	-0.22334626	-3595.061853

Table (6-2-c): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Zr*.

6-3- Palladium $_{46}Pd$

subshell	HF energy/a.u.	DHF energy/a.u.	Exp. energy/a.u.
1s	873.3159525	900.1392435469	895.23
2s	127.9665877	134.4528922469	132.51
2p*		124.3014355370	122.43
2p	118.5311179	118.4120400492	116.66
3s	24.2091113	25.54368738440	24.62
3p*		21.49016949852	20.55
3p	20.3742918	20.42934235649	19.54
3d*		13.31983228320	12.5
3d	13.36344555	13.11044072465	12.30
4s	3.5873098	3.842502740962	3.17
4p*		2.520253271042	}1.87
4p	2.33008935	2.347288902157	
4d*		0.3405483675449	
4d	0.3359993	0.3197920101766	0.306

Table (6-3-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Pd*.

subshell	r(a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.03310	0.03184288	45.48052	48.24487	0.00147	0.001370
2s	0.14355	0.13773109	10.35316	11.11257	0.02423	0.022430
2p*		0.11723214		11.05460		0.016882
2p	0.12298	0.12215664	10.32253	10.42200	0.01842	0.018204
3s	0.38930	0.37688010	3.68283	3.883676	0.17310	0.162560
3p*		0.36970714		3.779177		0.158880
3p	0.38231	0.38006786	3.58966	3.629061	0.16946	0.167713
3d*		0.35439535		3.447675		0.149635
3d	0.35614	0.35781413	3.42015	3.408186	0.15082	0.152388
4s	0.98596	0.95672639	1.37155	1.429692	1.10183	1.037855
4p*		1.0345489		1.306789		1.228897
4p	1.06857	1.0644817	1.25304	1.262114	1.31108	1.301720
4d*		1.5286007		0.896504		2.932442
4d	1.53306	1.5649343	0.89266	0.877628	2.95172	3.088464

Table (6-3-b): Comparison between Hartree-Fock and Dirac-Fock mean values for Pd.

HF/a.u.	Relativistic shift /a.u.	Total energy/a.u.
-4937.921022	-98.65317424	-5036.57419711

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-5041.179824	3.68936474	-0.37174935	-5037.862209

Table (6-3-c): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for Pd.

6-4- Tin $_{50}Sn$

subshell	HF energy/a.u.	DHF energy/a.u.	Exp. energy/a.u.
1s	1041.228093	1079.394674150	1073.53
2s	156.9822479	166.3260494435	164.14
2p*		154.8855614920	152.8
2p	146.493933	146.3720170634	144.44
3s	31.6036073	33.56634314677	32.5
3p*		28.87692561628	27.80
3p	27.21365225	27.27641298050	26.26
3d*		19.08751862976	18.13
3d	19.16798535	18.76168650354	17.82
4s	5.51704795	5.888774360434	5.01
4p*		4.251109059929	}3.25
4p	3.9735609	3.960580408411	
4d*		1.336228001524	}0.87
4d	1.37355275	1.294280184702	
5s	0.47932165	0.5102032849392	
5p*		0.2575348850635	0.269
5p	0.24858345	0.2413649545043	

Table (6-4-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Sn*.

subshell	r(a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.03042	0.02904621	49.47479	53.09223	0.00124	0.001142
2s	0.13125	0.12491709	11.33067	12.33461	0.02024	0.018464
2p*		0.10590566		12.27712		0.013790
2p	0.11217	0.11123637	11.30644	11.43968	0.01530	0.015085
3s	0.35053	0.33728888	4.10401	4.374595	0.14025	0.130169
3p*		0.32872594		4.272539		0.012556
3p	0.34211	0.33955071	4.01598	4.070937	0.13557	0.133773
3d*		0.31149024		3.904087		0.011506
3d	0.31362	0.31498110	3.86321	3.851536	0.11638	0.117511
4s	0.85043	0.82201584	1.60224	1.682161	0.81647	0.763475
4p*		0.87111936		1.564521		0.866003
4p	0.90219	0.89857575	1.49130	1.504034	0.92806	0.921547
4d*		1.0811642		1.225215		1.381474
4d	1.08028	1.0957187	1.22157	1.207162	1.37671	1.419484
5s	2.58341	2.4799582	0.49102	0.516377	7.63161	7.042617
5p*		3.1762282		0.399572		11.73203
5p	3.28586	3.3059498	0.38344	0.382510	12.5269	12.71073

Table (6-4-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Sn*.

HF/a.u.	Relativistic shift /a.u.	Total energy/a.u.
-6022.914166	-140.75083358	-6163.66499962

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-6171.862090	4.92727413	-0.50329172	-6167.438108

Table (6-4-c): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Sn*.

6-5- Cesium $_{55}Cs$

subshell	HF energy/a.u.	DHF energy/a.u.	Exp. energy/a.u.
1s	1272.768824	1330.059813571	1323.0
2s	198.1437753	212.3960633624	210.0
2p*		199.2453587919	197
2p	186.3161698	186.2520882130	184.26
3s	42.6930285	45.78947928941	44.74
3p*		40.26461802883	39.15
3p	37.5959298	37.71052339219	36.67
3d*		28.12573610028	27.18
3d	28.226188	27.59139320075	26.67
4s	8.6954872	9.330613319766	8.48
4p*		7.262985612054	6.33
4p	6.7685309	6.737673932827	5.94
4d*		3.302461758338	2.89
4d	3.37953935	3.213745834889	2.81
5s	1.23160675	1.309148584373	0.83
5p*		0.7266858273581	0.48
5p	0.68347445	0.6593484481467	0.42
6s	0.12366835	0.1282450820039	0.143

Table (6-5-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Cs*.

subshell	r(a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	**DHF**	**HF**	**DHF**	**HF**	**DHF**
1s	0.02762	0.0261014	54.46797	59.408808	0.00102	0.0009246
2s	0.11853	0.1115467	12.55506	13.941277	0.01650	0.0147403
2p*		0.0941291		13.882531		0.0109109
2p	0.10103	0.0999758	12.53821	12.723509	0.01240	0.0127943
3s	0.31160	0.2972905	4.63353	5.0145036	0.11075	0.1011274
3p*		0.2877925		4.9149687		0.0962332
3p	0.30219	0.2992532	4.55191	4.6314064	0.10568	0.1038562
3d*		0.2705271		4.4768768		0.0864328
3d	0.27310	0.2741620	4.41455	4.4039434	0.08784	0.0886293
4s	0.72279	0.6947239	1.90341	2.0187276	0.58818	0.5440048
4p*		0.7215985		1.9105926		0.5916457
4p	0.75114	0.7471451	1.80409	1.8243695	0.64020	0.6341487
4d*		0.8306059		1.5876986		0.8015026
4d	0.83156	0.8408486	1.57837	1.5645559	0.80194	0.8212287
5s	1.83938	1.7700107	0.69941	0.7352554	3.80549	3.5293968
5p*		2.0289237		0.6369828		4.6849338
5p	2.11120	2.1192349	0.60628	0.6063363	5.06661	5.1155314
6s	6.30590	6.0842662	0.19217	0.2005899	44.9894	41.979965

Table (6-5-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Cs*.

HF/a.u.	Relativistic shift /a.u.	Total energy/a.u.
-7553.9336560	-211.26992752	-7765.20358361

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-7780.914981	6.8659267	-0.71111793	-7774.760172

Table (6-5-c):): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Cs*.

6-6- Barium $_{56}Ba$

subshell	HF energy/a.u.	DHF energy/a.u.	Exp. energy/a.u.
1s	1322.093397	1383.977150772	1377.0
2s	207.1544644	222.5947350564	220.4
2p*		209.0873996004	206.7
2p	195.0559587	195.0091354104	193
3s	45.28085235	48.65515494626	47.5
3p*		42.95638562344	41.8
3p	40.0397901	40.16696796652	39.0
3d*		30.29759356108	29.26
3d	30.4023086	29.71163735695	28.7
4s	9.5564001	10.25804413848	9.3
4p*		8.099057200357	7.05
4p	7.54931795	7.513114694635	6.6
4d*		3.913477420946	3.4
4d	4.0014955	3.812526222378	3.3
5s	1.5127214	1.603661296667	1.43
5p*		0.9563926188673	0.61
5p	0.9038624	0.8726359864140	0.536
6s	0.1575276	0.1631832615725	0.191

Table (6-6-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Ba*.

subshell	r(a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	**DHF**	**HF**	**DHF**	**HF**	**DHF**
1s	0.02713	0.025572	55.46669	60.71073	0.00098	0.000888
2s	0.11627	0.109158	12.80034	14.27456	0.01587	0.014119
2p*		0.092030		14.21520		0.010433
2p	0.09907	0.097981	12.78481	12.98194	0.01192	0.011697
3s	0.30480	0.290277	4.73995	5.146513	0.10596	0.096414
3p*		0.280674		5.047176		0.091534
3p	0.29528	0.292268	4.65942	4.744569	0.10088	0.099058
3d*		0.263571		4.592031		0.511120
3d	0.26623	0.267239	4.52471	4.514436	0.08341	0.084147
4s	0.70159	0.673497	1.96457	2.088308	0.55397	0.511120
4p*		0.697544		1.981147		0.552587
4p	0.72696	0.722873	1.86673	1.888831	0.59929	0.593292
4d*		7.950169		1.658385		0.732729
4d	0.79633	0.804862	1.64750	1.633855	0.73389	0.750789
5s	1.72119	1.656664	0.75008	0.788835	3.31905	3.079802
5p*		1.870453		0.693735		3.961754
5p	1.94459	1.950565	0.66037	0.661079	4.27611	4.311018
6s	5.25681	5.083188	0.23364	0.243395	31.2707	29.30057

Table (6-6-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Ba*..

HF/a.u.	Relativistic shift	Total energy/a.u.
-7883.54382577	-228.13405946	-8111.6778852

DHF/a.u.	Breit interaction		Total energy/a.u.
	magnetic	Retardation	
-8135.9844756	7.3108792015	-0.7589694	-8129.432565

Table (6-6-c):): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Ba*.

6-7- Lutetium $_{71}Lu$

subshell	HF energy/a.u.	DHF energy/a.u.	Experimental energy/a.u.
1s	2167.731423	2342.044741753	2327.70
2s	357.5722459	403.4314610494	399.64
2p*		384.0666754525	380.46
2p	341.4900667	342.9008597052	339.85
3s	82.26871065	93.54236622599	91.58
3p*		85.02725702380	83.21
3p	74.86027695	76.09871579864	74.40
3d*		61.88863915513	60.27
3d	61.23635795	59.95946868506	58.40
4s	16.9378601	19.69989598863	18.61
4p*		16.19344719935	15.07
4p	13.84504355	14.14372376181	13.21
4d*		8.380158584436	7.53
4d	8.26487015	7.997002286713	7.17
4f*		0.8551588934254	}0.25
4f	1.0768588	0.7906609684398	
5s	2.31704075	2.702522890592	2.07
5p*		1.62572187542	}1.03
5p	1.37584735	1.357794295550	
5d*		0.1912606431807	0.199
5d	0.24335145	0.1849517448900	
6s	0.1988556	0.2225540696485	

Table (6-7-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Lu*.

subshell	r(a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.02134	0.019312479	70.45377	82.249182	0.00061	0.00051178008
2s	0.09029	0.081165323	16.50701	19.909235	0.00956	0.0078487136E
2p*		0.067484987		19.825137		0.0056551088
2p	0.07653	0.075057083	16.50609	16.948865	0.00710	0.0068593612
3s	0.22980	0.21156628	6.33417	7.3147248	0.06020	0.051314755
3p*		2.0179759		7.2139881		4.7440601
3p	0.22008	0.21580100	6.26857	6.4789729	0.05601	5.4056037
3d*		0.18986645		6.3498059		0042374101
3d	0.19390	0.19420574	6.16924	6.1728644	0.04399	0.044202480
4s	0.51624	0.47845602	2.70048	3.0343242	0.30035	0.25851157
4p*		0.48658497		2.9199403		0.26960649
4p	0.52639	0.51742620	2.60171	2.6778857	0.31476	0.30469106

4d*		0.54258028		2.4499002		0.34198136
4d	0.55138	0.55401470	2.38944	2.3875109	0.35242	0.35640081
4f*		0.69420829		1.8658052		0.62264797
4f	0.67458	0.70807839	1.90014	1.8347633	0.58047	0.65060022
5s	1.29835	1.1922362	0.99640	1.1122093	1.89481	1.6008370
5p*		1.3336889	0.89816557	0.98500352		2.0245651
5p	1.46259	1.4435760	0.87912	0.89816557	2.43174	2.3754966
5d*		2.6948450		0.49603326		9.0469330
5d	2.48531	2.7796268	0.52663	0.47909852	7.52712	9.6085665
6s	4.25876	3.9017398	0.28969	0.31988955	20.71043	17.431553

Table (6-7-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Lu*.

HF/a.u.	Relativistic shift/a.u.	Total energy/a.u.
-13851.80800258	-619.69839062	-14471.50639321

EAL DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-14574.3353	16.625395669	-1.75788321	-14559.46779

Table (6-7-c):): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Lu*.

6-8- Iridium $_{77}Ir$

subshell	HF energy/a.u.	DHF energy/a.u.	Experimental energy/a.u.
1s	2566.492836	2816.769717273	2798.20
2s	413.476324	497.9201070751	493.32
2p*		475.7631479757	471.47
2p	413.476324	415.8273157794	412.32
3s	102.2296445	118.8670297820	116.68
3p*		109.0356550315	107.0
3p	93.9029701	95.72291221036	93.77
3d*		79.60507469305	77.80
3d	78.57743315	76.75682313619	75.0
4s	22.4970606	26.65494750198	25.37
4p*		22.47740708912	21.21
4p	18.89059335	19.29180916935	18.17
4d*		12.46064131309	11.44
4d	12.31636715	11.86007812200	10.84
4f*		3.103954818478	2.33
4f	3.52924545	2.982581636810	2.22
5s	3.55091525	4.255617370157	3.04
5p*		2.851258280234	1.67
5p	2.3440547	2.329384046235	1.27
5d*		0.4960532284069	
5d	0.55622765	0.4492513531464	0.33
6s	0.2465845	0.2995422282852	

Table (6-8-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Ir*.

subshell	r(a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.01967	0.017429738	76.44936	92.259207	0.00052	0.00041916051
2s	0.08288	0.072897930	17.99019	22.590037	0.00805	0.0063505819
2p*		0.060247054		22.487266		0.0045283876
2p	0.07015	0.068518345	17.99437	18.576810	0.00596	0.0057171979
3s	0.20934	0.18949192	6.96719	8.3049982	0.04995	0.041212949
3p*		0.17999796		8.1998192		0.037802924
3p	0.19987	0.19512633	6.90659	7.1892819	0.04619	0.044221819
3d*		0.17058506		7.0659465		0.034181991
3d	0.17511	0.17522768	0.19987	6.8318126	0.03582	0.035939337
4s	0.46267	0.42320190	3.02540	3.4806914	0.24101	0.20220510
4p*		0.42735371		3.3666553		0.20785373
4p	0.46839	0.45925150	2.93211	3.0331045	0.24885	0.23979800
4d*		0.47164604		2.8199513		0.25743278
4d	0.48027	0.48268898	2.73895	2.7381929	0.26620	0.26941527
4f*		0.52674481		2.3408129		0.33783880
4f	0.51719	0.53402559	2.36955	2.3083360	0.32375	0.34735517
5s	1.08800	0.99162982	1.20318	1.3610277	1.32628	
5p*		1.0794631		1.2371984		1.3190533
5p	1.19054	1.1743397	1.09212	1.1176722	1.60241	1.5629590
5d*		1.6369936		0.80313031		3.1877203
5d	0.80152	1.7081034	0.80152	0.76853862	3.11470	3.4823189
6s	3.52372	3.0784249	0.35438	0.41361825	14.29196	10.923699

Table (6-8-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Ir*.

HF/a.u.	Relativistic shift/a.u.	Total energy/a.u.
-16806.03919934	-872.03448532	-17678.07368467

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-17850.22677	22.13122787	-2.34607469	-17830.44162

Table (6-8-c):): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Ir*.

6-9- Mercury $_{80}Hg$

subshell	HF energy/a.u.	DHF energy/a.u.	Experimental energy/a.u.
1s	2778.80244	3076.157554210	3055.23
2s	470.7350853	550.5410728539	545.56
2p*		526.8622564809	522.37
2p	452.1803406	455.1452287241	451.61
3s	113.1366448	133.1796109750	131.0
3p*		122.6406246691	120.53
3p	104.3408156	106.5418018949	104.67
3d*		89.43372040739	87.68
3d	88.1454023	86.01719722699	84.37
4s	25.57341055	30.66500184950	29.42
4p*		26.12428675636	25.0
4p	21.698963	22.18751205796	21.0
4d*		14.79580445872	14.0
4d	14.60965375	14.05168540175	13.27
4f*		4.472273593914	3.75

4f	5.01242675	4.311084618092	3.3
5s	4.1820087	5.106219616269	4.47
5p*		3.537751923932	3.0
5p	2.8508716	2.841583097980	2.16
5d*		0.6497963810141	}0.23
5d	0.7141968	0.5743919981951	
6s	0.26104675	0.3283017581484	0.383

Table (6-9-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Hg*.

subshell	r (a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.01892	0.016579436	79.44732	97.671314	0.00048	0.00038043900
2s	0.07961	0.069188789	18.73183	24.055844	0.00743	0.0057307117
2p*		0.056998215		23.941119		0.0040642199
2p	0.06734	0.065632647	18.73846	19.400887	0.00549	0.0052465742
3s	0.20041	0.17973450	7.28399	8.8372200	0.04577	0.037101758
3p*		0.17040042		8.7288062		0.033908265
3p	0.19109	0.18611712	7.22576	7.5500790	0.04221	0.040245478
3d*		0.16225202		7.4291290		0.030916540
3d	0.16701	0.16704625	7.14355	7.1620827	0.03256	0.032642610
4s	0.43929	0.39893263	3.19313	3.7224000	0.21719	0.17967175
4p*		0.40155360		3.6084460		0.18349285
4p	0.44332	0.43398234	3.10267	3.2189562	0.22281	0.21406808
4d*		0.44158401		3.0138438		0.22532650
4d	0.45034	0.45248856	2.91956	2.9207164	0.23364	0.23636495
4f*		0.47673673		2.5570488		0.27331899
4f	0.46920	0.48316600	2.58352	2.5212134	0.26336	0.28070490
5s	1.01020	0.91491233	1.30258	1.4884478	1.14287	0.93907345
5p*		0.98712089		1.3642503		1.1018495
5p	1.09541	1.0791773	1.19287	1.2233091	1.35517	1.3185623
5d*		1.4312762		0.92005878		2.4196019
5d	1.43269	1.4988644	0.91032	0.87704474	2.40982	2.6649264
6s	3.32841	2.8419295	0.37607	4.5091349	12.79929	9.3432495

Table (6-9-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Hg*.

HF/a.u.	Relativistic shift/a.u.	Total energy/a.u.
-18408.99149576	-1024.21656420	-19433.20805995

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	**retardation**	
-19653.65019	25.353410795	-2.68849576	19630.98458

Table (6-9-c)): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for Hg.

6-10- Thallium $_{81}Tl$

subshell	HF energy/a.u.	DHF energy/a.u.	Experimental energy/a.u.
1s	2851.547193	3166.308184345	3144.5
2s	484.5601593	569.1669046273	564.21
2p*		544.9589610768	540.36
2p	465.7267086	468.9044589310	465.35
3s	117.1504551	138.4376961420	136.18
3p*		127.6546623131	125.57
3p	108.1967842	110.5244472696	108.70
3d*		93.08040877486	91.36
3d	91.7084766	89.45676913337	87.84
4s	26.883433865	32.31139981174	31.08
4p*		27.64462343548	26.51
4p	22.91769375	23.42631013338	22.38
4d*		15.84255936561	15.0
4d	15.6529619	15.04553331168	14.20
4f*		5.190097303497	4.51
4f	5.7852471	5.014096150090	4.35
5s	4.6187855	5.622767123731	5.01
5p*		3.985032947972	3.66
5p	3.2313775	3.216939791481	2.77
5d*		0.8942155033847	0.57
5d	0.9682785	0.8059087053937	0.5
6s	0.36111135	0.4495846047062	
6p*		0.2112787916735	0.22
6p	0.19239735	0.1764633953805	

Table (6-10-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Tl*

subshell	r(a. u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.01869	0.016307686	80.44664	99.544738	0.00047	0.00036847149
2s	0.07858	0.068006602	18.97909	24.565949	0.00724	0.0055399369
2p*		0.055962349		24.446750		0.0039216248
2p	0.06646	0.064719990	18.98651	19.677184	0.00535	0.0051019848
3s	0.19759	0.17664201	7.38978	9.0210831	0.04449	0.035844090
3p*		0.16736324		8.9113966		0.032720167
3p	0.18833	0.18328002	7.33231	7.6713562	0.04100	0.039032159
3d*		0.15963844		7.5510169		0.029926565
3d	0.16448	0.16448286	7.25179	7.2723345	0.03157	0.031642624
4s	0.43194	0.39128757	3.24972	3.8058975	0.20996	0.17285319
4p*		0.39347005		3.6917550		0.17617847
4p	0.43549	0.42608730	3.16008	3.2818215	0.21497	0.20633416
4d*		0.43240183		3.0787293		0.21597364
4d	0.44121	0.44326555	2.97969	2.9816215	0.22416	0.22673201
4f*		0.46236886		2.6279989		0.25615651
4f	0.45539	0.46861498	2.65366	2.5908051	0.24723	0.26306176
5s	0.98219	0.88901477	1.34196	1.5364901	1.07922	0.88593861
5p*		0.95503300		1.4138987		1.0298521
5p	1.05962	1.0442453	1.23476	1.2662367	1.26566	1.2322683
5d*		1.3388539		0.97981021		2.0941789
5d	1.34120	1.3941057	0.96892	0.93798396	2.09050	2.2759320
6s	2.96691	2.5778926	0.42173	0.49747485	10.07303	7.6217582
6p*		3.5169952		0.36102694		14.476469
6p	3.92625	4.0131578	0.31623	0.31299260	17.87610	18.831657

Table (6-10-b) Comparison between Hartree-Fock and Dirac-Fock mean values for *Tl.*

HF/a.u.	Relativistic shift/a.u.	Total energy/a.u.
-18961.82482530	-1079.26782112	-20041.09264642

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-20280.14899	26.504299489	-2.81043639	-20256.45513

Table (6-10-c):): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Tl*.

6-11- Bismuth $_{83}Bi$

subshell	HF energy/a.u.	DHF energy/a.u.	Experimental energy/a.u.
1s	3000.163695	3352.039012195	3328.15
2s	512.8525685	607.7970736180	602.48
2p*		582.4967654221	577.61
2p	493.4598305	497.0931657494	493.33
3s	125.415705	149.3877218463	147.0
3p*		138.1044173532	135.89
3p	116.1448459	118.7419931058	116.80
3d*		100.6180725296	98.80
3d	99.06714215	96.55142406126	94.83
4s	29.59819615	35.75784275696	34.50
4p*		30.83293021256	29.60
4p	25.4483815	25.99901421086	25.0
4d*		18.02529421073	17.04
4d	17.828882	17.11319487489	16.17
4f*		6.703887589064	6.0
4f	7.41940175	6.495227183120	5.78
5s	5.50820315	6.69118530790	5.85
5p*		4.909504871763	4.30
5p	4.00503835	3.976443483196	3.4
5d*		1.389084564932	1.0
5d	1.48743145	1.270617536207	0.89
6s	0.55816945	0.6868477023406	
6p*		0.3384212953894	
6p	0.28618835	0.2610827027547	0.26

Table (6-11-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Bi*.

subshell	r(a.u)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.01823	0.015780292	82.44526	103.40543	0.00044	0.00034580866
2s	0.07660	0.065716921	19.47367	25.621493	0.00688	0.0051797704
2p*		0.053955294		25.492565		0.0036527607
2p	0.06475	0.062962804	19.48264	20.232288	0.00507	0.0048293534
3s	0.19219	0.17067767	7.60157	9.3992799	0.04209	0.033480077
3p*		0.16151089		9.2868077		0.030491004
3p	0.18303	0.17783421	7.54562	7.9154819	0.03872	0.036755386
3d*		0.15463411		7.7961567		0.028076556
3d	0.15963	0.15957911	7.46834	7.4931312	0.02973	0.029773422
4s	0.41790	0.37662661	3.36364	3.9773019	0.19649	0.16015021
4p*		0.37800319		3.8627392		0.16260405
4p	0.42055	0.41101239	3.27571	3.4089561	0.20042	0.019196790

4d*		0.41504373		3.2095221		0.19885233
4d	0.42397	0.42584118	3.10040	3.1040405	0.20681	0.20909878
4f*		0.43646732		2.7683686		0.22683600
4f	0.43042	0.44241489	2.79236	2.7282743	0.21956	0.23295962
5s	0.93008	0.84039179	1.42221	1.6358198	0.96610	0.79055807
5p*		0.89564729		1.5166224		0.90361388
5p	0.99444	0.98011630	1.31982	1.3541794	1.11153	1.0824889
5d*		1.2012479		1.0904069		1.6655843
5d	1.20462	1.2439741	1.07702	1.0483735	1.66728	1.7877964
6s	2.53935	2.2417493	0.49430	0.57481123	7.30706	5.7125770
6p*		2.7802116		0.45898240		8.9073112
6p	3.13655	3.1865733	0.39851	0.39637608	11.29532	11.742169

Table (6-11-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Bi.*

HF/a.u.	Relativistic shift/a.u.	Total energy/a.u.
-20095.53020854	-1196.13921144	-21291.66941998

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-21572.23210	28.926792665	-3.06642773	-21546.37174

Table (6-11-c):): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Bi*.

6-12- Radon $_{86}Rn$

subshell	HF energy/a.u.	DHF energy/a.u.	Experimental energy/a.u.
1s	3230.312867	3644.805562231	3617.8
2s	556.9131415	669.3866358768	663.56
2p*		642.3552965030	637.4
2p	536.6769975	541.0812900559	537.47
3s	138.421886	166.9674992004	164.78
3p*		154.9011522852	153
3p	128.6715766	131.7246145612	130.08
3d*		112.5611310987	111.1
3d	110.7013669	107.7534919633	106.34
4s	33.9207527	41.34873761635	40.33
4p*		36.02085746636	34.17
4p	29.49118815	30.11864807260	28.25
4d*		21.54639343934	21.0
4d	21.33131915	20.43710056305	
4f*		9.192674466125	
4f	10.10763175	8.926994059932	
5s	6.90581565	8.416808159130	
5p*		6.409030793993	
5p	5.2252085	5.175233686579	
5d*		2.189222179225	
5d	2.32631655	2.016139908905	
6s	0.87399265	1.072703722240	
6p*		0.5403444673918	
6p	0.4280064	0.3838897263296	0.4

Table (6-12-a): Comparison between Hartree-Fock and Dirac-Fock subshell energies compared with corresponding experimental values for *Rn*.

subshell	r(a.u.)		1/r (a.u.)		r**2 (a.u.)	
	HF	DHF	HF	DHF	HF	DHF
1s	0.01759	0.015026252	85.44322	109.50906	0.00041	0.00031469660
2s	0.07380	0.062454250	20.21571	27.302050	0.00638	0.0046877961
2p*		0.051093205		27.156313		0.0032862715
2p	0.06235	0.060484749	20.22695	21.071434	0.00470	0.0044577436
3s	0.18460	0.16223740	7.91979	9.9952145	0.03883	0.030273340
3p*		0.15324119		9.8778612		0.027476178
3p	0.17561	0.17019172	7.86610	8.2857118	0.03564	0.033676025
3d*		0.14763762		8.1674259		0.025590340
3d	0.15286	0.15273391	7.79337	7.8251083	0.02724	0.027260279
4s	0.39834	0.35609165	3.53610	4.2460235	0.17848	0.14318108
4p*		0.35642394		4.1306142		0.14458692
4p	0.39981	0.390063620	3.45080	3.6029106	0.18107	0.17287663
4d*		0.39127898		3.4081284		0.17659336
4d	0.40040	0.40201012	3.28236	3.2890205	0.18425	0.18617444
4f*		0.40332097		2.9757391		0.19226692
4f	0.39837	0.40895543	2.99705	2.9307994	0.18675	0.19754451
5s	0.86160	0.77550469	1.54390	1.7908823	0.82768	0.67220009
5p*		0.81802755		1.6767969		0.75190299
5p	0.91088	0.89731915	1.44839	1.4884392	0.92986	0.90465379
5d*		1.0562860		1.2435927		1.2765914
5d	1.06049	1.0901174	1.22608	1.1987798	1.28138	1.3599057
6s	2.15662	1.9195492	0.58551	0.67677525	5.23267	4.1600068
6p*		2.2415261		0.57500865		5.7309278
6p	2.54338	2.5826272	0.49527	0.49268289	7.37002	7.6506582

Table (6-12-b): Comparison between Hartree-Fock and Dirac-Fock mean values for *Rn*.

HF/a.u.	Relativistic shift/a.u.	Total energy/a.u.
-21866.77224332	-1389.30383643	-23256.07607976

DHF/a.u.	Breit interaction/a.u.		Total energy/a.u.
	Magnetic	retardation	
-23611.1925	32.878641287	-3.48189413	-23581.80

Table (6-12-c):): Average energy of configuration and their corresponding corrections for Hartree-Fock and Dirac-Fock calculations for *Rn*.

CONCLUSIONS

The relativistic effect on the binding energies is important on the inner subshells especially for the ١s and 2s-subshells and this effect becomes more pronounced as Z increases. For the other subshells, this effect is contracted due to the screening by the inner subshells. The contribution of the relativistic two body effect (Breit interaction) is about 2% of the relativistic single-particle effect (mass-velocity and Darwin correction). Finally the Hartree-Fock calculations and single-particle relativistic correction gives reasonably good results for heavy atoms while Dirac-Fock calculation and Breit interaction gives high precision calculations.

FUTURE WORK

This work can be extended to include the Breit interaction in the unperturbed Hamiltonian and introduced it in the self consistent field process. Also we can take into account the radiative corrections quantum electrodynamics (QED) (self energy and vacuum polarization corrections).

REFERENCES

[1]- I. I. Sobel'man, Introduction to The Theory of Atomic Spectra, Pergamon Press Ltd. (1972).

[2]- C. F. Fischer, The Hartree-Fock Method For Atoms, John Wiley and Sons, Inc. (1977).

[3]- D. R. Hartree, Proc. Cambridge Phil. Soc. 24(1928)89.

[4]- D. R. Hartree, Proc. Cambridge Phil. Soc. 24(1928)111.

[5]- V. Fock, Z. Physik 61(1930)126.

[6]- J. C. Slater, Phys. Rev. 35 (1930) 509.

[7]- G. H. Shortley, Phys. Rev., 50, 1072 (1936).

[8]- J. C. Slater, Quantum Theory of Atomic Structure, Mc Graw-Hill, New York, (1960).

[9]- B. Swrirles, Proc. Roy. Soc. A 152(1935)652.

[10]- A. O. Williams, Phys. Rev. 58(1940)723.

[11]- D. F. Mayers, Proc. Roy. Soc. A 241(1957)93.

[12]- S. Cohen**,** Phys. Rev. 118(1960)489.

[13]- J. L. Schonfelder, Proc. Phys. Soc. 87(1966)163**.**

[14]- D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. 137(1965)A27**.**

[15]- I. P. Grant, Proc. Roy. Soc. A 262(1961)555.

[16]- I. P. Grant, Proc. Roy. Soc. A 86(1965)563.

[17]- Y. K. Kim, Phys. Rev. 154(1967)17.

[18]- J. P. Desclaux, At. Data Nucl. Data tables 12(1973)311.

[19]- J. P. Desclaux, Comput. Phys. Commun. 9(1975)31.

[٢٠]- B. J. McKenzeie, I. P. Grant and P. H. Norrington, Comput. Phys. Commun. 21(1980)233

[21]- Markus Reiher and Karsten Kind, J. Phys. B: At. Mol. Opt. Phys. 34(2001)3133.

[22]- C.Z. Dong, S. Firtzsche, B. Fricke and W. D. Sepp, Physica Scripta. T92(2001)294.

[23]- A. Irimia and C. F. Fischer, J. Phys. B: At. Mol. Opt. Phys. 37(2004)1659.

[24]- Mitchel Weissbluth, Atoms and Molecules, Academic Press, Inc., New York, (1978).

[25]- I. Lindigren and J. Morrison, Atomic Many-Body Theory, Springer-Verlag, Berlin Heidelberg, (1982).

[26]- C. F. Fischer, comput. Phys. Reports 3(1986)273.

[27]- C. F. Fischer, comput. Phys. Commun. 43(1987)355.

[28]- J. P.. Desclaux, C. M. Moser, G. Verhaegen, J. Phys. B: Atom. Molec. Phys. 4(1971)296.

[29]- E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge University Press, London, (1935).

[30]- R. D. Cowan, The Theory of Atomic Structure and Spectra, University of California press, Ltd., London, (1981).

[31]- J. D. Jackson, Classical Electrodynamics, John Wiley and Sons, Inc., Canada, (1975).

[32]- A. R. Edmonds, Angular Momentum in Quantum Mechanics, Princeton University Press, New Jersy, (1960).

[33]- T. Koopmans, Physica 1(1934)104.

[34]- L. I. Schiff, Quantum Mechanics, McGraw-Hill, Inc., (1968).

[35]- Hans A. Bethe and Edwin E. Salpeter, Quantum Mechanics of One and Two electron Atoms, Springer-Verlag, Berlin (1957).

[3٦]- I. P. Grant, Comput. Phys. Commun. 17(1979)149.

[37]- S. Fritsche, Physica Scripta. T100(2002)37.

[3٨]- F. A. Parpia, C. F. Fischer and I. P. Grant, Comput. Phys. Commun. 94(1996)249.

[3٩]- V. B. Berestetskii, E. M. Lifshitz and L. P. Pitaeevskii, Relativistic Quantum Theory, part 1, Pergamon Press Ltd., Heading Hill Hall, Oxford, (1971).

[٤٠]- K. J. Dyall, I. P. Grant, C. J. Johnson, F. A. Parpia and E. P. Plummer, Comput. Phys. Commun. 25(1989)425.

[٤١]- V. V. Karasiev, E. V. Ludena and Olga A. Shukruto, Phys. Rev. A 69(2004)052509-1.

[42]- I. P. Grant, B. J. McKenzeie, P. H. Norrington, D. F. Mayers and N. C. Pyper, Comput. Phys. Commun. 21(1980)207.

[43]- S. Fritzsche and I. P. Grant, Comput. Phys. Commun. 92(1995)111.

[44]- I. P. Grant and N. C. Pyper, J. Phys. B: At. Mol. Phys. 9(1976)761.

[45]- D. F. Mayers, J. de Physique, 11-12 (1970)C4-221.

[46]- I. P. Grant, Adv. Phys. 19(1970)747.

[47]- J. B. Mann and W. R. Johnson, Phys. Rev. A 4(1971)41.

[48]- Markus Reiher and Juergen Hinze, J. Phys. B: At. Mol. Opt. Phys. 32(1999)5489.

[49]- P. Indelicato G. C. Rodrigues, E. Lindroth, M. A. Ourdane, F. Parente, J. P. Santos, P. Patte and J. Bieron, Physica Scripta. T92(2001)327.

[٥٠]- G. Breit, Phys. Rev. 34(1929)553.

[٥١]- G. Breit, Phys. Rev. 36(1930)383.

[٥٢]- G. Breit, Phys. Rev. 39(1932)616.

[٥٣]- S. S. Huang, Astrophysics. J. 108(1948)354.

[54]- C. F. Fischer, T. Brage and Per Jönsson, Computational Atomic Structure, Institute of Physics Publishing, Bristol, Philadelphia, (1997).

[55]- D. F. Mayers and F. O'Brien, J. Phys. B: At. Mol. Phys. 1(1968)145.

[56]- G. Dahlberg and A. Björck, Numerical Methods, Prentice Hall, New York, (1974).

[57]- C. F. Fischer, Can. J. Phys.,41(1963)1895.

[58]- J. P. Desclaux, D. F. Mayers and F. O'Brien, J. Phys. B: At. Mol. Phys. 4(1971)631.

[59]- J. A. Bearden and A. F. Burr, Rev. Mod. Phys. 39(1967)125.

[60]- C. E. Moore , Atomic Energy Levels I-III of Nat. Stand. Ref. Ser., Nat.Bur. Stand. (U. S.), 35. U. S. Government Printing Office, Washington D. C., (1971).

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جمهورية العراق
وزارة التعليم العالي
والبحث العلمي
جامعة النهرين
كلية العلوم

حسابات نسبيه لبعض خصائص اطياف الذرات المتوسطة و المرتفعة العدد الذري

اطروحة مقدمة الى كلية العلوم في جامعة النهرين
كجزء من متطلبات درجة دكتوراه فلسفه في الفيزياء

من قبل
عدنان يوسف حسين

ماجستير (١٩٩٨)

في

جمادا الآخرة ١٤٢٧هـ تموز ٢٠٠٦م

الخلاصة

تم تقديم دراسة منتظمة لطريقة هارتري-فوك غير النسبيه وكذلك نسختها النسبية (ديراك-فوك) لمعدل التوزيع. بالنسبه للطريقة غير النسبية؛ فقد تم اشتقاق معادلات هارتري-فوك وبشكل مفصل واخذ بنظر الاعتبار التصحيح النسبي (تاثير الكتله-السرعه وتاثير دارون وتاثير تفاعل البرم-المداري للاكترون) وقد اعتبر كرتبه اولى للاضطراب. اما بالنسبه للطريقه النسبيه؛ فقد تم اشتقاق معادلات ديراك-فوك واخذ بنظر الاعتبار تاثير تفاعل بريت كتصحيح نسبي للتفاعل الكولومي وقد اعتبر كرتبه اولى للاضطراب. تم تقديم معادلات عناصر

المصفوفه لتفاعل بريت (الحد المغناطيسي والحد الارتدادي) لمعدل التوزيع. تم تقديم النتائج لبعض خصائص الذرات في المستوى الارضي (Rb, Zr, Pd, Sn, Cs, Ba, Lu, Ir, Hg, Tl, Bi, Rn) وتمت مقارنتها بالنتائج العمليه. التأثير النسبي على طاقات الاغلفه الذريه مهم وخصوصا على الاغلفه الداخليه 1s و 2s وهذا التأثير يكون محسوسا كلما ارتفع العدد الذري. يكون تأثير بريت حوالي ٢% من تأثير التصحيح النسبي (تاثير الكتله-السرعه وتاثير دارون). حسابات هارتري-فوك والتصحيح النسبي يعطي نتائج مقبوله بينما حسابات ديراك-فوك وتاثير بريت تعطي حسابات عالية الدقه.