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Relativistic Hartree-Fock Computations of Group15 Atoms and Some Diatomic Molecules

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To whom it may concern

Toulouse, May 5, 2015

Confirmation of research stay

I hereby confirm that since April 1 2015 Bilal Khalid Jasim has been working in my group at the Laboratoire de Chimie et Physique Quantiques (LCPQ) at the university of Toulouse (Paul Sabatier). We have started a collaboration on relativistic molecular quantum mechanics.

Best regards

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Summary

Atoms and molecules are the fundamental constituents of materials and they are the main key that can open the door to understand the materials' structures and dynamics. The goal of a computational atomic and molecular physics is to determine numerical solutions of approximate equations. All measurable properties of the atoms and molecules can be obtained by these solutions.

In the present work, accurate treatments for both non-relativistic quantum mechanics and relativistic quantum mechanics have been presented. The treatments were applied for the atoms group15 (in periodic table) that comprises ${}_{7}N$, ${}_{15}P$, ${}_{33}As$, ${}_{51}Sb$, ${}_{83}Bi$ and ${}_{115}Uup$ and for diatomic molecules, such as Li_2, N_2, F_2 and Se_2. The treatments depended on three essential techniques, which are basis-set, Hamiltonian and type of method. The obtained results, from modified GRASP1.0.0 and DIRAC14.2 programs, were compared with experimental results, non-relativistic C.F.Fischer treatment and relativistic Visscher treatment.

The first technique depended on approximate 4-component spinors and the expanded spinor into a finite basis set. Each 4-components are a linear combination of scalar basis function (atomic basis set). The scalar basis set was formed by primitive Cartesian Gaussian basis function and subdivided into a large (L) and small (S) components sets, which were used to describe the upper and lower two components of the 4- spinors, respectively. Gaussian basis function type Dunning basis set for the non-relativistic treatment and the type Dyall basis set for the case of relativistic treatment have been adopted. The small component Gaussian basis function was derived from the large component Gaussian basis function by using kinetic balance relationship. The second technique depended on the type of Hamiltonian, especially on the potential term. In this technique, two models were utilized to describe the nuclear charge distribution. The first model is called point charge model, whereas the second model is called the Gaussian charge model, which can be combined with Gaussian basis set for the two cases non-relativistic and relativistic treatments to solve the singularity. Accurate calculations for the

atoms and molecules required methods that have more flexibility to treat the relativistic and non-relativistic treatments. The third technique depended on two methods. Firstly, Hartree-Fock method, which was used with Dunning-Gaussian basis-set in non-relativistic. Secondly, Dirac-Hartree-Fock method, which was used with Dyall-Gaussain basis-set in relativistic to treat the systems that have many-electrons in atoms and molecules.

The results showed that in the case of heavy atoms, such as $_{51}Sb$ and $_{83}Bi$ and super heavy atoms, such as $_{115}Uup$ the inner spinors $s_{1/2}$ and $p_{1/2}$ were strongly contracted. In addition, the result showed weak singularity. In order to describe the nuclear charge distribution and solve the issue of singularity at the origin for the $1s_{1/2}$ and $2p_{1/2}$ spinors, the Gaussian charge plus Gaussian basis set model was harnessed. For the atoms, the obtained results, that include the total energy, the energy of each spinor in atoms, the energy of valance configuration, the expectation value of $\langle r \rangle$, the energy of each molecular orbital, the behavior of the large and small components for closer orbitals and the behavior of the radial overlap density of $p_{1/2}$ and $p_{3/2}$ for each atom in group15, were better than the C.F.Fischer treatment in non-relativistic and Visscher treatment in relativistic.

The technique's accuracy was stemmed from the type of Gaussian basis-set, that containens Dunning-Gaussian type (non-relativistic treatment) and Dyall-Gausaaian type (relativistic treatment), which was used to describe the correlation and polarization wave functions for valance orbitals and the Gaussian charge model, which was used to describe the nuclear charge to solve the problem of singularity in closer orbitals.

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Bilal

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Contents

Acronyms

symbol	meaning
HF	Hartree-Fock
STF	*Slater Type Function*
GTF	*Gaussian Type Function*
cGTF	contracted Gaussian basis function
VDZ	Valence Double-Zeta
DZ	Double-Zeta
Zeta	The usual name for the exponent Gaussian function
AOs	Atomic orbitals
CBS	Complete Basis-Set
MCDHF	Multi-Configuration Dirac-Hartree-Fock
T.I.S.E	Time Independent Schrödinger Equation
CSF	Configuration State Function
SCF	Self-Consistent-Field
MCHF	Multi-Configuration Hartree-Fock
ASFs	Atomic State Functions
MOs	Molecular Orbitals
$cc-pVXZ$	correlation-consistent, polarized Valance, $X-zeta$ basis
$X-zeta$	$X = D, T, Q$, D is Double-zeta, T is Triple-zeta, Q is Quadruple-zeta
DHF	Dirac-Hartree-Fock
BOA	Born-Oppenheimer Approximation
LCAO	Linear Combination of Atomic Orbitals
L	Large component
S	Small component

List of Symbols

symbol	meaning
Ψ_i	The $i-th$ molecular orbital
$c_{\mu i}$	The coefficient of linear combination of atomic orbitals
ϕ_μ	The $\mu-th$ atomic orbital
N	A normalization constant
α	The control the width of the orbital called exponent
r, θ and φ	Spherical coordinates
$Y_{lm}(\theta, \varphi)$	The angular momentum part
ζ	The Gaussian orbital exponent
n, l, m	The principle, angular momentum,and magnetic quantum numbers
x, y, z	The Cartesian coordinates
a,b,c	The control angular momentum
$d_{\mu k}$	The fixed coefficient of Gaussian primitive k
g_k	Gaussian primitive
H	Non-Relativistic Hamiltonian
$\hat{H}_1$	The sum of the N identical one-body Hamiltonians
$\hat{H}_2$	The sum of $N(N-1)/2$ identical terms $\frac{1}{r_{ij}}$,
$\hat{h}_i$	Hamiltonian for one-body
∇_i^2	
$\frac{1}{r_{ij}}$	represent the two-body interactions between each pair of electrons
Z	nuclear charge
L^2	The square of the angular momentum operator
L_Z	The z-projection of angular momentum
S^2	The square of the spin operator
S_Z	The z-projection of the spin operator
$\rho(r)$	The nuclear charge density distribution
$V(r)$	potential energy function
$\delta(r)$	The three-dimensional Dirac delta function
$\phi(r_i)$	Coulomb potential
$\rho_N(r_i)$	The Gaussian nuclear charge distribution
η	The exponential parameter chosen to give a root-mean-square value
$\left\langle r^2 \right\rangle^{1/2}$	root-mean-square value of the nuclear charge distribution
A	The atomic mass of a nucleus
$U_{nlm_lm_s}$	The central field orbital
$R_{nl}(r)$	The radial function

$\chi_{1/2,m_s}$	The spin function
$\hat{A}$	The anti symmetrizing operator
$\hat{P}$	The permutation operator
$\hat{g}(i,j)$	represent the two-electron interaction, means $\hat{g}(i,j) = \frac{1}{r_{ij}}$
P_{ij}	operator that interchanged linking coordinates (spatial and spin) of the electrons i and j,
$J_{\lambda\mu}$	called the Coulomb term or a Coulomb operator
$K_{\lambda\mu}$	called the exchange term exchange operator
E_{HF}	The energy Hartree-Fock
$u_{nlm}(r)$	a single-electron orbital in the central field
$\Phi(\gamma LS)$	denote configuration state function
γ	represent the set on nl quantum numbers and the angular coupling scheme
λ	Lagrange multiple
$I(n_il_i, n_jl_j)$	The radial part integral of the orbitals for each occupied sub-shell the
$F^k(n_il_i, n_il_i)$	The radial integral
$G^k(n_il_i, n_jl_j)$	The radial integral
$R^k(nln'l', n'l'nl)$	represent the two particle slater integral
$Y^k(n_1l_1n_3l_3)$	The exchange energy produced from the interaction between the electron and the electrons in other shells
f_k and g_k	The coefficients depend on the angular coupling
$\chi(n_il_i;r)$	The function arises from the exchange with in configuration stat
ε_{ii} and ε_{ij}	represented the energy diagonal and off diagonal respectively
$\Psi(r,R)$	The function for the stationary state
r and R	denote to the set of electronic and nuclear coordinates respectively
$r_{iA} = \lvert r_i - R_A \rvert$	The distance between the electron i and the nucleus A
$r_{ij} = \lvert r_i - r_j \rvert$	denotes the distance between the electrons i and j
$R_{AB} = \lvert R_A - R_B \rvert$	The distance between the nucleus A and the nucleus B
Z_A	The atomic number
$\hat{T}_N$	The kinetic energy of nuclei
$\hat{T}_e$	The kinetic energy of electrons
$\hat{V}_{e-N}$	The electrostatic interaction between the electrons and the nuclei
ϕ_A	The scalar potential of the nucleus
$-e$	The electrons charge
$\hat{V}_{e-e}$	The electrostatic interaction between the electrons
$\hat{V}_{N-N}$	The repulsion energy between nuclei

$\hat{F}$	Fock operator
$F_{\mu\nu}$	The Fock integrals
$S_{\nu\mu}$	The overlap integral
$\Psi_{n\kappa m}$	The one-electron Dirac wave function
h_D	The Dirac Hamiltonian
α and β in	Dirac Matrices
$\sigma_x, \sigma_y, \sigma_z$	Pauli matrices
$P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$	The large and small component radial wave functions
$\delta_{nn'}\delta_{\kappa\kappa'}$	The Kronecker delta
$\chi_{\kappa}^{m_j}(\theta,\phi)$	The spin-orbit parts
κ	The Dirac quantum number
l	The orbital angular momentum of large component
l^{-}	The orbital angular momentum of small component
$\hat{H}_{DC}$	Dirac-Coulomb Hamiltonian
$u_{n\kappa}(r)$ and $v_{n\kappa}(r)$	The large and small components of the electron wave functions respectively
$\xi_{n\kappa p}, \eta_{n\kappa q}$	linear variation parameters
$f_{\kappa p}^{L}(r)$ and $f_{\kappa q}^{S}(r)$	The relativistic Gaussian basis-set
ζ_L and ζ_S	parameters usually called the exponents of the basis function
$F_l(a,b)$	The radial integrals
$\gamma_{ij}^{A}, \Gamma_{ijkl}^{A}$	structure factor or coupling coefficient

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Chapter One

Chapter 1

Introduction and Literature Review

1.1 Introduction

The laws and equations that govern the behavior of the electrons in atoms and molecules are, of course, unknown exactly, but only to a certain approximation. The goal of atomic and molecular computational physics is to determine the numerical solutions to these approximate equations. From these solutions, most measurable properties of atoms and molecules can be obtained, and can be compared with experiments. For the calculated properties to be of any practical use, it must be possible to provide error estimates for them. To do so, a number of calculations have to be performed, where the convergence of the properties is studied as the approximate solution improved. Variational methods, such as Multi-Configuration-Hartree-Fock or Dirac-Hartree-Fock, are well suited for this purpose, since the function space spanned by the trial functions can be extended in a natural way. In addition, most variational methods are very general, and allow different types of atoms and states to be studied within the same formalism. The starting point of non-relativistic quantum mechanics is the Schrödinger equation that describes the motion of electrons and nuclei. Many-particle equations can not be solved exactly and ways to obtain approximation solution must be found. The 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. For the study of such a system we rely on some approximation methods, such as the Hartree-Fock method (HF). 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 equation is solved in an iterative manner until a chosen level of self-consistent accuracy is achieved. To study the properties of molecular systems as many particle systems, fundamental concepts of quantum physics must be applied. Molecular systems involve, fast and slow degrees of freedom, these would be electronic and nuclear variables, respectively. Such systems can be analyzed by means of the Born-Oppenheimer approximation [1]. Atomic data are of great importance in astrophysics. Computational atomic physics has provided data for many atoms and ions, but the need for additional data is enormous [2], especially for more complicated atoms, where little progress has been made so far. By developing reliable computational methods in order to provide these data, atomic physics can help to answer fundamental questions about the universe and its evolution. Atomic data are also essential for understanding processes in plasmas. such data can also be applied, to fusion plasmas, laser physics, and transition probabilities. They are also needed in the search for new and efficient laser transitions. This is particularly important in the context of the current research in X-ray laser generation in dense plasmas.

1.2 Hartree–Fock Algorithm

In computational physics, the Hartree–Fock (HF) method is a method of approximation for the determination of the wave function and the energy of a quantum many-body system in a stationary state. The Hartree–Fock method often assumes that the exact N-body wave function of the system can be approximated by a single Slater determinant in the case of fermions. By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. A solution of these equations yields the Hartree–Fock wave function and energy of the system [3]. The Hartree–Fock method is typically used to solve the time-independent Schrödinger equation for a multi-electron atom or molecule as described in the Born–Oppenheimer approximation. Since there aren't exact known solutions for many-electron systems, the problem is solved numerically. Due to the nonlinearities introduced by the Hartree–Fock approximation, the equations are solved using a nonlinear method such as iteration, which gives rise to the name "self-consistent field method".

1.3 Basis set

Basis sets are a mathematical convenience, this is because of the quantum mechanical equations which describe the behavior of electrons in atoms and molecules are most easily solved by expanding the wave function or density in terms of a finite set. The molecular orbitals can be created by linear combinations of a set of functions called atomic orbitals as [4]:

$$\Psi_i = \sum_{\mu=1}^{n} c_{\mu i}\phi_{\mu} \tag{1.1}$$

where Ψ_i is the $i-th$ molecular orbital, $c_{\mu i}$ are the coefficients of linear combination of atomic orbitals, ϕ_{μ} is the $\mu-th$ atomic orbital, and n is the number of atomic orbitals. The basis sets typically model atomic orbitals centered on the atoms. There are two general categories of basis sets. The first minimal basis-set, is a basis set that describes only the most basic aspects of the orbitals, and secondly extended basis set, is a basis set that describes the orbitals in a great detail. In quantum molecules approximate calculations are used for atomic orbitals with different forms. One type of basis functions is the *Slater Type Function* (STF) which is similar to the hydrogen wave function. Another type of basis functions is the *Gaussian Type Function* (GTF).

1.3.1 Slater Type Function

Slater type function (STF) which is similar to the hydrogen wave function, has the form in spherical coordinate as:

$$\phi_i\left(\xi, n, l, m; r, \theta, \varphi\right) = Nr^{n-1}e^{-\alpha r}Y_{lm}\left(\theta, \varphi\right) \tag{1.2}$$

where N is a normalization constant, α is the control width of the orbital called exponent, r, θ and φ are spherical coordinates, and $Y_{lm}\left(\theta, \varphi\right)$ is the angular momentum part. The n, l, m are the principal, angular momentum, and magnetic quantum numbers, respectively. The exponential depends on the distance between the nucleus and electron mirrors of the exact orbitals. However, the STFs do not have any radial nodes; nodes in the radial part are introduced by making linear combinations of $STFs$. The exponential dependence ensures a fairly rapid convergence with increasing number of functions. The Slater type orbital for 1s type atomic orbital have a cusp at the origin.

1.3.2 Gaussian Type Function

Gaussian type function(GTF) is an atomic orbital used in linear combinations forming molecular orbitals, has the form in spherical coordinate as.

$$\phi\left(\zeta, n, l, m; r, \theta, \varphi\right) = Nr^{n}e^{-\zeta r^2}Y_{lm}\left(\theta, \varphi\right) \tag{1.3}$$

where ζ is the Gaussian orbital exponent, N, is a normalization constant, The r, θ and φ are spherical coordinates, and $Y_{lm}\left(\theta, \varphi\right)$ is the angular momentum part. The Gaussian function can be written in Cartesian coordinates, and it is given by:

$$\phi^{GTF}\left(\zeta, a, b, c; x, y, z\right) = Ne^{-\zeta r^2}x^a y^b z^c \tag{1.4}$$

where N is a normalization constant which insures that the square of the Gaussian gives a value of 1.0 when integrated over all space x, y, z in Cartesian coordinates. The a, b, c are angular momentum control parameters; $L = a + b + c$, and ζ controls the width of the orbital. ζ is the Gaussian orbital exponent, which helped to determine the radial size of the function. The variable r represents the distance of the electron from the origin of the Gaussian functions with $L = a + b + c = 0$, are spherically symmetric about the origin and are known as "s" functions. Similarly, the three functions corresponding to $a + b + c = 1$ are the p_x, p_y, p_z functions, etc. The Cartesian Gaussian possesses six functions with $a+b+c=2$, from which the five spherical components, d_{xy}, d_{xz}, d_{yz}, d_{xx-yy} and $d_{2zz-xx-yy}$, can be constructed.

1.3.3 Gaussian Primitive Functions

Gaussian primitives are added together in linear combinations to produce basis functions which are approximations to natural orbitals. The primitive function is usually obtained from quantum calculations on atoms. The primitive functions describe isolated atoms and cannot accurately describe deformations of atomic orbitals brought by the presence of other atoms in the molecule. For molecular calculations, these Gaussian primitives have to be contracted. The contraction means a linear combination of Gaussian primitives which can be used as basis function. A Gaussian primitive is given by :

$$\phi_{\mu} = \sum_{k} d_{\mu k} g_k \tag{1.5}$$

where ϕ_{μ} is the atomic basis function, $d_{\mu k}$ is the fixed coefficient of Gaussian primitive k, and called contraction coefficient in atomic orbitals, and g_k is Gaussian primitive. The designers of basis sets have optimized the set of coefficients $d_{\mu k}$ and the set of exponents ζ in equation (1.4) used in the Gaussian primitive g_k to give a balanced set of orbitals for a certain set of elements. The individual Gaussian functions are summed to produce a contracted Gaussian basis function (cGTF). So a set of p-functions is three basis functions, but may be many primitive basis functions.

1.3.4 Contracted Gaussian Basis Function (cGTF)

Contracted Gaussian-type Function (cGTF) is the usual basis-set function, a linear combination of Gaussian functions with the linear coefficients fixed, multiplied by an angular function. Contracted Gaussian basis sets for atom and molecule calculations are derived from primitive basis-sets. So, one set of p-functions contains three cGTF's $(p_x, p_y, and p_z)$, i.e, three basis functions.

Contraction refers to the particular choice of scheme for generating the linear combinations of Gaussian functions that constitute a contracted basis set. A "generally-contracted" basis set is one in which each primitive is used in many basis functions.

1.3.5 Valence Double-Zeta (VDZ) Basis-Set

A basis consisting of a minimal basis set for the core electrons and a double zeta basis set for the valence electrons would be called a split valence double zeta basis set. A Valence Double-Zeta (VDZ) is a minimal basis-set used to describe core electrons, but the valence electrons have twice the minimum number of functions which mean double zeta. This means the valance orbitals are split into two parts: an inner, compact orbital and an outer, expanded orbital. The coefficients of these two kinds of orbitals can be varied independently during the construction of the molecular orbitals as shown in Fig (1.1). The Double-Zeta (DZ) is a basis set for which there are twice as many basis functions as are minimally necessary.

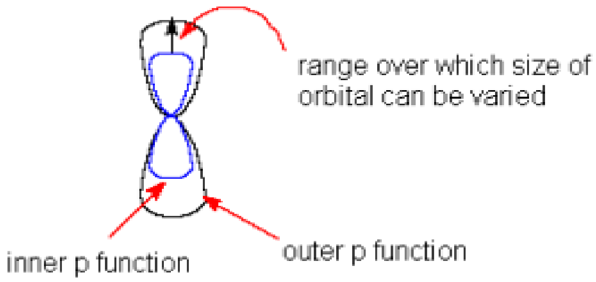


Figure 1.1: **Split-valance for p-type basis functions**

1.3.6 Polarized Basis-Set

When the wave function includes polarization functions, this means increasing basis-set to get closer to the exact electronic energy. A polarized basis set includes functions that are of higher angular momentum than minimally required. For example, nitrogen atom has 1s, 2s, and 2p orbitals, so a polarized basis set would also include at least a set of d-functions. The added functions are often called polarization functions. Polarization functions are included to improve the flexibility of the basis set, particularly to better represent electron density in bonding regions. The outer shell have two (or more) valence shell basis functions for each natural valence shell orbital. The tails of the Atomic Orbitals (AOs) are allowed to vary to account for the different electronic properties of an element in different molecular environments. Usually, need at least one extra basis function and allow electron cloud to be polarized off-center from the nucleus, this is called a polarization function. Polarization functions help to account for the fact that atoms within molecules are not spherical. The use of polarization basis functions allows for the atomic electron densities to be polarized in order to better represent the electron density of the molecule. Consider the sum of an s-type orbital and a p-type orbital, as shown in Fig (2.1). One lobe of the p-type orbital is enhanced by the addition of the s-type orbital, while the lobe of opposite sign cancels and a few are left. This has the effect of polarizing the electron density from its original spherical shape into a form that is polarized in one direction.

Figure 1.2: **The polarization s-type basis with p-type basis functions**

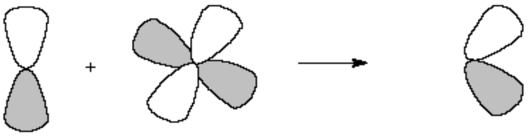


Figure 1.3: **The polarization p-type basis with d-type basis functions**

1.3.7 Double-zeta with polarization (DZP)

The Double Zeta (DZ) basis set is polarized with two basis functions added of each type found in the separated atoms. A polarization set generally has an angular momentum one unit higher than the highest valence function. So a polarization set on nitrogen is added to the set of d-functions. For the nitrogen atom, a double zeta basis set would consist of two $1s$, two $2s$, and two each of $2p_x$, $2p_y$, and $2p_z$ orbitals, for a total of 10 $basis\ functions$. The two $1s$ orbitals employed in the basis set are not identical. Rather, they have different orbital exponents. The same is true for the 2s and 2p orbitals. The basis functions in the double zeta basis set are denoted $1s$, $1s'$, $2s$, $2s'$, $2p(3)$, and $2p'(3)$.

1.3.8 Correlation-Consistent Polarized Valence Double-Zeta Basis-Set cc-pVDZ

The smallest in a series of "correlation consistent" basis sets was developed by Dunning and coworkers for high-level calculations. It has been observed that properties computed using successively larger basis sets of this series appear to converge exponentially, presumably to the corresponding Complete Basis-Set (CBS) values. Complete basis set indicates that some method of basis set extrapolation is applied in an attempt to determine the result that would have been obtained using an infinitely large basis set. The two major extrapolation methods are (1) repeating the calculation with increasingly large basis sets and making an empirical extrapolation, and (2) using analytical formulas that are correct to second-order.

1.4 Historical Background

Hartree published two important papers in 1927 [5,6]. In the first paper Hartree described a numerical method for the solution of radial equation with a non-Coulomb central-field, and in a second paper he used these methods to find a field of force such that the distribution of a charge given by the wave functions,shall reproduce the field. Hartree called this field the self-consistent field. The system of differential equations that he solved later, are known as the Hartree equations but Hartree equation with out exchange field. In 1929, Egli Hylleraas concluded a very successful variational calculation of the energy levels in Helium[4]. In 1934, *E. Wigner* explained, Fock pointed out that the Hartree wave function was involved, as it did not satisfy the Pauli exclusion principle, that the wave function 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) wave functions [7]. Slater showed that the resulting wave function was simply the determinant of matrix, called a Slater determinant in 1930 [8]. In 1936 the idea of the configuration average was discussed early by Shortly[9] and has been treated in detail by Slater [10]. S.F.Boys in 1950 obtained numerical accuracy electronic wave functions for the stationary states of atoms and molecules by using Gaussian functions for molecular orbitals and and linear combination of many slater determinant treatment by the variational procedure [11]. E.Clementi and D.L.Raimondi in 1963 used minimum basis set of Slater-type orbitals for atoms with 2 to 36 electrons [12]. In 1964 E.Clementi presented simple basis set by taking inner and outer regions of the wave function for the ground state of the first and second row atom, using self consistent field functions, with two slater type orbitals (STO) [13]. Liberman et al., calculated numerical wave functions for closed shell configuration of some atoms by approximating the exchange term by Slater's method in 1965 [14]. W.J.Hehre, R.F.Stewart and J.A.Pople fixed Slater atomic orbital in 1969, by linear combination of Gaussian orbitals. The sum of Gaussian-type orbital type (STO-nG) to represent STO and Gaussian exponent are shared between Slater-type 2s and 2p functions in self consistent field molecular-orbital calculations [15]. R.Ditchfield, W.J.Hehre and J.A.Pople extended the basis set of atomic functions. The basis set type 4-31G described each inner shell and valance shell for atoms from carbon to flourine. The expansion coefficient and Gaussian exponents are determined by minimizing the total calculated energy of the electron ground state in 1971 [16]. In 1971 Dunning's concentrated on energy optimized GTOs, where each exponent had been variational optimized in an atomic HF linear combination of atomic orbital calculation. He used Huzinaga GTO, which consist of ten primitive S-type GTO and six primitive GTO for each first row atom (10s,6p) to constract contracted (5s,3p) and (5s,4p) GTO [17]. Bungeo et al. in 1992, studied the atoms from (He-Xe) with atomic orbital expressed in terms of Slater type functions. When the the basis set size is increased with respect to the Cleimenti basis , they yield to the total energy becomes better using HF method under MCHF program [18]. M.B.Ruiz and M.Rojas in 2003 studied variational calculation of the $2p_{1/2}$ ground state of boron atom of using a single term reference wave function without inter electronic distance using a 4-31G basis set [19]. The attempts in 1935 to set up relativistic self-consistent field calculation were initiated by Swirles [20]. Swirles showed that Dirac's equation is able to carry through the relativistic version of Fock and Slater's formulation of the Hartree-Fock equations. For a closed shell configuration some relativistic self-consistent calculations were made by various authors, but most of these calculations either omitted the exchange term or made some approximation to avoid the numerical difficulties. For instance, Schonfelder computed for various atoms numerical wave functions without the exchange terms [21]. In 1973 Desclaux calculated highly accurate spinor energies, total energies,and other expectation values for closed shell atoms [22]. Desclaux also published a program for calculation on Multi-Configuration Dirac-Hartree-Fock(MCDHF) in 1975 [23]. B.Fricke presented in 1984 a relativistic atomic structure calculation with Multi-configuration-Dirac-Fock method to study charge density for one-electron Mercury atom in (1s,2s,2p) levels [24]. Matveen et al.,in 1998 analytically calculated the ground state wave function and the energy term of the relativistic electronic moving in the field of two Coulomb center by the method of LCOA to calculate of the critical distance between two nuclei Z=35,Z=68 [25]. Paolo et al., in 2002 studied relativistic correction of the simple one electron mass velocity Darwin approximation and two electron to the ground state electronic energy of H_2S molecule [26]. Hiroshi et al.,in 2005 solved analytically relativistic Dirac-Coulomb (DC) equation for atoms and molecules. Appling this method on the hydrogen like and helium like atoms gives satisfactory results implying a high potentiality in relativistic case [27]. Jacek Bieron et al., used MCDHF model to calculate the expectation value for the $D_{3/2}$ and $D_{5/2}$levels of atomic gold. The approximation employed in this study is equivalent to a complete active space approach [28]. D.M.Gitman, A.D.Levin, I.V.Tyutin, and B.L.Voronov in 2013 used Dirac equation with the Coulomb field of a point charge model to study the electronic spectrum for heavy elements[29]. V.P.Neznamov and I.I.Safronov in 2014 determined the energy level for hydrogen-like atom for $Z > 105$ by using a new method. This method included finite nuclear size effects, suggested for heavy elements encountered in solving the Dirac equation for an electron in the field of a point charge Ze. In this method, the boundary condition for the numerical solution of the equations for the Dirac radial wave functions is taken so that the components of the electron current density are zero at the boundary of the nucleus [30].

1.5 The Aims of The Thesis

The main goal of this work is to find accurate and flexible treatments for both non-relativistic and relativistic quantum mechanics and to develop GRASP1.0.0 program based on these treatments. In addition, the work aims to expand one-component in case of non-relativistic and four-component spinors in case of relativistic into a finite basis-set and to investigate the atomic level properties of heavy and super heavy atoms for group15. Moreover, DIRAC14.2 program was used to compute the properties of diatomic molecules via evaluate the total energy and the spinor energy, which depend on the type potential model and Gaussian Dyall basis set functions.

1.6 Outline of Thesis

The first chapter will briefly review the history of non-relativistic quantum mechanics and relativistic quantum mechanics and the development of the basis-set. The second chapter is divided into two parts, the first part describes Hartree-Fock (HF) approach with Gaussian basis set in case of non-relativistic quantum mechanics for atoms. In the second part, the Schrödinger equation for molecular systems in general is presented. The standard method for quantum molecules is solved for the electronic part problem by using Born-Oppenheimer approximation to find total energy and find energy for grad state and ungrad state. Chapter three have two parts. Part one describes the relativistic atomic structure by using Dirac-Hartree-Fock (DHF) approach for atoms and part two describes the molecular structure theory using DHF approach for molecules. It also gives the relativistic wave function described by Dyall basis set type Gaussian $dyall - 2zp$. In chapter four we present and discuss the results and figures achieved in this project. Finaly, capter five gives the main conclusion, and some suggested future work.

Chapter 2

Non-Relativistic Hartree-Fock for Atoms and Molecules

Part One

Non-Relativistic Hartree-Fock for Atomic Structure Theory

2.1 The Non-Relativistic Hamiltonian

For an N-electron system (atoms or molecules), with a nuclear charge Z, the normal starting point is the Hamiltonian. The non-relativistic Hamiltonian can be written, in atomic units,$(\hbar = m = {e^2}/{4\pi\varepsilon_\circ} = 1)$,as [31].

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \tag{2.1}$$

where,

$$\hat{H}_1 = \sum_{i=1}^{N} \hat{h}_i \qquad ; \hat{h}_i = -\frac{1}{2}\nabla^2_{r_i} - \frac{Z}{r_i} \tag{2.2}$$

and

$$\hat{H}_2 = \sum_{i<j}^{N} \frac{1}{r_{ij}} \qquad ; r_{ij} = \left|\vec{r}_i - \vec{r}_j\right| \tag{2.3}$$

The first term of equation (2.1), $\hat{H}_1$ is the sum of the N identical one-body Hamiltonians $\hat{h}_i$; each individual Hamiltonian $\hat{h}_i$, containing the kinetic energy operator of an electron and its potential energy due to the attraction of the nucleus. The second term, $\hat{H}_2$, is the sum of $N(N-1)/2$ identical terms $\frac{1}{r_{ij}}$, which represent the two-body interactions between each pair of electrons, where $\vec{r}_i$ denotes the relative coordinate of the electron i with respect to the nucleus, the Hamiltonian can be write, as [32],

$$\hat{H} = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla^2_{r_i} - \frac{Z}{r_i}\right) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{2.4}$$

The non-relativistic Hamiltonian commutes with the angular momentum operators $\hat{L}^2, \hat{L}_Z, \hat{S}^2, \hat{S}_Z$ and with the inversion operator $\hat{I}$, and thus the eigenfunctions of $\hat{H}$ must also be eigenfunctions of these operators. In the Hamiltonian above, it is assumed that the atomic nucleus can be treated as a point charge and Gaussian nucleus model.

2.2 Nuclear Charge Distribution Model

In a large part of previous studies, atomic nuclei are considered mainly as massive point-like centers of positive charge, which attract the surrounding electrons and repel other nuclei. The attractive and repulsive Coulomb interactions between the constituting particles, i.e., nuclei and electrons, as well as their kinetic energy, must be balanced if stable structures are to be formed. The application of quantum mechanics which describes behavior of electrons and nuclei under these interactions, finally leads to connection with structure optimization according to the energy minimization principle. The charge distribution within a nucleus can be described by two types of model, using both the point nucleus model and Gaussian nuclear model [33]. The important effects on a single particle function and energy are due to the change from the point like nucleus to an extended nucleus. The models included here are either frequently used in electronic structure calculations or are of importance due to their use for representing nuclear charge density distribution as obtained from experiment. As long as one is interested only in the total energy of the atomic electron system, the change from the simple but unrealistic point nuclear charge to a roughly realistic Gaussian nuclear charge is much more important than finer details due to the variation of the finite nucleus. In the non-relativistic treatment, based on the Schrödinger equation, solutions exist for any nuclear charge Z for both, the point model and the Gaussian model, and the change from the point model to the Gaussian model induces only a slight change in the short-range behavior of non-relativistic radial functions (removal of the cusp). The nuclear charge density distribution $\rho(r)$ is related to the resulting potential energy function $V(r)$.

2.2.1 Point Charge Model

In non-relativistic theory, nuclei are usually treated as point charges. The charge density distribution $\rho(r)$ for the atomic nucleus can be given in terms of Dirac delta distribution [34],

$$\rho_N(\vec{r}_i) = Z_N \delta(\vec{r}_N) \tag{2.5}$$

where δ is the three-dimensional Dirac delta function and $\vec{r}_N$ is the nuclear position . And the scalar potential due to a nucleus N determined by the nuclear charge Z is given by [35],

$$\phi\left(r_i\right) = \int \frac{\rho_N\left(r'\right)}{\left|\vec{r}_i - \vec{r}'\right|} d^3 r' \tag{2.6}$$

giving a Coulomb potential

$$\phi\left(r_i\right) = \frac{Z_N}{r_{iN}} \qquad ; r_{iN} = \left|\vec{r}_i - \vec{r}_N\right| \tag{2.7}$$

However, this introduces weak singularities in the relativistic wave functions at the nuclear origins, which are hard to model in a finite basis approximation [36]. With the introduction of a Gaussian nucleus model, which in any case is a better physical model, the wave functions attain a Gaussian shape at the nuclear origins [37].

2.2.2 Gaussian Charge Model

The Gaussian nuclear charge distribution has the following form,[33]

$$\rho_N\left(r_i\right) = Z_N \left(\frac{\eta_N}{\pi}\right)^{3/2} exp\left(-\eta_N r_{iN}^2\right) \tag{2.8}$$

where the exponent of the normalized Gaussian type function representing the nuclear distribution is determined by the root-mean-square radius of the nuclear charge distribution via the relation [38],

$$\eta_N = \frac{3}{2\left\langle r^2 \right\rangle} \tag{2.9}$$

where η is the exponential parameter chosen to give a root-mean-square value $\left\langle r^2 \right\rangle^{1/2}$of the nuclear charge distribution and, equal to the empirical formula [39, 40]

$$\left\langle r^2 \right\rangle^{1/2} = \left[0.836A^{1/3} + 0.570\right] * 10^{-15} mbohr \tag{2.10}$$

where A is the atomic mass of the nucleus .This gives the formula

$$\eta = \frac{3}{2}\left[\frac{0.529167}{0.836A^{1/3} + 0.570}\right]^2 * 10^{10} \tag{2.11}$$

The electrostatic potential for this charge density distribution is given in terms of the incomplete gamma function as $F_n(x)$: [41],

$$\phi\left(r_{iN}\right)=Z_N\sqrt{\frac{4\eta_N}{\pi}}F\left(\eta_N r_{iN}^2\right)\;;whrer\;F_n(x)=\int\limits_0^1 exp\left[-xt^2\right]t^{2n}dt \quad (2.12)$$

The Gaussian charge distribution leads to a long-range behavior of the potential identical to that of a Coulomb potential, but value at the nuclear origin is finite:

$$\phi\left(r_{iN}\right)=2Z_N\sqrt{\frac{\eta_N}{\pi}} \quad (2.13)$$

This model is popular, due to the easy computational implementation, since the electronic wave function is usually also expanded to Gaussian-type function and electron-electron repulsion integrals.

2.3 Slater Determinants

For a single particle, or electron in a central potential created by static proton, a single wave function is required to describe the system. It would seem reasonable then to form the total wave function of a system of particles as a product of individual wave functions. This describes the simplest approximation. Hartree assumed that each electron moves only in the average field of all the other electrons of the system, where for N-electron system the total wave function can be written as a simple product of one-particle wave functions [42]:

$$\Psi=\prod_{q=1}^{N}u_{\alpha,\beta,\ldots,\nu}(q_N)=u_\alpha\left(q_1\right)u_\beta\left(q_2\right)\ldots u_\nu\left(q_N\right) \quad (2.14)$$

Each of the symbols $\alpha,\beta,\ldots,\nu$ represents a set of four quantum numbers(n,l,m_l,m_s). The one-particle wave function $u_{\alpha,\beta,\ldots,\nu}(q_N)$ is composed of a spatial function and a spin function. And $q_i=(\vec{r}_i,\sigma_i)$, is the space and spin coordinate of the electron labeled i. The problem with this assumption is that electrons are a among a class of particles called fermions. According to Pauli exclusion principle two fermions can not be in the same state and same location, at the same time. This means any wave function describing a system of such particles must be antisymmetric under exchange of particles [39], to build up out of single-electron spin orbitals, a total N-electron wave function $\Psi(q_1, q_2, ..., q_N)$, which is antisymmetric in the spatial and spin coordinates of any two electrons, in order to satisfy the requirements of the Pauli exclusion principle. The total wave function describing an atom in which one electron is in state α and another in state β and so on may be written as a NxN determinant [43]. To satisfy this requirement, Fock and Slater re-derived the equations of Hartree, such that the wave function can be written as a Slater determinant given by [44]:

$$\Psi(q_1, q_2, ..., q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \dots & u_\nu(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) & \cdots & u_\nu(q_2) \\ \vdots & \vdots & & \vdots \\ u_\alpha(q_N) & u_\beta(q_N) & & u_\nu(q_N) \end{vmatrix} \tag{2.15}$$

This wave function is obviously antisymmetric because if we interchange the (spatial and spin) coordinates of two electrons (say q_1 and q_2) this is equivalent to interchanging two rows, so that the determinant changes sign, to satisfy the requirements of the Pauli exclusion principle. The factor $\frac{1}{\sqrt{N!}}$ appearing in equation (2.15) is a normalization factor arising from the fact that there are $N!$ permutations of the electron coordinates, $q_1, q_2, ..., q_N$. A more convenient notation for the total wave function uses the anti symmetrizing operator $\hat{A}$ and is given by [45].

$$\Psi = \hat{A}\left[\Psi(q_1, q_2, ..., q_N)\right] = \hat{A}\prod_{q=1}^{N} u_{\alpha,\beta,...,\nu} \tag{2.16}$$

where

$$\hat{A} = \frac{1}{\sqrt{N!}}\sum_p (-1)^p \hat{P} = \frac{1}{\sqrt{N!}}\left[1 - \sum_{ij}\hat{p}_{\alpha\beta} + \sum_{ijk}\hat{P}_{\alpha\beta\nu} - ...\right] \tag{2.17}$$

and $\hat{P}$ is the permutation operator. $\hat{P}_{\alpha\beta}$ permutes the coordinates of electron α and β, and p is the number of permutations of two indices. If an even number of permutations occurs, the term $(-1)^p$is positive while if odd, the term $(-1)^p$ is -ve. In terms of electron coordinate permutations, we can rewrite the Slater determinant (2-15) in the more compact form. That is [46]

$$\Psi\left(q_1,q_2,\ldots,q_N\right)=\frac{1}{\sqrt{N!}}\sum_P\left(-1\right)^p P u_\alpha\left(q_1\right)u_\beta\left(q_2\right)\ldots u_\nu\left(q_N\right) \qquad (2.18)$$

2.4 The Variational Principle

The variational principle is a method for approximation to the exact solution of the Schrödinger equation, which is very useful in obtaining the bound state energies and wave functions of a time-independent Hamiltonian H. We denote by E_j the eigenvalues of this Hamiltonian and by Ψ_j the corresponding orthonormal eigenfunctions. We choose a trial function with a flexible form, with some parameters that we can vary. The best approximatation to the exact solution for this class of trial wave function is known. Suppose we know that the exact solution of the ground state is given by [47]:

$$\hat{H}|\Psi_j>=E_j|\Psi_j> \qquad (2.19)$$

where Ψ_j is arbitrary wave function. The solutions for any function Ψ_{trial} can be expressed as a linear combination of the eigenfunctions of a Hermitian operator, for instance

$$|\Psi_{trial}>=\sum_j c_j|\Psi_j> \qquad (2.20)$$

where $|\Psi_{trial}>$ is an approximate ground state eigenfunction for the Hamiltonian. The approximate energy function $E^{approxi}\left[\Psi\right]$ is given by:

$$E^{approxi}\left[\Psi_{trial}\right]=\frac{\left\langle\Psi_{trial}\left|\hat{H}\right|\Psi_{trial}\right\rangle}{\left\langle\Psi_{trial}|\Psi_{trial}\right\rangle} \qquad (2.21)$$

An important additional property of the functional $E^{approxi}\left[\Psi_{trial}\right]$ is that it provides an upper bound to the exact ground state energy $E_\circ$. To prove this result, we substitute equation (2-20) in equation (2-21), to get

$$E^{approxi}\left[\Psi_{trial}\right]=\frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} \tag{2.22}$$

If we now subtract $E_\circ$, the energy eigenvalue, from both sides of equation (2-21) we obtain

$$E^{approxi}\left[\Psi_{trial}\right]-E_\circ=\frac{\sum_i |c_i|^2 (E_i-E_\circ)}{\sum_i |c_i|^2} \tag{2.23}$$

We can write the above equation in another form

$$E^{approxi}\left[\Psi_{trial}\right]=\frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} \geqslant \frac{\sum_i |c_i|^2 E_\circ}{\sum_i |c_i|^2} \tag{2.24}$$

Since $E_i \geqslant E_\circ$, the right-hand side of above equation (2.24) is non-negative so that $E_\circ \leq E^{approxi}\left[\Psi_{trial}\right]$. The functional $E^{approxi}\left[\Psi_{trial}\right]$ gives an upper bound, i.e., we can show the exact ground state energy is lower than any approximation.

2.5 The Hartree-Fock Approach

The Hartree-Fock (HF) approach is a method for obtaing approximate total wave functions for many-electron systems. It has been applied successfully for many areas of quantum mechanics including atomic, molecular and solid state systems. This method is based on both central field approximation and the variational principle [48]. To study details of many-electron atoms is a very difficult task in which approximation must be made. The starting point of this approximation is that each of the atomic electrons moves in an effective spherically symmetric potential created by the nucleus and all the other electrons [41]. This approximation is based on an independent particle model, in which each electron moves in an effective potential which represents the attraction of the nucleus and the average effect of the repulsive interactions between this electron and the $(N-1)$ other electrons.

2.5.1 Hartree-Fock Energy Expression for Atoms

The non-relativistic Hamiltonian is explained in section (2.1), and can written in another form, in atomic units i.e. ($\hbar = m = e^2/4\pi\varepsilon_\circ = 1$), as

$$\hat{H} = \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2}\sum_{i\neq j} \hat{g}(i,j) \tag{2.25}$$

The first term in above equation is the sum of the N identical one body Hamiltonians and the second term $\hat{g}(i,j)$ represents the two-electron interaction, i.e., $\hat{g}(i,j) = \frac{1}{r_{ij}}$. To calculate the Hartree-Fock energy for atoms, we take the expectation value of the Hamiltonian (2-25)

$$E_{HF} = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \int \Psi^\star(1,...,N)\,\hat{H}\Psi(1,...,N)\,d_1...d_N \tag{2.26}$$

Now, we take the expectation value for the 1st term in equation (2-25),

$$\sum_{i=1}^{N} \left\langle \Psi \middle| \hat{h}(i) \middle| \Psi \right\rangle = \sum_{i=1}^{N} \int \Psi^\star(1,...,N)\,\hat{h}(i)\,\Psi(1,..,N)\,d_1...d_N \tag{2.27}$$

Since electrons are indistinguishable, therefore each term in this sum must have the same value and we can select one term and multiply with the number of terms, i.e.

$$\sum_{i=1}^{N} \left\langle \Psi \middle| \hat{h}(i) \middle| \Psi \right\rangle = N \int \Psi^\star(1,...,N)\,\hat{h}(1)\,\Psi(1,..,N)\,d_1...d_N \tag{2.28}$$

Following the same argument, we can write the two-electron term in equation (2-25) as,

$$\frac{1}{2}\sum_{i\neq j}^{N} \langle \Psi | \hat{g}(i,j) | \Psi \rangle = \frac{1}{2}\sum_{i\neq j}^{N} \int \Psi^\star(1,...,N)\,g(i,j)\,\Psi(1,...,N)\,d_1...d_N \tag{2.29}$$

$$= \frac{1}{2}N(N-1) \int \Psi^\star(1,...,N)\,\hat{g}(i,j)\,\Psi(1,...,N)\,d_1...d_N \tag{2.30}$$

Now, can write the energy expression by summing equation (2-28) and equation (2-30), to obtain:

$$E = N\int \Psi^{\star}(1,...,N)\,\hat{h}(1)\,\Psi(1,..,N)\,d_1...d_N + \frac{1}{2}N(N-1)\int \Psi^{\star}(1,...,N)\,\hat{g}(i,j)\,\Psi(1,...,N)\,d_1...d_N \tag{2.31}$$

Substituting equation (2-18) in equation (2-28), the first term can be written,

$$N\int \Psi^{\star}(1,...,N)\,\hat{h}(1)\,\Psi(1,..,N)\,d_1...d_N = N\int \frac{1}{\sqrt{N!}}$$

$$\sum(-1)^{p}u_{\alpha}(q_1)\,u_{\beta}(q_2)...u_{\nu}(q_N)\,\hat{h}(1)\times\frac{1}{\sqrt{N!}}\sum(-1)^{p'}u_{\alpha'}(q_1)\,u_{\beta'}(q_2)...u_{\nu'}(q_N) \tag{2.32}$$

To simplify equation (3.32), we replace symbols $(\alpha,\beta,...,\nu)$ by λ, i.e., $\lambda = \alpha,\beta,...,\nu$, we can rewrite equation (2-32),

$$N\int \Psi^{\star}(1,...,N)\,\hat{h}(1)\,\Psi(1,..,N)\,d_1...d_N = \sum_{\lambda}\left\langle u_{\lambda}(q_i)\left|\hat{h}_i\right|u_{\lambda}(q_i)\right\rangle \tag{2.33}$$

where the sum over λ runs over the N individual quantum states (i.e. the N spin orbitals) occupied by the electron, therefore, we introduc a new definition as:

$$I_{\lambda} = \left\langle u_{\lambda}(q_i)\left|\hat{h}_i\right|u_{\lambda}(q_i)\right\rangle \tag{2.34}$$

to be the average value of the individual Hamiltonian $\hat{h}_i$ relative to the spin orbital u_{λ}, as

$$\left\langle \Psi\left|\hat{h}(i)\right|\Psi\right\rangle = \sum_{\lambda} I_{\lambda} \tag{2.35}$$

The second term in equation (2.31) can be written after substituting equation (2-18) as:

$$\frac{1}{2}N(N-1)\int \Psi^{\star}(1,...,N)\,\hat{g}(i,j)\,\Psi(1,...,N)\,d_1...d_N = \frac{1}{2}\sum_{i\neq j}^{N}\langle\Psi|\hat{g}(i,j)|\Psi\rangle$$

$$= \frac{1}{2}N(N-1)\int \frac{1}{\sqrt{N!}}\sum(-1)^{p}u_{\alpha}(q_1)\,u_{\beta}(q_2)...u_{\nu}(q_{\nu})\,\hat{g}(i,j)$$

$$\frac{1}{\sqrt{N!}}\sum(-1)^{p'}u_{\alpha\prime}(q_1)\,u_{\beta\prime}(q_2)...u_{\nu\prime}(q_N) \tag{2.36}$$

The antisymmetrizer operator of equation (2-17) acting on second term in equation (2-31), gives :

$$\hat{A}\left[\frac{1}{2}\sum_{i<j}^{N}\langle\Psi|\hat{g}(i,j)|\Psi\rangle\right]=\frac{1}{2}\sum_{i<j}^{N}\sum_{P}(-1)^{p}\left\langle\Psi\left|\hat{g}(i,j)\hat{P}\right|\Psi\right\rangle \tag{2.37}$$

$$=\frac{1}{2}\sum_{i<j}^{N}\left\langle\Psi\left|\hat{g}(i,j)\left(1-\hat{P}_{ij}\right)\right|\Psi\right\rangle \tag{2.38}$$

where $\hat{P}_{ij}$ an operator that interchanges linked coordinates (spatial and spin) of the electrons i and j. Combining equations (2-18) and (2-38) of two body operators, where the sum over λ and μ runs over the $N(N-1)/2$ pairs of orbitals, we can write

$$\frac{1}{2}\sum_{i<j}^{N}\left\langle\Psi\left|\hat{g}(i,j)\left(1-\hat{P}_{ij}\right)\right|\Psi\right\rangle=\left[\frac{1}{2}\sum_{\lambda}\sum_{\mu}\left\langle u_{\lambda}(q_i)u_{\mu}(q_i)\left|\frac{1}{r_{ij}}\right|u_{\lambda}(q_i)u_{\mu}(q_i)\right\rangle\right.$$
$$\left.-\left\langle u_{\lambda}(q_i)u_{\mu}(q_j)\left|\frac{1}{r_{ij}}\right|u_{\mu}(q_i)u_{\lambda}(q_j)\right\rangle\right] \tag{2.39}$$

where $\lambda,\mu=\alpha,\beta,...,\nu$, The first Dirac notation bracket in equation (2.39) represents the direct term

$$J_{\lambda\mu}=\left\langle u_{\lambda}(q_i)u_{\mu}(q_i)\left|\frac{1}{r_{ij}}\right|u_{\lambda}(q_i)u_{\mu}(q_i)\right\rangle \tag{2.40}$$

which is the average value of the interaction$\frac{1}{r_{ij}}$ relative to the state $u_{\lambda}(q_i)u_{\mu}(q_j)$, such that electron i is in the spin orbital $u_{\lambda}$and electron$j$ in the spin orbital u_{μ}. Also, we can introduced the exchange term representing the second Dirac notation bracket in equation (2.39),

$$K_{\lambda\mu}=\left\langle u_{\lambda}(q_i)u_{\mu}(q_j)\left|\frac{1}{r_{ij}}\right|u_{\mu}(q_i)u_{\lambda}(q_j)\right\rangle \tag{2.41}$$

which is the matrix element of the interaction $\frac{1}{r_{ij}}$ between the two states $u_{\lambda}(q_i)u_{\mu}(q_j)$ and $u_{\mu}(q_i)u_{\lambda}(q_j)$ obtained by interchanging the electrons i and j. Combining eqs. (2-40), and (2-41), we get

$$\frac{1}{2}\sum_{i\neq j}^{N}\langle\Psi|\hat{g}(i,j)|\Psi\rangle=\frac{1}{2}\sum_{\lambda}\sum_{\mu}\left[J_{\lambda\mu}-K_{\lambda\mu}\right] \tag{2.42}$$

Using eqs. (2-25),(2-35), and(2-42), the Hartree-Fock energy (E_{HF}) can written as

$$E_{HF} = \sum_{\lambda} I_{\lambda} + \frac{1}{2} \sum_{\lambda} \sum \left[J_{\lambda\mu} - K_{\lambda\mu} \right]_{\mu} \tag{2.43}$$

2.5.2 The Hartree-Fock (HF) Equations for Atoms

The form $u_{nlm}(r)$ of a single-electron orbital, in the central field approximation is given by

$$u_{nlm}(r) = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \phi) \xi_{ms}(\sigma) \tag{2.44}$$

where Y_{lm_l} is a spherical harmonic and ξ_{ms} is a spin function. The radial orbital can be assigned a principal quantum number n, dependent on the number of radial nodes, and the single-electron orbitals can be entirely specified in terms of the four quantum numbers n, l, m_l and m_s. All orbitals with the same n and l quantum numbers have the same energy and are said to belong to the same nl shell. The equation (2.44), is referred to as a configuration state function CSF and is denoted by $\Phi(\gamma LS)$, where γ represents the set of nl quantum numbers and the angular coupling scheme. Usually , an orthonormal constraint is imposed on the radial orbitals

$$\int_0^{\infty} P_{nl}(r) P_{n'l}(r) dr = \delta_{nn'} \tag{2.45}$$

In the variational procedure, the energy is minimized with respect to variations in the radial orbitals in above equations. This is a non-linear problem, and an iterative procedure is required to determine the solution. Instead of minimizing the energy directly, a set of integro-differential equations for the radial orbitals that can be obtained by applying the radial variational condition to the functional, and introducing a Lagrange multiplier λ_{ij}, as:

$$E\left(\gamma LS\right)+\sum_{i,j}\delta_{l_i,l_j}\lambda_{ij}\left\langle P_{n_il_i}|P_{n_jl_j}\right\rangle-\lambda\sum_{i=1}^{m}c_i^2=0 \tag{2.46}$$

where $E\left(\gamma LS\right)$ is the energy functional of the configuration state function $\Phi\left(\gamma LS\right)$ with

$$\gamma=\left(n_1l_1\right)^{q_1}\left(n_2l_2\right)^{q_2}\ldots\left(n_m\right)^{q_m} \tag{2.47}$$

The energy can be written as [49],

$$E\left(\gamma LS\right)=\left\langle\gamma LS\left|\hat{H}\right|\gamma LS\right\rangle \tag{2.48}$$

$$=\sum_{i=1}^{m}q_i\left[I\left(n_il_i,n_jl_j\right)+\left(\frac{q_i-1}{2}\right)\sum_{k=0}^{2l_i}f_k\left(i\right)F^k\left(n_il_i,n_il_i\right)\right]+$$

$$\sum_{i=2}^{m}\left\{\sum_{j=1}^{i-1}q_iq_j\left[F\left(n_il_i,n_jl_j\right)+\sum_{k=\left|l_{i-l_j}\right|}^{\left(l_i+l_j\right)}g_k\left(i,j\right)G^k\left(n_il_i,n_jl_j\right)\right]\right\} \tag{2.49}$$

where $I\left(n_il_i,n_jl_j\right)$, $F^k\left(n_il_i,n_il_i\right)$, and $G^k\left(n_il_i,n_jl_j\right)$ are radial integrals, given by

$$I\left(n_il_i,n_jl_j\right)=\int_0^\infty P_{nl}\left(r\right)\left(-\frac{1}{2}\frac{d^2}{dr^2}-\frac{Z}{r}+\frac{l'\left(l'+1\right)}{2r^2}\right)P_{n'l'}\left(r\right)dr \tag{2.50}$$

$$F^k\left(n_il_i,n_il_i\right)=R^k\left(nln'l',nln'l'\right) \tag{2.51}$$

$$G^k\left(n_il_i,n_jl_j\right)=R^k\left(nln'l',n'l'nl\right) \tag{2.52}$$

and $R^k\left(nln'l',n'l'nl\right)$ is given by [50]:

$$R^k\left(n_1l_1n_2l_2,n_3l_3n_4l_4\right)=\int_0^\infty\frac{1}{r_2}Y^k\left(n_1l_1n_3l_3\right)P_{n_2l_2}\left(r_2\right)P_{n_4l_4}\left(r_2\right)dr_2 \tag{2.53}$$

where the function $Y^k\left(n_1l_1n_3l_3\right)$ is given by:

$$Y^k\left(n_1l_1n_3l_3,r_3\right)=r_2\int_0^\infty\frac{r_<^k}{r_>^{k+1}}P_{n_1l_1}\left(r_1\right)P_{n_3l_3}\left(r_1\right)dr_1 \tag{2.54}$$

The coefficients f_k and g_k depend on the angular coupling and can be determined analytically using Racah algebra techniques [51]. The integro-differential equations for each radial orbital, has the form,

$$\left(\frac{d^2}{dr^2}+\frac{2}{r}\left[Z-Y\left(n_il_i;r\right)\right]-\frac{l_i\left(l_i+1\right)}{r^2}-\varepsilon_{ii}\right)P_{n_il_i}=\frac{2}{r}\chi\left(n_il_i;r\right)+\sum_{j\neq i}\delta_{l_i,l_j}\varepsilon_{ij}P_{n_jl_j}\left(r\right) \tag{2.55}$$

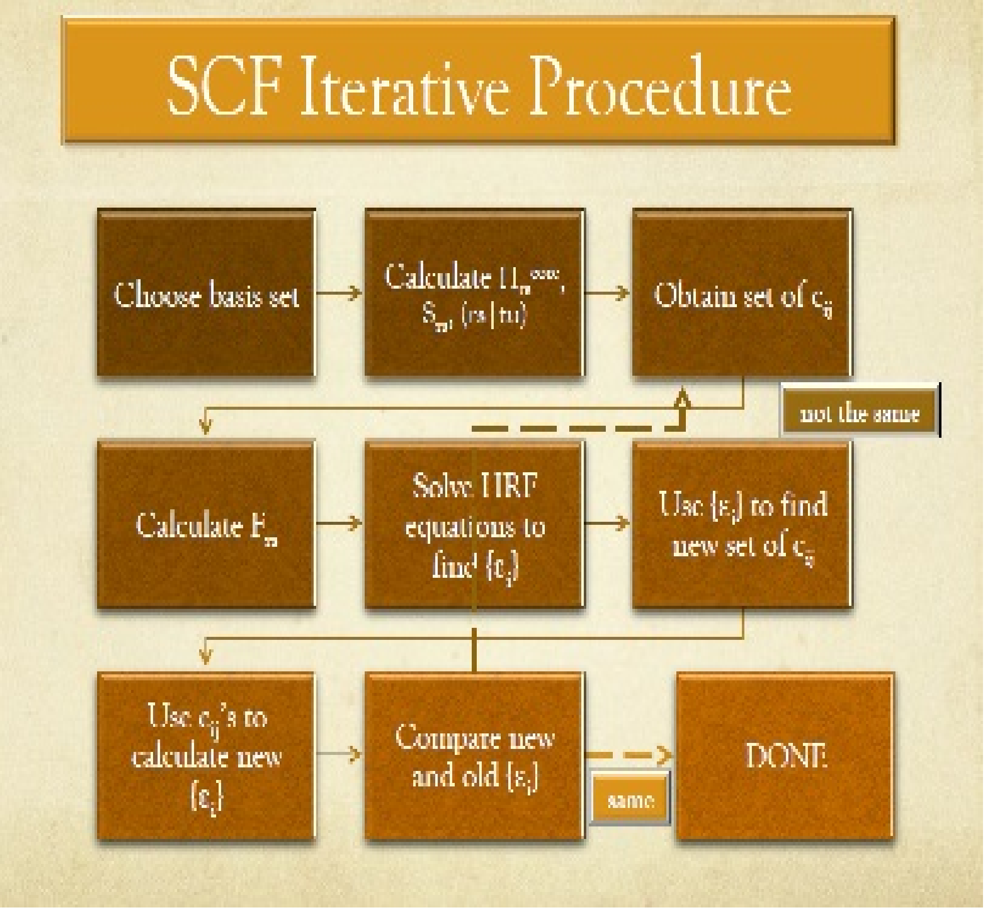
Eq. (2.55) is the Hartree-Fock equation for the radial part of the orbitals for each occupied sub-shell, where $Y\left(n_il_i;r\right)$ is given by [52]

$$Y\left(n_il_i;r\right)=2\left(q_i-1\right)\sum_{k=0}^{2l_i}f_k\left(i\right)Y^k\left(n_il_in_il_i,r\right)+\sum_{j\neq i}q_jY^{\circ}\left(n_jl_jn_jl_j;r\right) \tag{2.56}$$

and the function $\chi\left(n_il_i;r\right)$ arises from exchange with configuration state function and from interaction between configuration states is as,

$$\chi\left(n_il_i;r\right)=\sum_{j\neq i}q_j\sum_{k=\left|l_i-l_j\right|}^{\left(l_i+l_j\right)}g_k\left(i,j\right)Y^k\left(n_jl_jn_jl_j;r\right)P_{n_jl_j}\left(r\right) \tag{2.57}$$

where ε_{ii} and ε_{ij} represent the diagonal and off diagonal energies ,respectively in equation(2-55). These parameters ε_{ii} and ε_{ij} are related to the Lagrange multipliers by,$\varepsilon_{ii}=\frac{\lambda_{ii}}{q_i}$ and $\varepsilon_{ij}=\frac{\lambda_{ij}}{q_i}$. The integro-differential equations are non-linear and must be solved iteratively by the so called Self-Consistent Field (SCF) procedure explained in Fig (2.1).



SCF Iterative Procedure

Choose basis set

Calculate H_{rs}^{core}, S_{rs}, $(rs|tu)$

Obtain set of c_{ij}

not the same

Calculate F_{rs}

Solve HRF equations to find $\{\varepsilon_i\}$

Use $\{\varepsilon_i\}$ to find new set of c_{ij}

Use c_{ij}'s to calculate new $\{\varepsilon_i\}$

Compare new and old $\{\varepsilon_i\}$

same

DONE

Figure 2.1: **The Iterative Self-Consistent -Field (SCF) Procedure**

2.5.3 Multiconfiguration Hartree-Fock (MCHF) Calculations

In the Multi-Configuration Hartree-Fock (MCHF) method, the trial wave function is given as a linear combination of orthogonal configuration state functions [50,52]. The Atomic State Functions (ASFs) can now be defined by taking a linear combination of $CSFs$ with the same total angular momentum J value as,

$$\Psi(\gamma Ls) = \sum_{i=1}^{m} c_i \phi(\gamma_i LS) \tag{2.58}$$

where m is the number of $CSFs$ included in the expansion and the c_i are the configuration mixing coefficients for state Ψ, where $\phi(\gamma_i LS)$configuration state function.

$$\sum_{i=1}^{m} c_i^2 = 1 \tag{2.59}$$

The energy functional for state Ψ is given by ,

$$E\Psi = \left\langle \Psi(\gamma LS) \left| \hat{H} \right| \Psi(\gamma LS) \right\rangle \tag{2.60}$$

$$= \sum_{i=1}^{m} \sum_{j=1}^{m} c_i c_j \left\langle \phi(\gamma_i LS) \left| \hat{H} \right| \phi(\gamma_j LS) \right\rangle \tag{2.61}$$

$$= \sum_{i=1}^{m} c_i^2 H_{ii} + 2 \sum_{i>j}^{m} c_i c_j H_{ij} \tag{2.62}$$

The first term in above equation represents the non-relativistic average energy of a configuration, and this term can be called the diagonal contribution to the Hamiltonian matrix which can be written as [53],

$$E_{av} = \sum_{i=1}^{m} c_i^2 H_{ii} \tag{2.63}$$

and the second term in equation (2.62) represents the interaction matrix, where the Hamiltonian matrix element H_{ij} as,

$$H_{ij} = \int_0^\infty \phi_i^*(\gamma LS) \hat{H} \phi_j(\gamma LS) d^3r \tag{2.64}$$

The energy function in Eq. (2.60) for state Ψ, can be written

$$E\left(\gamma LS\right) = \sum_{i=1}^{m}\sum_{j=1}^{m} c_i c_j H_{ij} \tag{2.65}$$

where H_{ij} can be expressed in terms of radial integrals is given by

$$H_{ij} = \sum_{ab} q_{ab}^{ij} I\left(a,b\right) + \sum_{abcdk} v_{abcd;k}^{ij} R^k\left(ab,cd\right) \tag{2.66}$$

where a and b denote nl quantum numbers of the orbitals. The sums ab and $abcd$ are over the occupied orbitals in configuration i and j. In MCHF calculations the energy functional is minimized with respect to variations in the radial orbitals and the expansion coefficient subject to the orthonormal restrictions in Eqs. (2-45) and (2-54). The stationary condition with respect to variations in the expansion leads to the matrix eigenvalue equation ,

$$HC = EC \tag{2.67}$$

which is coupled to the radial equations. These equations are solved iteratively as follows [54,55]. The first step is initial estimates of the radial functions and the second step is solving the matrix eigenvalue equation. The next step is improving the radial function by solving the integro-differential equations and the last step is solving the matrix eigenvalue equation. As for the minimization, steps 3 and 4 are repeated until both the energy and the orbitals have converged within some specified tolerance.

Chapter-2

Part Two

Non-Relativistic Hartree-Fock for Molecular Structure

2.6 Molecular Schrödinger Equation

For calculating molecular properties, the quantum mechanics for molecule seems to be the obvious tool to use. Calculations use the Schrödinger equation, and are acceptable only to the extent that they produce the result of high level quantum mechanical calculation [56]. A number of experimental observations have shown that the motion of microscopic particles cannot be correctly described with the framework of classical or Newtonian mechanics. This tool has become essential in understanding phenomena at the microscopic scale. Meanwhile, the quantum mechanics for molecules gives us the possibility to describe the fundamental behavior of molecular systems by applying quantum mechanics theory [57]. To study a molecule as a microscopic system, we start from solving the time-independent molecular Schrödinger equation ,

$$\hat{H}\Psi\left(\vec{r},\vec{R}\right) = E\Psi\left(\vec{r},\vec{R}\right) \tag{2.68}$$

where the Hamiltonian $\hat{H}$ is for the system describing the atomic nuclei and the electrons, and it is composed of the kinetic and potential energies. $\Psi\left(r,R\right)$ is the wave function for the stationary state with energy E, While $\vec{r}$ and $\vec{R}$ are used to denote the set of electronic and nuclear coordinates respectively. The non-relativistic Hamiltonian of a molecular system in atomic units for N-electrons and N_a nuclei is given by,

$$\hat{H} = -\sum_{A=1}^{N_a}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{N_a}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{i<j}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{N_a}\sum_{A<B}^{N_a}\frac{Z_A Z_B}{R_{AB}} \tag{2.69}$$

where $r_{iA} = \left|\vec{r}_i - \vec{R}_A\right|$ is the distance between the electron i and the nucleus A, $r_{ij} = \left|\vec{r}_i - \vec{r}_j\right|$ denotes the distance between the electrons i and j. The distance between the nucleus A and the nucleus B is $R_{AB} = \left|\vec{R}_A - \vec{R}_B\right|$. M_A is the mass for the nucleus A and Z_A is the atomic number.

For convenience, we write the Hamiltonian as

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{e-N}(r,R) + \hat{V}_{e-e}(r) + \hat{V}_{N-N}(R) \tag{2.70}$$

where $\hat{T}_N$ is the kinetic energy of nuclei in atomic units,

$$\hat{T}_N = -\sum_{A=1}^{N_a} \frac{1}{2M_A}\nabla_A^2 \tag{2.71}$$

and $\hat{T}_e$ is the kinetic energy of electrons

$$\hat{T}_e = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 \tag{2.72}$$

For a molecule with N_e electrons and N_n nuclei there are three types of interactions between these components, which contribute with the potential term $\hat{V}$. Here $\hat{V}_{e-N}$ is the electron-nuclear attraction or electrostatic interaction between the electrons and the nuclei

$$\hat{V}_{e-N} = -e\sum_{i=1}^{N}\sum_{A=1}^{N_a} \phi_A \tag{2.73}$$

where $-e$ is the electron charge and ϕ_A is the scalar potential of the nucleus given by:

$$\phi_A(\vec{r}_1) = \int \frac{\rho_A(\vec{r}_2)}{r_{12}} dr_2 \tag{2.74}$$

For a point charge, the charge density can be expressed via the Dirac delta function as:

$$\rho_A(\vec{r}_2) = Z_A e \delta\left(\vec{r}_2 - \vec{R}_A\right) \tag{2.75}$$

where R_A is the nuclear position. Substituting equation (2-75) in equation (2-74), yields

$$\phi_A(\vec{r}_1) = \int \frac{Z_A e \delta\left(\vec{r}_2 - \vec{R}_A\right)}{r_{12}} dr_2 = \frac{Z_A e}{r_{1A}} \tag{2.76}$$

and $\hat{V}_{e-e}$ is the repulsion energy between electrons or is the electrostatic interaction between the electrons. It is given by the instantaneous Coulomb interaction

$$\hat{V}_{e-e} = \frac{1}{2}\sum_{i=1}^{N}\sum_{i\neq j}^{N}\frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} \tag{2.77}$$

where indices's i and j run over all electrons and $\hat{V}_{N-N}$ is the repulsion energy between nuclei given by:

$$\hat{V}_{N-N} = \frac{1}{2}\sum_{A=1}^{N_N}\sum_{A\neq B}^{N_N}\frac{Z_A Z_B}{\left|\vec{R}_A - \vec{R}_B\right|} \tag{2.78}$$

Due to the impossibility to get the exact solution of the molecular Schrödinger equation, a number of approximations must be introduced.

2.7 The Born-Oppenheimer Approximation

It is well-known that the Schrödinger equation for the hydrogen atom composed of one nucleus (proton) and one electron can be solved analytically. The molecular system has many-body problem to solve the Schrödinger equation approximations must be applied [58]. As a result of the great difference in masses between an electron and a nucleus, one can separate the motions of the electrons, from the motions of the nuclei. It means that electrons move much faster than the nuclei [59]. Assuming the nuclei to be fixed, we can omit the nuclear kinetic energy term from the Hamiltonian (2-70), obtaining :

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{e-N}(r,R) + \hat{V}_{e-e}(r) + \hat{V}_{N-N}(R) \tag{2.79}$$

To obtain the Schrödinger equation for the electronic motion

$$\hat{H}_{el}\Psi\left(\vec{r};\vec{R}\right) = E(R)\Psi\left(\vec{r};\vec{R}\right) \tag{2.80}$$

The wave function and the potential energy depend, parametrically, on the nuclear configuration, R. The repulsion between the nuclei is considered to be constant. It adds to the eigenvalue of the electronic Hamiltonian operator. Then, it has no effect on the operator eigenfunctions or other properties. This term shifts only the eigenvalue by same constant. In the adiabatic approximation, the nuclear configuration R will change slowly and the motions of the electrons will immediately adjust to the new nuclear configuration and remain in the same electronic eigenstate. When R is changing to R', the electronic wave function change from $\Psi\left(\vec{r};\vec{R}\right)$ to $\Psi\left(\vec{r};\vec{R}'\right)$ and the potential energy changes from $E(R)$ to $E(R')$. Solving the electronic Schrödinger equation for different nuclear configurations allow us to construct the potential energy curve for (diatomic molecules) or in general, a potential energy surface for a diatomic molecule. When the electronic Schrödinger equation (2-80) is solved, an infinite number of eigenfunctions, $\Psi_i\left(\vec{r};\vec{R}\right)$, are obtained with the energies $E_i(R)$, where $i = 1, 2, 3, \ldots$. The eigenfunctions form complete set of states and to go beyond the adiabatic approximation the full molecular wave function can be expanded in the adiabatic electronic wave function.

$$\Psi\left(\vec{r};\vec{R}\right) = \sum_i \Psi_i\left(\vec{r};\vec{R}\right)\chi_i(R) \tag{2.81}$$

where the expansion coefficients $\chi_i(R)$ are functions of nuclear coordinates. Inserting wave function in Eq.(2.81) into the total Schrödinger equation (2.68) and multiplying from left with $\Psi_j^*\left(\vec{r};\vec{R}\right)$ and integrating over the electronic coordinates, yields :

$$\sum_i \left\langle \Psi_j\left(\vec{r};\vec{R}\right) \middle| \left[\hat{T}_N + \hat{H}_{el}\right]\chi_i(R) \middle| \Psi_i\left(\vec{r};\vec{R}\right)\right\rangle = \sum_i \left\langle \Psi_j\left(\vec{r};\vec{R}\right) \middle| E\chi_i(R) \middle| \Psi_i\left(\vec{r};\vec{R}\right)\right\rangle \tag{2.82}$$

Here, the Dirac bracket notation implies integration over all electron coordinates. The right hand side of equation (2.82) can be written as

$$RHS = E\sum_i \chi_i(R)\left\langle \Psi_j\left(\vec{r};\vec{R}\right) \middle| \Psi_i\left(\vec{r};\vec{R}\right)\right\rangle \tag{2.83}$$

$$= E\sum_i \chi_i(R)\,\delta_{ij} = E\chi_j(R) \tag{2.84}$$

Since the integration is over r, $\chi_i(R)$ has been brought out of the bracket, and by using the orthonormal properties of the electronic state, the sum is eliminated. And the left hand side in equation (2.82)

$$LHS = \sum_i \left\{ \left\langle \Psi_j\left(\vec{r};\vec{R}\right) \middle| \hat{T}_N\chi_i(R) \middle| \Psi_i\left(\vec{r};\vec{R}\right)\right\rangle + \left\langle \Psi_j\left(\vec{r};\vec{R}\right) \middle| \hat{H}_{el}\chi_i(R) \middle| \Psi_i\left(\vec{r};\vec{R}\right)\right\rangle \right\} \tag{2.85}$$

We should notice that the nuclear kinetic energy operator contained derivatives with respect to the nuclear coordinates R, and it acts on the both factors in the product $\Psi_i\left(\vec{r};\vec{R}\right)\chi_i(R)$, so the first term in parenthesis, in the LHS of equation (2.85) becomes

$$\left\langle \Psi_j\left(\vec{r};\vec{R}\right)\left|\hat{T}_N\chi_i(R)\right|\Psi_i\left(\vec{r};\vec{R}\right)\right\rangle = \{T_N\chi_i(R)\}\left\langle \Psi_j\left(\vec{r};\vec{R}\right)\middle|\Psi_i\left(\vec{r};\vec{R}\right)\right\rangle + \chi_i(R)\left\{\left\langle \Psi_j\left(\vec{r};\vec{R}\right)\left|\hat{T}_N\right|\Psi_i\left(\vec{r};\vec{R}\right)\right\rangle\right. \tag{2.86}$$

Since we use adiabatic eigenfunctions that by definition diagonalize the electronic Hamiltonian, the second term in parenthesis, in the LHS of equation (2.85) becomes

$$\left\langle \Psi_j\left(\vec{r};\vec{R}\right)\left|\hat{H}_{el}\right|\Psi_i\left(\vec{r};\vec{R}\right)\right\rangle = E_i(R)\,\delta_{ij} \tag{2.87}$$

By substituting Eqs. (2.86) and (2.87) into Eq. (2.85) and once again using the orthonormality of the electronic states, the sum is eliminated and we finally obtain

$$\left[\hat{T}_N + E_j(R)\right]\chi_j(R) + \sum_i \left\{\left\langle \Psi_j\left(\vec{r};\vec{R}\right)\left|\hat{T}_N\right|\Psi_i\left(\vec{r};\vec{R}\right)\right\rangle\right\}\chi_i(R) = E\chi_j(R) \tag{2.88}$$

The second term in above equation is usually small when compared to $E_j(R)$, and the interaction between different electrostatic states can be neglected, thus we obtain the Schrödinger equation:

$$\left[\hat{T}_N + E_j(R)\right]\chi_j(R) = E\chi_j(R) \tag{2.89}$$

The eigenvalue E is the total energy of the molecule within the Born-Oppenheimer approximation.

2.8 Electronic Energy Expression for Molecules

By freezing the molecular positions (nuclear kinetic energy is zero), we can write the Hamiltonian alternatively as [60]:

$$\hat{H}_{el} = \hat{V}_{N-N} + \sum_{i=1}^{N} \hat{h}\,(i) + \frac{1}{2}\sum_{i \neq j}^{N} \hat{g}(i,j) \tag{2.90}$$

where $\hat{h} = \hat{H} + \hat{V}_{e-N}$, $\hat{H}_{el}$ is the Hamiltonian for a charged particle, $\hat{V}_{e-N}$ is the electrostatic interaction between the electron and the nuclei and $\hat{g}(i,j)$ is the two electron interaction. Now, the expectation value of the electronic Hamiltonian in above equation is

$$E = \left\langle \Psi \middle| \hat{H}_{el} \middle| \Psi \right\rangle = \int \Psi^{*}\,(1,..,N)\,\hat{H}_{el}\Psi\,(1,...,N)\,d_1...d_N \tag{2.91}$$

The firs term in equation (2-90) is constant

$$\left\langle \Psi \middle| \hat{V}_{N-N} \middle| \Psi \right\rangle = V_{N-N}\,\langle \Psi | \Psi \rangle = V_{N-N} \tag{2.92}$$

The expectation value of second term, can be written as:

$$\sum_{i=1}^{N} \left\langle \Psi \middle| \hat{h}\,(i) \middle| \Psi \right\rangle = \sum_{i=1}^{N} \int \Psi^{*}\,(1,..,N)\,\hat{h}\,(i)\,\Psi\,(1,...,N)\,d_1...d_N \tag{2.93}$$

Each of these terms must have the same value, since the electrons are indistinguishable. We select one and multiply with the number of the terms, so we can rewrite the equation (2-93) as:

$$\sum_{i=1}^{N} \left\langle \Psi \middle| \hat{h}\,(i) \middle| \Psi \right\rangle = N \int \Psi^{*}\,(1,..,N)\,\hat{h}\,(1)\,\Psi\,(1,...,N)\,d_1...d_N \tag{2.94}$$

The expectation value of last term in equation (2.90), for two electrons, can be written as:

$$\sum_{i=1}^{N} \langle \Psi | \hat{g}\,(i,j) | \Psi \rangle = \frac{1}{2}\sum_{i \neq j}^{N} \int \Psi^{*}\,(1,..,N)\,\hat{g}\,(i,j)\,\Psi\,(1,...,N)\,d_1...d_N \tag{2.95}$$

$$= \frac{1}{2}N(N-1)\int \Psi^*(1,..,N)\,\hat{g}(i,j)\,\Psi(1,...,N)\,d_1...d_N \tag{2.96}$$

By combining Eqs. (2.92), (2.94) and (2.96), we get the electron energy

$$\begin{aligned} E = V_{NN} + N\int \Psi^*(1,..,N)\,\hat{h}(1)\,\Psi(1,...,N)\,d_1...d_N \\ +\frac{1}{2}N(N-1)\int \Psi^*(1,..,N)\,\hat{g}(i,j)\,\Psi(1,...,N)\,d_1...d_N \end{aligned} \tag{2.97}$$

2.9 Electronic Schrödinger Equation for Molecules

As we have seen in the Born-Oppenheimer approximation, the electronic motions can be separated from nuclear motions and solved the electronic Schrödinger equation (2-80). For molecular systems containing more than one electron, the electronic Schrödinger equation is still a many-body problem and approximation have to be applied. Now, we will discuss how to solve the electronic Schrödinger equation, given by

$$\left(V_{N-N} + \sum_{i=1}^{N}\hat{h}(i) + \frac{1}{2}\sum_{i\neq j}^{N}\hat{g}(i,j)\right)\Psi_{el}\left(\vec{r};\vec{R}\right) = E_{el}\Psi_{el}\left(\vec{r};\vec{R}\right) \tag{2.98}$$

In a simpler system containing one-electron interaction, i.e., $\hat{g}(i,j) = 0$, and V_{N-N} is just constant for the fixed set of nuclear coordinates (R), we ignore it (V_{N-N} does not change the eigenfunctions and only shifts the eigenvalue) [61]. Then the Schrödinger electronic equation for an electronic system can be written

$$\sum_{i=1}^{N}\hat{h}(i)\,\Psi_{el}\left(\vec{r};\vec{R}\right) = E_{el}\Psi_{el}\left(\vec{r};\vec{R}\right) \tag{2.99}$$

If we have N-electrons, the Schrödinger equation is written as:

$$\left[\hat{h}_1 + \hat{h}_2 + ... + \hat{h}_N\right]\Psi(1,2,...,N) = E\Psi(1,2,...,N) \tag{2.100}$$

and the wave function for many-body system in the independent particle approximation can be expressed as

$$\Psi(1,2,...,N) = \phi_{(1)}\phi_{(2)}...\phi_{(N)} \tag{2.101}$$

Substituting equation (2-78) into equation (2-77), yields

$$\left[\hat{h}_1 + \hat{h}_2 + ... + \hat{h}_N\right]\phi_{(1)}\phi_{(2)}...\phi_{(N)} = E\phi_{(1)}\phi_{(2)}...\phi_{(N)} \tag{2.102}$$

The electronic Schrödinger equation can be solved by the method of separation of variables and a set of orthonormal eigenfunctions, $\{\phi_j\}$, can be obtained

$$\hat{h}(i)\,\phi_j(\vec{r}_i) = \varepsilon_i\phi_j(\vec{r}_i) \tag{2.103}$$

where $\phi_j(\vec{r}_i)$ is spin-orbital describing the one-electron wave function.

2.10 Developing Hartree-Fock Approximation for Molecules

The Hartree-Fock method seeks to approximately solve the electronic Schrödinger equation, and it assumes that the wave function can be approximated by a single Slater determinant made up of one spin orbital per electron [62]. For an N-electron system, the orbital $\phi_j(\vec{r}_i)$ consists of a spatial part $\varphi_j(\vec{r})$ (molecular orbital) and a spin part. The spin up and the spin down states are denoted by α and β, respectively, and we can write the orbital form as:

$$\phi_j^{(s)}(\vec{r}) = \begin{cases} \varphi_j(\vec{r})\,\alpha \\ \varphi_j(\vec{r})\,\beta \end{cases} \tag{2.104}$$

where s denotes the spin state. The molecular orbitals can be describe by the linear combination of atomic orbital approximation (LCOA) as [63].

$$\varphi_i(\vec{r}) = \sum_j c_{ij}\xi_j(\vec{r}) \tag{2.105}$$

In equation (2.105), the c_{ij}'s are coefficients or weights of the atomic orbitals $\xi_j(\vec{r})$ for the molecular orbitals $\varphi_i(\vec{r})$. The orbitals satisfy the orthonormality condition. For a system having many particles, the wave function $\Psi(1,2,...,N)$ must be antisymmetric with respect to the exchange of the coordinates of any two electrons to satisfy the Pauli principle, as : [64].

$$\begin{aligned} P_{ij}\Psi(r_1,...,r_i,...,r_j,...,r_N) &= \Psi(r_1,...,r_j,...,r_i,...,r_N) \\ &= -\Psi(r_1,...,r_i,...,r_j,...,r_N). \end{aligned} \tag{2.106}$$

A single Slater determinant can be used to describe the ground state of the N-electron system, and is given by [65]

$$\Psi(1,2,...,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & & \vdots \\ \phi_1(N) & \phi_2(N) & & \phi_N(N) \end{vmatrix} \tag{2.107}$$

when act antisymmetric operator on the Slater determinant, the wave function has the form:

$$\Psi(1,2,...,N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^p \phi_{p_1}(1)\phi_{p_2}(2)...\phi_{p_N}(N) \tag{2.108}$$

Choosing $\Psi^{HF} = \Psi^{Slater}$, where Ψ^{HF} is the trial wave function in the HF approach for many particle, and $\Psi^{Slater} = \Psi$. Substituting $\Psi^{HF} = \Psi^{Slater}$ in the one electron energy (2.94), yields:

$$\begin{aligned} \sum_{i=1}^{N} \left\langle \Psi^{HF} \left| \hat{h}(i) \right| \Psi^{HF} \right\rangle = N \int \frac{1}{\sqrt{N!}} \sum_P (-1)^p \phi_{P_1}(1)\phi_{P_2}(2)...\phi_{P_N}(N) \\ \hat{h}(1) \frac{1}{\sqrt{N!}} \sum_Q (-1)^q \phi_{Q_1}(1)\phi_{Q_2}(2)...\phi_{Q_N}(N)\, d_1...d_N \end{aligned} \tag{2.109}$$

When $P_i = Q_i$, we obtain

$$\sum_{i=1}^{N} \left\langle \Psi^{HF} \left| \hat{h}(i) \right| \Psi^{HF} \right\rangle = \sum_{i=1}^{N} \left\langle \phi_i \left| \hat{h} \right| \phi_i \right\rangle \tag{2.110}$$

The second term for two electron energy in equation (2.96), after substituting $\Psi^{HF} = \Psi^{Slater}$, becomes

$$\sum_{i=1}^{N}\left\langle\Psi^{HF}\left|\hat{g}\left(i,j\right)\right|\Psi^{HF}\right\rangle=\frac{1}{2}N\left(N-1\right)\int\frac{1}{\sqrt{N!}}\sum_{P}\left(-1\right)^{p}\phi_{P_1}\left(1\right)\phi_{P_2}\left(2\right)...\phi_{P_N}\left(N\right)$$
$$\times\hat{g}\left(i,j\right)\frac{1}{\sqrt{N!}}\sum_{Q}\left(-1\right)^{q}\phi_{Q_1}\left(1\right)\phi_{Q_2}\left(2\right)...\phi_{Q_N}\left(N\right)d_1...d_N \tag{2.111}$$

$$=\frac{1}{2}N\left(N-1\right)\frac{1}{N!}\sum_{P}\left(-1\right)^{p}\sum_{Q}\left(-1\right)^{q}\left\langle\phi_{P_1}\left(1\right)\phi_{P_2}\left(2\right)\left|\hat{g}\left(i,j\right)\right|\phi_{Q_1}\left(1\right)\phi_{Q_2}\left(2\right)\right\rangle$$
$$\times\left\langle\phi_{P_3}\left(3\right)\left|\phi_{Q_3}\left(3\right)\right.\right\rangle...\left\langle\phi_{P_N}\left(N\right)\left|\phi_{Q_N}\left(N\right)\right.\right\rangle \tag{2.112}$$

Orthonormality condition applied on the last two terms in above equation, and $P_1 = Q_1$ and $P_2 = Q_2$, yields

$$\sum_{i=1}^{N}\left\langle\Psi^{HF}\left|\hat{g}\left(i,j\right)\right|\Psi^{HF}\right\rangle=\frac{1}{2}\sum_{i\neq j}^{N}\left[\left\langle\phi_i\phi_j\left|\hat{g}\left(i,j\right)\right|\phi_i\phi_j\right\rangle-\left\langle\phi_i\phi_j\left|\hat{g}\left(i,j\right)\right|\phi_j\phi_i\right\rangle\right] \tag{2.113}$$

Thus, we can write the Hartree-Fock energy by combination between the Eqs. (2.110) and (2.113) and substituting in equation (2-97), as:

$$E^{HF}=V_{N-N}+\sum_{i=1}^{N}\left\langle\phi_i\left|\hat{h}\right|\phi_i\right\rangle+\frac{1}{2}\sum_{i\neq j}^{N}\left[\left\langle\phi_i\phi_j\left|\hat{g}\left(i,j\right)\right|\phi_i\phi_j\right\rangle-\left\langle\phi_i\phi_j\left|\hat{g}\left(i,j\right)\right|\phi_j\phi_i\right\rangle\right] \tag{2.114}$$

Since the energy expression is symmetric, and the variation theorem holds, and since the Slater determinant with the lowest energy is close to the true wave function of, we obtain a single Slater determinant. The Hartree-Fock method determines the set of spin orbitals which minimize the energy and gives us this best single determinant [66]. So, we need to minimize the HF energy expression with respect to changes in the orbitals $\phi_i \rightarrow \phi_i + \delta\phi_i$. We also assume that the orbital ϕ is orthonormal. We want to ensure that our variational procedure leaves them orthonormal. We can accomplish this by Lagrange's multipliers method to keep the set of orbitals $\{\phi_k\}$ orthonormal through the minimization process, where we employ a functional L defined as :

$$L\left[\{\phi_i\}\right] = E^{HF}\left[\{\phi_i\}\right] - \sum_{ij}\lambda_{ij}\left\{\langle\phi_i|\phi_j\rangle - \delta_{ij}\right\} \tag{2.115}$$

where λ_{ij} are the Lagrange multipliers and $\langle\phi_i|\phi_j\rangle$ is the overlap between spin orbitals i and j, i.e:

$$\langle\phi_i|\phi_j\rangle = \int \phi_i^*(r)\,\phi_j(r)\,dr \tag{2.116}$$

The variational Lagrangian is given by:

$$\delta L\left[\{\phi_i\}\right] = \sum_i \int \frac{\delta L}{\delta\phi_i(1)}\delta\phi_i(1)\,d1 + \sum_i \int \frac{\delta L}{\delta\phi_i^*(1)}\delta\phi^*(1)\,d1 \tag{2.117}$$

We seek a stationary point, i.e. $\delta L = 0$, which implies

$$\frac{\delta L}{\delta\phi_i(r)} = 0 \qquad , \frac{\delta L}{\delta\phi_i^*(r)} = 0 \tag{2.118}$$

and working through some algebra, we eventually arrive at the Hartree-Fock equation defining the orbitals:

$$\hat{h}(1)\,\phi_k(1) + \left[\sum_j^N \int \phi_j^*(2)\,\hat{g}(1,2)\,\phi_j(2)\,d2\right]\phi_k(1) - \left[\sum_j^N \int \phi_j^*(2)\,\hat{g}(1,2)\,\phi_k(2)\,d2\right]\phi_j(1) = \sum_j \lambda_{kj}\phi_j(1) \tag{2.119}$$

The first term in square brackets gives the Coulomb interaction of an electron in spin orbital ϕ_k with the average charge distribution of the other electrons. This is called the Coulomb term and it is convenient to define a Coulomb operator as [67] :

$$\hat{J}_j(1)\,\phi_k(1) = \int \phi_j^*(2)\,\hat{g}(1,2)\,\phi_j(2)\,d2\phi_k(1) \tag{2.120}$$

which gives the average potential due to the charge distribution from the electron in orbital ϕ_j. The other term in square bracket in equation (2-119) is difficult to explain because it does not have a simple classical analog. It arises from the antisymmetry requirement of the wave function. It looks much like the Coulomb term, except that it switches or exchanges spin orbitals ϕ_j and ϕ_k. Hence, it is called the exchange term, and we can define an exchange operator in terms of its action on a spin orbital ϕ_i as:

$$\hat{K}_j(1)\,\phi_k(1) = \int \phi_j^*(2)\,\hat{g}(1,2)\,\phi_k(2)\,d2\phi_j(1) \tag{2.121}$$

In terms of Coulomb and exchange operators, the Hartree-Fock equations become considerably more compact as:

$$\left[\hat{h}(1) + \sum_{j=1}^{N}\left(\hat{J}_i(1) + \hat{K}_j(1)\right)\right]\phi_k(1) = \sum_j \lambda_{kj}\phi_j(1) \tag{2.122}$$

We can introduce a Fock operator as:

$$\hat{F}(1) = \hat{h}(1) + \sum_{j=1}^{N}\left(\hat{J}_i(1) + \hat{K}_j(1)\right) \tag{2.123}$$

The Hartree-Fock equations become after substituting Eq. (2.123) in Eq. (2.122), as

$$\hat{F}(1)\,\phi_k(1) = \sum_j \lambda_{kj}\phi_j(1) \tag{2.124}$$

By the unitary transformation of the orbitals, we can transform the Lagrange multipliers λ_{kj} in the diagonal matrix form

$$\lambda_{kj} = U^{\dagger}\varepsilon_k U \tag{2.125}$$

The Hartree-Fock equation can be written,

$$\hat{F}|\phi_k> = \varepsilon_k|\phi_k> \tag{2.126}$$

The above equation is called the canonical Hartree Fock equations, where ε_k is the energy associated with the orbital ϕ_k. We notice that the HF operator depends on the orbitals ϕ_k because it consists of Coulomb operator $\hat{J}_j$ and exchange operator $\hat{K}_j$. The Hartree-Fock equation is *developed* by expanding the Molecular Orbitals (MOs) $|\phi_k>$ as a linear combination of a number of linearly independent functions, using basis set as:

$$|\phi_k> = \sum_{\mu=1}^{n} c_{\mu k}|\chi_\mu> \qquad (2.127)$$

where ϕ_k is the molecular orbitals, $c_{\mu k}$ are the coefficient of atomic orbitals and χ_μ is the basis set function for atomic orbitals. Substitution equation (2.127) into equation (2.126), yields

$$\hat{F}\sum_{\mu=1}^{n} c_{\mu k}|\chi_\mu> = \varepsilon_k \sum_{\mu=1}^{n} c_{\mu k}|\chi_\mu> \qquad (2.128)$$

Multiplication on the left by χ_ν and integration over the range of the coordinates of the electron gives :

$$\sum_{\mu=1}^{n}\int \chi_\nu \hat{F}\chi_\mu d\tau c_{\mu k} = \sum_{\mu=1}^{n}\int c_{\mu k}\varepsilon_k \chi_\nu \chi_\mu d\tau \qquad (2.129)$$

The above equation can be written by another form as :

$$\sum_{\mu=1}^{n} F_{\mu\nu}c_{\mu k} = \sum_{\mu=1}^{n} S_{\nu\mu}c_{\mu k}\varepsilon_k \qquad (2.130)$$

where $F_{\mu\nu}$ are the Fock integrals defined as:

$$F_{\mu\nu} = \int \chi_\nu \hat{F}\chi_\mu d\tau \qquad (2.131)$$

The Fock integrals are constructed from kinetic energy integrals, nuclear-electron attraction integrals, and two-electron repulsion integrals, and $S_{\nu\mu}$ in equation (2-130) is the overlap integral which is defined as:

$$S_{\nu\mu} = \int \chi_\nu \chi_\mu d\tau \qquad (2.132)$$

If the basis functions are normalized, so $S_{ii} = 1$, but are not orthogonal, $S_{ij} \neq 0$ in general. Equation (2.130) can be cast as a matrix equation,

$$Fc = Sc\varepsilon \qquad (2.133)$$

This equation is called the Fock equation, where F is the Fock matrix operator, S is the overlap matrix, ε is the orbital energy or the diagonal Fock matrix elements in atomic orbitals basis. To construct the Fock matrix, one must already know the molecular orbitals, since the electron repulsion integrals require them. For this reason, the Fock equation (2.133) must be solved iteratively. One makes an initial guess at the molecular orbitals and uses this guess to construct an approximate Fock matrix. Solution of the Fock equations will produce a set of MOs from which a better Fock matrix can be constructed . After repeating this operation a number of times, if everything goes well, a point will be reached where the MOs obtained from solution of the Fock equations are the same as those obtained from the previous cycle and used to make up the Fock matrix [68].

2.11 Basis-Set Considerations

The accuracy of the electronic structure does not depend only on which level of theory should be chosen, but also on the quality of the finite set of basis functions used to expand the orbitals. The basis set is a mathematical convenience, because the quantum mechanics equations which describe the behavior of electrons in molecules are most easily solved by expanding the wave function in terms of a finite basis set [69]. The molecular orbitals can be created by linear combinations of a set of functions called atomic orbitals, given by equation (1.1) . The basis set typically models atomic orbitals centered on the atoms. When the minimum number of the basis functions are used to describe the orbitals in each atom, this means, we have the minimal basis sets [70]. In quantum molecule calculations, approximate atomic orbitals are used with different forms. One type of basis functions is the Slater Type Function (STF), which is similar to the hydrogen wave function, described by the function depending on spherical coordinate, given by equation(1.2). Another type of normalized basis set functions is the Gaussian Type Function (GTF), given by equation (1.3). The important difference between these two type of basis functions occurs when $r \to 0$ and, at large value of r. At $r = 0$ the Slater type function (STF) has finite slope, but the slope of the Gaussian type function (GTF) is zero. At large r the Gaussian type function(GTF) decays more rapidly than the Slater type function(STF). For comparable results, the Slater type function(STF) orbitals are more correct, but difficult to integrate. However, they are esear to obtain from Gaussian type functions (GFT) orbitals. The essential difference is that, there is squared r [71]. In our work use Gaussian type function(GTF) basis set functions type $cc - pVXZ$, which means Dunning correlation-consistent, polarized valance, $X - zeta$ basis, where $X = D, T, Q, D$ is Double-zeta, T is Triple-zeta, and Q is Quadruple-zeta. The calculation of the two electron integrals in the Hartree-Fock equation is much easier and faster in the Self-Consist-Field SCF processes, because the product of the two Gaussian functions with two different centers, will be a Gaussian function on a third center. And another reason to use GTF, if we had more basis function than STF, is that we need more coefficients $c'es$ to optimize in our SCF calculation for our particular molecule . This will give a better quality Molecular Orbitals (MOs) and energy. A large basis-set can give a more accurate result. For better and improved description, the number of basis functions per atom can be increased by multiplying a minimal basis-set and obtain the double, triple, quadrupole zeta,... basis sets [72].

2.12 Hartree-Fock Approach With Basis-Set

In this section, the Hartree-Fock equations and total energy with Gaussian basis-set wave function in matrix form will be derived. The wave function is:

$$\phi_{nlm}(\vec{r}) = \frac{1}{r} P_{nl}(r) Y_{lm}(\Omega) \tag{2.134}$$

where $P_{nl}(r)$ is the radial part and $Y_{lm}(\Omega)$ is the spherical harmonic part. The Gaussian type basis-set function for the radial part $P_{nl}(\vec{r})$ is given by

$$P_{n\xi}(\vec{r}) = N_{n\xi} r^n e^{-\xi r^2} \tag{2.135}$$

where $N_{n\xi}$ is the normalization constant and ζ is the controle width of orbital or the Gaussian orbital exponent. The Gaussian type function is normalized as the radial wave function $P_{n\xi}(\vec{r})$. The Hartree-Fock equation developed by using basis-set in section (2.10), can be written as:

$$\sum_{\mu=1}^{n} F_{\mu\nu} c_{\mu k} = \sum_{\mu=1}^{n} S_{\nu\mu} c_{\mu k} \varepsilon_k \tag{2.136}$$

where the $F_{\mu\nu}$ is the Fock integrals which are constructed from kinetic energy integrals, nuclear-electron attraction integrals two-electron repulsion integrals is defined as:

$$\hat{F}_{\mu\nu} = \hat{T}_{\mu\nu} + \hat{V}_{\mu\nu} + \hat{G}_{\mu\nu} \tag{2.137}$$

The kinetic matrix element denoted by $\hat{T}_{\mu\nu}$, represents the kinetic energy integral in equation (2.137) defined as:

$$\hat{T}_{\mu\nu} = \int \phi_\mu^* \left(-\frac{1}{2}\nabla^2\right) \phi_\nu d^3 r \tag{2.138}$$

where ϕ_μ is the Gaussian type wave function given by

$$\phi_\mu \left(\xi, n_\mu, l_\mu, m_\mu; r, \theta, \varphi\right) = \frac{1}{r} N_\mu r^{n_\mu} e^{-\xi_\mu r_\mu^2} Y_{l_\mu m_\mu}(\theta, \varphi) \tag{2.139}$$

The radial part is $P_{n\xi}(r) = N_{n\xi} r^n e^{-\xi r^2}$, substituting in eqn. (2.139) , to get

$$\phi_\mu \left(\xi, n_\mu, l_\mu, m_\mu; r, \theta, \varphi\right) = \frac{1}{r} P_{n_\mu l_\mu} Y_{l_\mu m_\mu}(\theta, \varphi) \tag{2.140}$$

To evaluate kinetic energy integrals using Gaussian basis-set type function, we substitute equation (2.140) into kinetic energy integrals, to obtain:

$$\hat{T}_{\mu\nu} = \int_0^\infty \left(\frac{1}{2} P'_{n_\mu \xi_\mu}(r) P'_{n_\nu \xi_\nu}(\vec{r}) + P_{n_\mu \xi_\mu}(r) \frac{l(l+1)}{2r^2} P_{n_\nu \xi_\nu}(\vec{r}) \right) dr \tag{2.141}$$

Substituting Gaussian type orbital basis function, equation (2.135) into equation (2.141), yields

$$\begin{aligned}T_{\mu\nu}=\frac{1}{2}N_{n_\mu\xi_\mu}N_{n_\nu\xi_\nu}\Bigg(\Bigg(&n_\mu n_\nu+l\left(l+1\right)\left(n_\mu+n_\nu-3\right)!\sqrt{\frac{\pi}{2\left(2\xi_\mu+2\xi_\nu\right)^{n_\mu+n_\nu-1}}}\Bigg)\\&-2\left(n_\mu\xi_\nu+n_\nu\xi_\mu\right)\left(n_\mu+n_\nu-1\right)!\sqrt{\frac{\pi}{2\left(2\xi_\mu+2\xi_\nu\right)^{n_\mu+n_\nu+1}}}\\&+4\xi_\mu\xi_\nu\left(n_\mu+n_\nu-1\right)!\sqrt{\frac{\pi}{2\left(2\xi_\mu+2\xi_\nu\right)^{n_\mu+n_\nu+1}}}\Bigg)dr\end{aligned}\qquad(2.142)$$

The nuclear-electron attraction energy integrals can be evaluated by using Gaussian type function. The potential matrix element $\hat{V}_{\mu\nu}$, represents the nuclear-electron attraction integrals in equation (2.137). The energy caused by the attraction between an electron in the region described by the overlap of orbitals ϕ_μ and ϕ_ν and a nuclear charge Z is expressed by the nuclear-electron attraction integral , defined as:

$$\hat{V}_{\mu\nu}=\int\phi_\mu^*\left(-\frac{Z}{r}\right)\phi_\nu d^3r \qquad (2.143)$$

When involving Gaussian type function with nuclear electron attraction energy integrals, and substituting equation (2.139) into equation (2.143), we get :

$$\hat{V}_{\mu\nu}=\int_0^\infty P_{n_\mu\xi_\mu}\left(\vec{r}\right)\left(-\frac{Z}{r}\right)P_{n_\nu\xi_\nu}\left(\vec{r}\right)dr \qquad (2.144)$$

Substituting Gaussian type orbital basis function (2.135) into (2.144), yields

$$\hat{V}_{\mu\nu}=-ZN_{n_\mu\xi_\mu}N_{n_\nu\xi_\nu}\frac{\left(\frac{n_\mu+n_\nu-2}{2}\right)!}{2\sqrt{\left(\xi_\mu+\xi_\nu\right)^{\frac{n_\mu+n_\nu}{2}}}} \qquad (2.145)$$

The two particle matrix element $G_{\mu\nu}$, represents the two-electron repulsion integrals in equation (2.137) defined as:

$$\hat{G}_{\mu\nu} = \int \phi_\mu^*(\vec{r}_1)\left(\int \frac{2\sum_{k=1}^{N/2}|\psi_k(\vec{r}_2)|^2}{|\vec{r}_1-\vec{r}_2|}d^3r_2\right)\phi_\nu(\vec{r}_1)\,d^3r$$
$$-\int \phi_\mu^*(r_1)\sum_{k=1}^{N/2}\int \frac{\phi_\nu(\vec{r}_2)\,\psi_k^*(r_2)}{|\vec{r}_1-\vec{r}_2|}d^3r_2\psi_k(\vec{r}_1)\,d^3r \tag{2.146}$$

Introducing the density matrix, defined as:

$$P_{\alpha\beta} = 2\sum_{k=1}^{N/2} C_{\alpha k}C_{\beta k}^* \tag{2.147}$$

and the probability density defined as:

$$\rho(r) = 2\sum_{k=1}^{N/2}|\psi_k(r)|^2 = \sum_{\alpha\beta}\phi_\alpha(\vec{r})\,P_{\alpha\beta}\phi_\beta^*(\vec{r}) \tag{2.148}$$

then, substituting equation (2.147) and equation (2.148) into equation (2.146), we get

$$\hat{G}_{\mu\nu} = \sum_{\alpha\beta}P_{\alpha\beta}\int \phi_\mu^*(\vec{r}_1)\left(\int \frac{\phi_\beta^*(\vec{r}_2)\,\phi_\alpha(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}d^3r_2\right)\phi_\nu(\vec{r}_1)\,d^3r_1$$
$$-\frac{1}{2}\sum_{\alpha\beta}P_{\alpha\beta}\int \phi_\mu^*(\vec{r}_1)\int \frac{\phi_\nu(\vec{r}_2)\,\phi_\beta^*(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}d^3r_2\phi_\alpha(\vec{r}_1)\,d^3r_1 \tag{2.149}$$

We can write the above equation in a more compact form

$$\hat{G}_{\mu\nu} = \sum_{\alpha\beta}P_{\alpha\beta}\int \frac{\phi_\mu^*(r_1)\,\phi_\nu(r_1)\,\phi_\beta^*(r_2)\,\phi_\alpha(r_2) - \frac{1}{2}\phi_\mu^*(r_1)\,\phi_\alpha(r_1)\,\phi_\beta^*(r_2)\,\phi_\nu(r_2)}{|r_1-r_2|}d^3r_1d^3r_2 \tag{2.150}$$

The above equation can be simplify to a form :

$$\hat{G}_{\mu\nu} = \sum_{\alpha\beta}P_{\alpha\beta}\left(\langle\mu\beta\,|\nu\alpha\rangle - \frac{1}{2}\langle\mu\beta\,|\alpha\nu\rangle\right) \tag{2.151}$$

It can also be written in matrix form as,

$$P_{\alpha\beta} = 2\sum_{i} C_{\alpha i} C_{\beta i} \tag{2.152}$$

where $P_{\alpha\beta}$ is the density matrix. The sum over all occupied orbitals i can be written as:

$$\sum_{i} = \sum_{n_i l_i m_i} = \sum_{n_l=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} \tag{2.153}$$

Then,

$$P_{n_\alpha l_\alpha m_\alpha ; n_\beta l_\beta m_\beta} = 2\sum_{i} C_{n_\alpha l_\alpha m_\alpha ; n_i l_i m_i} C_{n_\beta l_\beta m_\beta ; n_i l_i m_i} \tag{2.154}$$

$$= 2\sum_{i} \delta_{l_i l_\alpha} \delta_{m_i m_\alpha} \delta_{l_i l_\beta} \delta_{m_i m_\beta} C^{l_i}_{n_\alpha n_i} C^{l_i}_{n_\beta n_i}$$

$$= 2\delta_{l_\alpha l_\beta} \delta_{m_\alpha m_\beta} \sum_{n_i} C^{l_\alpha}_{n_\alpha n_i} C^{l_\alpha}_{n_\beta n_i} \tag{2.155}$$

and we get

$$\hat{G}_{\mu\nu} = \hat{G}_{n_\mu l_\mu m_\mu n_\nu l_\nu m_\nu} = \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} P_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \left(\langle \mu\beta | \nu\alpha \rangle - \frac{1}{2} \langle \mu\beta | \alpha\nu \rangle \right) = \hat{J}_{\mu\nu} - \hat{K}_{\mu\nu} \tag{2.156}$$

The first part in the above equation is the direct term $\hat{J}_{\mu\nu}$, and the second part represents the exchange term $\hat{K}_{\mu\nu}$. Let us treat the direct term first:

$$\hat{J}_{\mu\nu} = \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} P_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \langle \mu\beta | \nu\alpha \rangle \tag{2.157}$$

$$= \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} P_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \sum_{k=max\left(|l_\mu - l_\nu|, |l_\beta - l_\alpha|, |m_\mu - m_\nu|\right)}^{min\left(l_\mu + l_\nu, l_\beta + l_\alpha\right)} c^k\left(l_\mu, m_\mu, l_\nu, m_\nu\right) c^k\left(l_\alpha, m_\alpha, l_\beta, m_\beta\right) \delta_{m_\mu + m_\beta - m_\nu - m_\alpha, 0} \times R^k\left(n_\mu l_\mu, n_\beta l_\beta, n_\nu l_\nu, n_\alpha l_\alpha\right) \tag{2.158}$$

where $R^k\left(n_\mu l_\mu, n_\beta l_\beta, n_\nu l_\nu, n_\alpha l_\alpha\right)$ represents the two particle integral,

$$\hat{J}_{\mu\nu} = \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \delta_{l_\alpha l_\beta} \delta_{m_\alpha m_\beta} P^{l_\alpha}_{n_\alpha n_\beta} \sum_{k=max\left(|l_\mu - l_\nu|, |l_\beta - l_\alpha|, |m_\mu - m_\nu|\right)}^{min\left(l_\mu + l_\nu, l_\beta + l_\alpha\right)} c^k\left(l_\mu, m_\mu, l_\nu, m_\nu\right) c^k\left(l_\alpha, m_\alpha, l_\beta, m_\beta\right) \delta_{m_\mu + m_\beta - m_\nu - m_\alpha, 0}$$

$$\times R^{k}\left(n_{\mu}l_{\mu},n_{\beta}l_{\beta},n_{\nu}l_{\nu},n_{\alpha}l_{\alpha}\right) \tag{2.159}$$

$$= \sum_{n_{\alpha}n_{\beta}}\sum_{lm}P^{l}_{n_{\alpha}n_{\beta}}\sum_{k=max\left(\left|l_{\mu}-l_{\nu}\right|,\left|m_{\mu}-m_{\nu}\right|\right)}^{min\left(l_{\mu}+l_{\nu},2l\right)} c^{k}\left(l_{\mu},m_{\mu},l_{\nu},m_{\nu}\right)c^{k}\left(l,m,l,m\right)\delta_{m_{\mu}-m_{\nu},0}R^{k}\left(n_{\mu}l_{\mu},n_{\beta}l,n_{\nu}l_{\nu},n_{\alpha}l\right) \tag{2.160}$$

$$= \delta_{m_{\mu}m_{\nu}}\sum_{n_{\alpha}n_{\beta}}\sum_{l}P^{l}_{n_{\alpha}n_{\beta}}c^{0}\left(l_{\mu},m_{\mu},l_{\nu},m_{\nu}\right)\left(2l+1\right)R^{0}\left(n_{\mu}l_{\mu},n_{\beta}l,n_{\nu}l_{\nu},n_{\alpha}l\right) \tag{2.161}$$

$$J_{\mu\nu} = \delta_{l_{\mu}l_{\nu}}\delta_{m_{\mu}m_{\nu}}\sum_{l}\left(2l+1\right)\sum_{n_{\alpha}n_{\beta}}P^{l}_{n_{\alpha}n_{\beta}}R^{0}\left(n_{\mu}l_{\mu},n_{\beta}l,n_{\nu}l_{\nu},n_{\alpha}l\right) \tag{2.162}$$

The exchange term can be treated in equation (2.156), can be written as:

$$\hat{K}_{\mu\nu} = \frac{1}{2}\sum_{n_{\alpha}l_{\alpha}m_{\alpha}n_{\beta}l_{\beta}m_{\beta}}P_{n_{\alpha}l_{\alpha}m_{\alpha}n_{\beta}l_{\beta}m_{\beta}}\left\langle\mu\beta\left|\alpha\nu\right.\right\rangle \tag{2.163}$$

$$= \frac{1}{2}\sum_{n_{\alpha}l_{\alpha}m_{\alpha}n_{\beta}l_{\beta}m_{\beta}}P_{n_{\alpha}l_{\alpha}m_{\alpha}n_{\beta}l_{\beta}m_{\beta}}\sum_{k=max\left(\left|l_{\mu}-l_{\alpha}\right|,\left|l_{\beta}-l_{\nu}\right|,\left|m_{\mu}-m_{\alpha}\right|\right)}^{min\left(l_{\mu}+l_{\alpha},l_{\beta}+l_{\nu}\right)} c^{k}\left(l_{\mu},m_{\mu},l_{\alpha},m_{\alpha}\right)c^{k}\left(l_{\nu},m_{\nu},l_{\beta},m_{\beta}\right)$$

$$\times\delta_{m_{\mu}+m_{\beta}-m_{\alpha}-m_{\nu},0}\,R^{k}\left(n_{\mu}l_{\mu},n_{\beta}l_{\beta},n_{\alpha}l_{\alpha},n_{\nu}l_{\nu}\right) \tag{2.164}$$

$$= \frac{1}{2}\sum_{n_{\alpha}l_{\alpha}m_{\alpha}n_{\beta}l_{\beta}m_{\beta}}\delta_{l_{\alpha}l_{\beta}}\delta_{m_{\alpha}m_{\beta}}P^{l_{\alpha}}_{n_{\alpha}n_{\beta}}\sum_{k=max\left(\left|l_{\mu}-l_{\alpha}\right|,\left|l_{\beta}-l_{\nu}\right|,\left|m_{\mu}-m_{\alpha}\right|\right)}^{min\left(l_{\mu}+l_{\alpha},l_{\beta}+l_{\nu}\right)} c^{k}\left(l_{\mu},m_{\mu},l_{\alpha},m_{\alpha}\right)c^{k}\left(l_{\nu},m_{\nu},l_{\beta},m_{\beta}\right)$$

$$\times\delta_{m_{\mu}+m_{\beta}-m_{\alpha}-m_{\nu},0}\,R^{k}\left(n_{\mu}l_{\mu},n_{\beta}l_{\beta},n_{\alpha}l_{\alpha},n_{\nu}l_{\nu}\right) \tag{2.165}$$

$$= \frac{1}{2}\delta_{m_{\mu}m_{\nu}}\sum_{n_{\alpha}n_{\beta}}\sum_{lm}P^{l}_{n_{\alpha}n_{\beta}}\sum_{k=max\left(\left|l_{\mu}-l\right|,\left|l-l_{\nu}\right|,\left|m_{\mu}-m\right|\right)}^{min\left(l_{\mu}+l,l+l_{\nu}\right)} c^{k}\left(l_{\mu},m_{\mu},l,m\right)c^{k}\left(l_{\nu},m_{\nu},l,m\right)R^{k}\left(n_{\mu}l_{\mu},n_{\beta}l,n_{\alpha}l,n_{\nu}l_{\nu}\right) \tag{2.166}$$

$$= \frac{1}{2}\delta_{m_{\mu}m_{\nu}}\sum_{n_{\alpha}n_{\beta}}\sum_{lm}P^{l}_{n_{\alpha}n_{\beta}}\sum_{k=max\left(\left|l_{\mu}-l\right|,\left|l-l_{\nu}\right|,\left|m_{\mu}-m\right|\right)}^{min\left(l_{\mu}+l,l+l_{\nu}\right)} c^{k}\left(l_{\mu},m_{\mu},l,m\right)c^{k}\left(l_{\nu},m_{\mu},l,m\right)R^{k}\left(n_{\mu}l_{\mu},n_{\beta}l,n_{\alpha}l,n_{\nu}l_{\nu}\right) \tag{2.167}$$

For $l_{\mu} = l_{\nu}$, we can be write the above equation as

$$K_{\mu\nu} = \delta_{l_{\mu}l_{\nu}}\delta_{m_{\mu}m_{\nu}}\sum_{l}\left(2l+1\right)\sum_{n_{\alpha}n_{\beta}}P^{l}_{n_{\alpha}n_{\beta}}\sum_{k=\left|l_{\mu}-l\right|}^{l_{\mu}+l}\frac{1}{2}\begin{pmatrix} l_{\mu} & k & l \\ 0 & 0 & 0 \end{pmatrix}^{2}R^{k}\left(n_{\mu}l_{\mu},n_{\beta}l,n_{\alpha}l,n_{\nu}l_{\nu}\right) \tag{2.168}$$

Substituting equation (2.168) and equation (2.162) into equation (2.156), we obtain

$$G_{\mu\nu} = \delta_{l_\mu l_\nu}\delta_{m_\mu m_\nu}\sum_{l}(2l+1)\sum_{n_\alpha n_\beta}P^{l}_{n_\alpha n_\beta}$$

$$\left(R^0\left(n_\mu l_\mu, n_\beta l, n_\nu l_\nu, n_\alpha l\right) - \sum_{k=\left|l_\mu - l\right|}^{l_\mu + l}\frac{1}{2}\begin{pmatrix} l_\mu & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 R^k\left(n_\mu l_\mu, n_\beta l, n_\alpha l, n_\nu l_\nu\right)\right) \quad (2.169)$$

The two particle integrals $R^k\left(n_\mu l_\mu, n_\beta l_\beta, n_\nu l_\nu, n_\alpha l_\alpha\right)$ can be written as:

$$R^k(\mu,\nu,\alpha,\beta) = \int_0^\infty dr' \int_{r'}^\infty dr \frac{r'^k}{r^{k+1}} P_\mu(r) P_\alpha(r) P_\nu(r') P_\beta(r') \quad (2.170)$$

Substituting Gaussian type orbital basis function (2.135) into (2.170), yields

$$R^k(\mu,\nu,\alpha,\beta) = N_{n_\mu\xi_\mu}N_{n_\nu\xi_\nu}N_{n_\alpha\xi_\alpha}N_{n_\beta\xi_\beta}\frac{\left(\frac{n_\mu+n_\alpha-k}{2}-1\right)!}{2\left(\xi_\mu+\xi_\alpha\right)^{\frac{n_\mu+n_\alpha-k}{2}}}\sum_{\nu=0}^{n_\mu+n_\alpha-k-2}\frac{\left(\xi_\mu+\xi_\alpha\right)^\nu}{\nu!}$$

$$\times\frac{\left(n_\nu+n_\beta+k+2\nu-1\right)!\sqrt{\pi}}{2^{\frac{n_\nu+n_\beta+k+2\nu+2}{2}}\left(\xi_\mu+\xi_\alpha+\xi_\alpha+\xi_\beta\right)^{\frac{n_\nu+n_\beta+k+2\nu+1}{2}}} \quad (2.171)$$

The overlap matrix element $S_{\mu\nu}$ represents the overlap integrals in equation (2.137) and can be evaluated with Gaussian type functions, defined as:

$$S_{\mu\nu} = S_{n_\mu l_\mu m_\mu n_\nu l_\nu m_\nu} = \int \phi^*_\mu(r)\,\phi_\nu(r)\,d^3r \quad (2.172)$$

$$S_{\mu\nu} == \int \frac{P_{n_\mu l_\mu}(r)}{r} Y^*_{l_\mu m_\mu}(\theta,\varphi)\frac{P_{n_\nu l_\nu}(r)}{r} Y_{l_\nu m_\nu}(\theta,\varphi)\, r^2 dr d\theta d\varphi \quad (2.173)$$

$$= \delta_{l_\mu l_\nu}\delta_{m_\mu m_\nu}\int_0^\infty P_{n_\mu l_\mu}(r)\,P_{n_\nu l_\nu}(r)\,dr$$

$$= \delta_{l_\mu l_\nu}\delta_{m_\mu m_\nu}\int_0^\infty P_{n_\mu l_\mu}(r)\,P_{n_\nu l_\mu}(r)\,dr \quad (2.174)$$

Substituting Gaussian type orbital basis function (2.135) into (2.174), yields

$$S_{\mu\nu} = N_{n_\mu\xi_\mu}N_{n_\nu\xi_\nu}\left(n_\mu+n_\nu-1\right)!\sqrt{\frac{\pi}{2\left(\xi_\mu+\xi_\nu\right)^{\left(\frac{n_\mu+n_\nu+1}{2}\right)}}} \quad (2.175)$$

Combining Eqs. (2.142), (2.145), (2.156), and Eq.(2.175), we get to the Hartree-Fock equation with Gaussian basis-set function

$$\sum_{n_i}(T+V+G)^l_{n_\mu n_\nu}C^l_{n_\nu n_i}=\varepsilon_{n_i l}\sum_{n_\nu}S^l_{n_\mu n_\nu}C^l_{n_\mu n_i} \tag{2.176}$$

$$\begin{aligned}
&\sum_{n_i}\left(\frac{1}{2}N_{n_\mu\xi_\mu}N_{n_\nu\xi_\nu}\left(\left(n_\mu n_\nu+l\left(l+1\right)\left(n_\mu+n_\nu-3\right)!\sqrt{\frac{\pi}{2\left(2\xi_\mu+2\xi_\nu\right)^{n_\mu+n_\nu-1}}}\right)\right.\right.\\
&\left.-2\left(n_\mu\xi_\nu+n_\nu\xi_\mu\right)\left(n_\mu+n_\nu-1\right)!\sqrt{\frac{\pi}{2\left(2\xi_\mu+2\xi_\nu\right)^{n_\mu+n_\nu+1}}}+4\xi_\mu\xi_\nu\left(n_\mu+n_\nu-1\right)!\sqrt{\frac{\pi}{2\left(2\xi_\mu+2\xi_\nu\right)^{n_\mu+n_\nu+1}}}\right)dr\\
&-ZN_{n_\mu\xi_\mu}N_{n_\nu\xi_\nu}\frac{\left(\frac{n_\mu+n_\nu-2}{2}\right)!}{2\sqrt{\left(\xi_\mu+\xi_\nu\right)^{\frac{n_\mu+n_\nu}{2}}}}+\left(\delta_{l_\mu l_\nu}\delta_{m_\mu m_\nu}\sum_{l}\left(2l+1\right)\sum_{n_\alpha n_\beta}P^l_{n_\alpha n_\beta}R^0\left(n_\mu l_\mu,n_\beta l,n_\nu l_\nu,n_\alpha l\right)\right.\\
&\left.\left.\delta_{l_\mu l_\nu}\delta_{m_\mu m_\nu}\sum_{l}\left(2l+1\right)\sum_{n_\alpha n_\beta}P^l_{n_\alpha n_\beta}\sum_{k=\left|l_\mu-l\right|}^{l_\mu+l}\frac{1}{2}\begin{pmatrix} l_\mu & k & l\\ 0 & 0 & 0\end{pmatrix}^2R^k\left(n_\mu l_\mu,n_\beta l,n_\alpha l,n_\nu l_\nu\right)\right)\right)C^l_{n_\nu n_i}\\
&=\varepsilon_{n_i l}C^l_{n_\mu n_i}\sum_{n_\nu}\left(N_{n_\mu\xi_\mu}N_{n_\nu\xi_\nu}\left(n_\mu+n_\nu-1\right)!\sqrt{\frac{\pi}{2\left(\xi_\mu+\xi_\nu\right)^{\left(\frac{n_\mu+n_\nu+1}{2}\right)}}}\right)
\end{aligned} \tag{2.177}$$

The total Hartree-Fock energy can be written as:

$$E=\sum_{\mu\nu}P_{\mu\nu}\left(F_{\mu\nu}-\frac{1}{2}G_{\mu\nu}\right) \tag{2.178}$$

$$E=\sum_{l}\sum_{n}2\left(2l+1\right)\left(\varepsilon_{nl}-\sum_{l'}\sum_{n'}\left(2l'+1\right)\left(R^0\left(nl,n'l',n_\nu l,n'l'\right)-\frac{1}{2}\sum_{k=|l-l'|}^{k=l+l'}\begin{pmatrix} l & k & l'\\ 0 & 0 & 0\end{pmatrix}^2R^k\left(nl,n'l',n'l',n_\nu l\right)\right)\right) \tag{2.179}$$

Chapter 3

Relativistic Hartree-Fock for Atomic and Molecular Structure

Part One

The Issues of Complex Atoms

3.1 Introduction

In the phenomena that occur in every day life, we intuitively apply a series of notions which are at the base of the Newtonian physics. For example, when we cross a street and the traffic light is on red, we can quickly estimate the speed of car that is coming on our direction, provided that does not suddenly accelerate. If the measured time that reached our position is long enough, we could safely cross the road. Our guess depends on a certain description of the dynamics of the car that turns out to be the same for us and for the car's driver. The laws which describe this motion are said to be invariant under a Galileo transformation over all the inertial frames. The theory that explains the movement of these macroscopic objects is known as classical mechanics. Macroscopic objects can be pushed to move at very high speed, and if their velocities come close to the speed of light, then classical mechanics is no longer capable of predicting their trajectories. Einstein developed a new theory where space and time are not two distinct entities, like we intuitively expect, but are closely related. The equations of motion in this new domain are not invariant under Galileo transformation, but under a Lorentz transformation. We can explain what happens to these very fast objects by making paradoxical examples. One of these, is the famous twins paradox, in which one of two brothers is an astronaut who travels on a spaceship at speed of light and the other, less adventurous brother, prefers to live in a slow moving object, i.e. the earth. At the end of his trip, the first brother is younger than his brother, because of the phenomena of time contraction. A fast-moving person ages more slowly due to the relation that connects the coordinates of two different frames, $t' = \frac{t-(xv/c^2)}{\sqrt{1-v^2/c^2}}$, in the approximation we move along the X axis. The dynamics that explains the behavior of fast moving objects is called *the special theory* of relativity. At microscopic scale, it is more difficult to predict trajectories because of the dual wave-particle nature that each object intrinsically possesses. The Heisenberg principle teaches us that momentum and position can not be known exactly at the same time, the more accurately one is measured, the bigger is the uncertainty on the measurement of the other. The equation of motion of microscopic objects can be deduced from the Schrödinger equation and the theory that explains their behavior is called quantum mechanics. In the last fourty years the evolution of computer power has helped in finding an approximate solution to the Schrödinger equation for microscopic systems of increasing complexity. In particular, the movement of electrons can be decoupled from the much slower nuclei (Born-Oppenheimer approximation) in order to predict the properties of a molecular system. A very small object can also move at velocity close to the speed of light. For example, an electron moving in the vicinity of a heavy nucleus can increase its speed so much. Therefore its mass can be changed significantly and the orbital in which it moves gets deformed. This can affect certain properties of a system. The combination of quantum mechanics and the special theory of relativity is known as *relativistic quantum mechanics.*

3.2 Dirac Equation for One Particle System

The Dirac equation with the Coulomb potential describes the motion of an electron in the field of an atomic nucleus. This problem can be solved and the solution a agrees with experiments [73]. The one-electron Dirac wave function $\Psi_{n\kappa m}$ satisfies the single-particle Dirac equation [74]:

$$\hat{h}_D \Psi_{n\kappa m}(\vec{r}) = E_{n\kappa} \Psi_{n\kappa m}(\vec{r}) \tag{3.1}$$

where $\hat{h}_D$ is the Dirac Hamiltonian, given by [75]:

$$\hat{h}_D = c\hat{\vec{\alpha}}.\hat{\vec{p}} + \hat{\beta} mc^2 + V(r) \tag{3.2}$$

where r is the distance between electron and nucleus, and $V(r)$ is the potential energy. Obviously, the $\hat{\beta} mc^2$ term in equation (3.2) is independent of coordinates system. The Hamiltonian $\hat{h}_D$ is invariant under rotation and space, which means that it commutes with the operators of the total angular momentum and the parity [76]. The operators $\hat{\vec{\alpha}}$ and $\hat{\beta}$ in equation (3.2) involves

4×4 Dirac matrices that are hermitian and given by [77]:

$$\hat{\vec{\alpha}} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \quad ; \hat{\beta} = \begin{pmatrix} \hat{I} & 0 \\ 0 & -\hat{I} \end{pmatrix} \tag{3.3}$$

where $\hat{I}$ is the 2×2 unit matrix ,and the $\hat{\sigma}$'s are defined by [78] :

$$\hat{\vec{\sigma}}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \hat{\vec{\sigma}}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ \hat{\vec{\sigma}}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{3.4}$$

Equation (3.4) represents Pauli matrices that constitute with the unite matrix, a basis for 2×2 hermitian matrices. In a spherical coordinate system, the eigenstate or bound-state solution to the Dirac equation for one-electron has the 4-spinor structure [79].

$$\Psi_{n\kappa m}(\vec{r}) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(\vec{r}) & \chi_{\kappa}^{m_j}(\theta, \phi) \\ iQ_{n\kappa}(\vec{r}) & \chi_{-\kappa}^{m_j}(\theta, \phi) \end{pmatrix} \tag{3.5}$$

where $P_{n\kappa}(\vec{r})$ and $Q_{n\kappa}(\vec{r})$ are the large and small component radial wave functions of the one electron radial wave function respectively, and satisfy the orthonormal condition given by [80]

$$\int_0^{\infty} [P_{n\kappa}(\vec{r}) P_{n'\kappa}(\vec{r}) + Q_{n\kappa}(\vec{r}) Q_{n'\kappa}(\vec{r})] \, dr = \delta_{nn'} \delta_{\kappa\kappa'} \tag{3.6}$$

where $\delta_{nn'}\delta_{\kappa\kappa'}$ is the Kronecker delta, and $\chi_{\kappa}^{m_j}(\theta, \phi)$ terms in equation (3.5) are the spin-orbit parts which are two-dimensional vector harmonics. The spherical spinors satisfy the orthogonality relation too which is defined by the equation [81]:

$$\chi_{\kappa}^{m_j}(\theta, \phi) = \sum_{m_s = -1/2}^{1/2} C\left(l, 1/2\, j; m_j - m_s, m_s\right) Y_l^{m_j - m_s}(\theta, \phi) \chi^{m_s} \tag{3.7}$$

Here n is the principal quantum number, and κ is the Dirac quantum number which is related to the total angular momentum j and the orbital angular momenta $l, and\ l^{-}$ of the large and small components respectively, by [82]:

$$\begin{aligned} j &= |\kappa| - \tfrac{1}{2} \\ l &= \left|\kappa + \tfrac{1}{2}\right| - \tfrac{1}{2} \\ l^{-} &= \left|-\kappa + \tfrac{1}{2}\right| - \tfrac{1}{2} \end{aligned} \tag{3.8}$$

there is also another useful formfor the spherical spinors given by :

$$\chi_{\kappa}^{m_j}(\theta,\phi) = \begin{bmatrix} C\left(l, 1/2\, j; m_j - \tfrac{1}{2}, +\tfrac{1}{2}\right) Y_l^{m_j - \frac{1}{2}}(\theta,\phi)\chi^{m_s} \\ C\left(l, 1/2\, j; m_j + \tfrac{1}{2}, -\tfrac{1}{2}\right) Y_l^{m_j + \frac{1}{2}}(\theta,\phi)\chi^{m_s} \end{bmatrix} \tag{3.9}$$

But $\hat{h}_D$ does not commute with $\hat{L}^2$ and $\hat{S}^2$ and the quantum numbers j and m_j are not sufficient to describe one state (each value of j corresponds to two non-relativistic states). This is why it is useful to introduce the operator $\hat{\kappa}$:

$$\hat{\kappa} = (2\hat{\vec{L}}\cdot\hat{\vec{S}} + 1) = (\hat{\vec{\sigma}}\cdot\hat{\vec{L}} + 1) \tag{3.10}$$

that commutes with $\hat{h}_D$ as well as with $\hat{\vec{J}}$. Its application on an eigenvector gives

$$(\hat{\vec{\sigma}}\cdot\hat{\vec{L}} + 1)\chi_{\kappa}^{m_j}(\theta,\phi) = \kappa\chi_{\kappa}^{m_j}(\theta,\phi) \tag{3.11}$$

where the eigenvalue κ is

$$\begin{cases} \kappa = -\left(j + \tfrac{1}{2}\right), & if \quad l = j - \tfrac{1}{2} \\ \kappa = +\left(j + \tfrac{1}{2}\right) & if \quad l = j + \tfrac{1}{2} \end{cases} \tag{3.12}$$

The value of κ determines both j and l. As the Dirac Hamiltonian does not change under space-like reflections, the parity operator $\hat{P}$ that maps $\vec{r} \to -\vec{r}$, may also produce good quantum numbers. In spherical coordinates, the operator $\hat{P}$ transforms $\phi \to \phi + \pi$ and $\theta \to \pi - \theta$. Under a parity transformation, $\hat{P}Y_l^{m_j - m_s}(\theta,\phi) = Y_l^{m_j - m_s}(\pi - \theta, \phi + \pi) = (-1)^l Y_l^{m_j - m_s}(\theta,\phi)$. From the action of the 4-components operator $\hat{p} = \hat{\beta}\hat{P}$ on the 4-rank spinor, it follows that the spherical spinors are eigenfunctions of $\hat{P}$ having eigenvalues $\Pi = (-1)^l$. The two spinors $\chi_{\kappa}^{m_j}(\theta,\phi)$ and $\chi_{-\kappa}^{m_j}(\theta,\phi)$, corresponding to the same value of j, have values of l differing by one unit and, therefore, have opposite parity.

3.3 Dirac-Coulomb Equation for a Many-Body System

If more than one-electron is present in the system, an additional term, arising from the interaction between electrons, must be added in the Dirac-Coulomb Hamiltonian describing the problem, given by [83]:

$$\hat{H}_{DC} = \sum_{i=1}^{N} \left[c\hat{\vec{\alpha}}_i.\hat{\vec{p}}_i + (\hat{\beta}_i - 1)c^2 + V(r_i) \right] + \sum_{i<j}^{N} V(i,j) \tag{3.13}$$

where the first summation is over all electrons and the second summation is over all pairs of electrons. The first and second terms in the Dirac-Coulomb Hamiltonian represent the Dirac kinetic energy operator as [84]:

$$\hat{T}_i = c\hat{\vec{\alpha}}_i.\hat{\vec{p}}_i + (\hat{\beta}_i - 1)c^2 \tag{3.14}$$

and the terms in bracket represent the one-electron Hamiltonian $\hat{h}_D$ which is defined in section (3.2), $V(r_i)$ is the Coulomb potential for one-electron and the last term $V(i,j)$ in equation (3.2) represents the interaction energy of electrons i and j, where $V(i,j) = \frac{1}{r_{ij}}$, $r_{ij} = \left|\vec{r}_i - \vec{r}_j\right|$ is the inter electronic distance. The result of many-body Hamiltonian is called Dirac-Coulomb Hamiltonian. The study of the bound state of the atomic system consists of solving an eigenvalue problem of the form [85]

$$\hat{H}_{DC}\Psi_{n\kappa m} = E\Psi_{n\kappa m} \tag{3.15}$$

whose solutions are square-integrable. Such an equation can no longer be solved analytically and all the challenge consists in determining an approximate wave function for an N-electron atom. Furthermore, as the electrons are fermions, the exclusion Pauli Principle play a major role. This physical constraint implies that the wave function of any N-electron system $\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$, must be antisymmetric under the exchange of any pair of coordinates ($\vec{r}_i$, $\vec{r}_j$). Such function has the form [86]:

$$\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \frac{1}{\sqrt{N!}} \sum_{p} (-1)^p \hat{P} \left\{ \Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2)...\Psi_N(\vec{r}_N) \right\} \tag{3.16}$$

where $\hat{P}$ is an operator which permutes the coordinates of the electrons, $(-1)^p = 1$ for an even permutation, and -1 otherwise. In an equivalent and convenient writing, the latter function can also be written as a Slater determinant which is given by [87]:

$$\Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\vec{r}_1) & \psi_b(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_a(\vec{r}_2) & \psi_b(\vec{r}_2) & .... & \psi_N(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_a(\vec{r}_N) & \psi_b(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix} \tag{3.17}$$

Each element of the determinant is a Dirac four-spinor (eigenstate) associated with an orbital. In analyzing the commutation properties of the many-electron Hamiltonian, we are looking for functions characterized by the good quantum numbers $\hat{J}, M_j, \hat{\Pi}$. A single Slater determinant is usually not an eigenfunction of J^2 and a J^2 -symmetry adapted linear combination of Slater determinants is needed to define a single Configuration State Function (CSF). These state functions $\psi\left(\alpha_j J\right)$ are called $CSFs$ (Configuration State Functions), where α_j contains enough parameters to define each state uniquely.

3.4 Configuration State Functions

A configuration state function (CSF), $\psi\left(\alpha_j J\right)$, of an $N-electron$ system is formed by taking linear combinations of Slater determinants of order N constructed from the orbitals of eqn. (3.5) so as to obtain normalized $\left(\left\langle \psi\left(\alpha_j J\right) | \psi\left(\alpha_j J\right)\right\rangle = 1\right)$ eigenfunctions of the parity operator $\hat{P}$, and total angular-momentum operators $\hat{J}^2$ and $\hat{j}_z$. In general, one configuration gives rise to several $CSFs$, all have the same total quantum numbers for spin and spatial parts but differ in their intermediate couplings.

3.5 Dirac-Hartree-Fock (DHF) Approximation

The strategy of the Dirac-Hartree-Fock (DHF) approach for calculating the electronic structure of atoms is to set up an expansion for the expectation value of the Hamiltonian, and minimizing with respect to variations wave functions. This problem concerns, with the fact that we have a four-component wave function and we want to minimize the total energy of an N-electron atom. The Dirac-Coulomb Hamiltonian for a many-electron atom can be written in another form as [88]:

$$\hat{H}_{DC} = \sum_{i=1}^{N}\left[c\hat{\vec{\alpha}}_i.\hat{\vec{p}}_i + (\hat{\beta}_i - 1)c^2 + V(r_i)\right] + \sum_{i<j}^{N}\frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} \tag{3.18}$$

To find the total energy of an N-electron atom, we have to find the expectation value of the Dirac-Coulomb Hamiltonian for determinant wave functions of eqn. (3.18). We can write down the expectation energy as [89]

$$\begin{aligned}\left\langle\Psi\left|\hat{H}_{DC}\right|\Psi\right\rangle &= \sum_{i=1}^{occ}\int\Psi_i(\vec{r})\left(c\tilde{\vec{\alpha}}_i.\hat{\vec{p}}_i + \hat{\beta}_i m_i c^2 - \frac{Ze^2}{r_i}\right)\Psi_i(\vec{r}_i)\,d\vec{r}_i \\ &+ e^2\sum_{i<j}\int\int\Psi_i^{\dagger}(\vec{r}_1)\,\Psi_j^{\dagger}(\vec{r}_2)\,\frac{1}{|\vec{r}_1 - \vec{r}_2|}\Psi_i(\vec{r}_1)\,\Psi_j(\vec{r}_2)\,d\vec{r}_1 d\vec{r}_2 \\ &- e^2\sum_{i<j}\int\int\Psi_i^{\dagger}(\vec{r}_1)\,\Psi_j^{\dagger}(\vec{r}_2)\,\frac{1}{|\vec{r}_1 - \vec{r}_2|}\Psi_i(\vec{r}_2)\,\Psi_j(\vec{r}_1)\,d\vec{r}_1 d\vec{r}_2\end{aligned} \tag{3.19}$$

where the first term is summed over all occupied states, and the other terms are summed over pairs of electrons. The single-particle wave functions take on the usual form for solutions of the Dirac equation in a central field [90] :

$$\Psi_{n\kappa}^{m_j}(\vec{r}) = \frac{1}{r}\begin{pmatrix} u_{n\kappa}(\vec{r}) & \chi_{\kappa}^{m_j}(\theta,\phi) \\ -v_{n\kappa}(\vec{r}) & \chi_{-\kappa}^{m_j}(\theta,\phi)\end{pmatrix} \tag{3.20}$$

In this form, we note that the energy depends only on the radial part of the wave function, and this energy does not depend on the spin-angular functions. Therefore, it will be convenient that if we could integrate the spin-angular functions, then equation (3-20) has the form $\Psi(\vec{r}) = \begin{pmatrix} u(\vec{r}) \\ v(\vec{r})\end{pmatrix}$. This leaves us with integrals, involving $u(\vec{r})$and $v(\vec{r})$ only, where u and v are large and small component of the electron wave function respectively. The radial functions

$u_{n\kappa}(\vec{r})$ and $v_{n\kappa}(\vec{r})$ may be expanded using Gaussian basis-sets as [91].

$$u_{n\kappa}(\vec{r}) = \sum_{i=1}^{N} f_{\kappa p}^{L}(\vec{r})\,\xi_{n\kappa p} \tag{3.21}$$

$$v_{n\kappa}(\vec{r}) = \sum_{i=1}^{N} f_{\kappa q}^{S}(\vec{r})\,\eta_{n\kappa q} \tag{3.22}$$

where N is the expansion length. $\xi_{n\kappa p}$ and $\eta_{n\kappa q}$ are linear variation parameters, $f_{\kappa p}^{L}(\vec{r})$ and $f_{\kappa q}^{S}(\vec{r})$ are the relativistic Gaussian basis-sets given by [92]

$$f_{\kappa p}^{L}(\vec{r}) = N_L r\,exp\left(-\zeta_L r^2\right) \tag{3.23}$$

$$f_{\kappa q}^{S}(\vec{r}) = N_S r\,exp\left(-\zeta_S r^2\right) \tag{3.24}$$

The factors ζ_L and ζ_S in Eq. (3.23) and Eq. (3.24) are the only adjustable parameters of these basis functions and these parameters are usually called the exponents of the basis functions. N_L and N_S are normalization factors . Substituting Eq. (3.23) and Eq. (3.24) into Eq.(3.21) and Eq.(3.22), respectively, the radial functions become

$$u_{n\kappa}(\vec{r}) = \sum_{i=1}^{N} r\,exp\left(-\zeta_L r^2\right)\xi_{n\kappa p} \tag{3.25}$$

$$v_{n\kappa}(\vec{r}) = \sum_{i=1}^{N} r\,exp\left(-\zeta_S r^2\right)\eta_{n\kappa p} \tag{3.26}$$

In equation (3-20), the wave function is labeled with the quantum number κ and m_j. We will replace the subscripts κ and n with the letters a, b, c , which will represent both n and κ. Then, the total energy expression of an atom can be find. We start from the first term in first bracket, in equation (3.19), which represents the kinetic energy, the expectation value for this term is [93]:

$$\left\langle \Psi_a^{m_j} \middle| c\hat{\vec{\alpha}}_i.\hat{\vec{p}}_i \middle| \Psi_a^{m_j} \right\rangle = \int \Psi_a^{m_j^{\dagger}}(\vec{r})\, ic\hat{\gamma}_5\hat{\sigma}_r\left(\hbar\frac{\partial}{\partial r} + \frac{\hbar}{r} - \hat{\beta}\frac{k}{r}\right)\Psi_a^{m_j}(r)\,dr \tag{3.27}$$

Integrating equation (3-27) over angles and using the orthonormality of the spin-angular functions, we get

$$\begin{aligned}\left\langle \Psi_a^{m_j} \middle| c\tilde{\vec{\alpha}}_i.\hat{\vec{p}}_i \middle| \Psi_a^{m_j} \right\rangle = &\left(c\hbar \int v_a(r) \left(\frac{\partial u_a(\vec{r})}{\partial r} + \frac{k}{r} u_a(\vec{r}) \right) dr \right.\\ &\left. - \int u_a(r) \left(\frac{\partial v_a(\vec{r})}{\partial r} - \frac{k}{r} u_a(\vec{r}) \right) dr \right)\end{aligned} \tag{3.28}$$

The expectation value of second term in first bracket in equation (3-19) represent the rest mass energy as:

$$\left\langle \Psi_a^{m_j} \middle| \hat{\beta}_i mc^2 \middle| \Psi_a^{m_j} \right\rangle = mc^2 \int \Psi_a^{m_j^\dagger}(\vec{r})\, \hat{\beta} \Psi_a^{m_j}(\vec{r})\, dr \tag{3.29}$$

$$= mc^2 \int \left(u_a^2(\vec{r}) - v_a^2(\vec{r}) \right) dr \tag{3.30}$$

And finally, the last term in first bracket in eqn. (3.19) represents the nuclear potential term. The expectation value for this term is:

$$\left\langle \Psi_a^{m_j} \middle| \frac{Ze^2}{r_i} \middle| \Psi_a^{m_j} \right\rangle = Ze^2 \int \Psi_a^{m_j^\dagger}(\vec{r})\, \frac{1}{r} \Psi_a^{m_j}(\vec{r})\, dr \tag{3.31}$$

$$= Ze^2 \int \frac{1}{r} \left(u_a^2(\vec{r}) + v_a^2(\vec{r}) \right) dr \tag{3.32}$$

Combining Eqs. (3.28), (3.30), and (3.32), we obtain the total single-particle energy for one electron :

$$\left\langle \Psi \middle| \hat{h}_D \middle| \Psi \right\rangle = \sum_{a,m_j} \int \Psi_a^{m_j^\dagger}(r)\, \hat{h}_D(\kappa, m_j)\, \Psi_a^{m_j}(r)\, dr \tag{3.33}$$

$$\begin{aligned}= \sum_a n_a &\left(mc^2 \int \left(u_a^2(r) - v_a^2(r) \right) dr - Ze^2 \int \frac{1}{r} \left(u_a^2(r) + v_a^2(r) \right) dr + \right.\\ c\hbar \int &\left. \left(v_a(r) \left(\frac{\partial u_a(r)}{\partial r} + \frac{k_a}{r} u_a(r) \right) - u_a(r) \left(\frac{\partial v_a(r)}{\partial r} - \frac{k_a}{r} u_a(r) \right) dr \right) \right)\end{aligned} \tag{3.34}$$

This equation represents the single-particle part of the total energy in terms of the radial parts of the single-particle wave functions only. While the total energy for two-particles is given by :

$$\left\langle a,b\left|\frac{e^2}{r_{12}}\right|c,d\right\rangle = \int\int \Psi_a^\dagger(r_1)\Psi_b^\dagger(r_2)\frac{e^2}{r_{12}}\Psi_c(r_1)\Psi_d(r_2)\,dr_1dr_2 \tag{3.35}$$

The Coulomb operator can be expanded as

$$\frac{1}{|\vec{r}_1-\vec{r}_2|} = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\left(\frac{4\pi}{2l+1}\right)\frac{r_<^l}{r_>^{l+1}}Y_l^{m^*}(\hat{r}_<)Y_l^m(\hat{r}_>) \tag{3.36}$$

where $r_> \equiv max(r_i, r_j)$ and $r_< \equiv min(r_i, r_j)$, represent longer (shorter) distance of the center of the nucleus for the ith and jth electron. Substituting Eqs. (3.20) and (3.36) into equations (3.35) and multiplying out the 4-component wave functions, we get :

$$\begin{aligned}
\left\langle a,b\left|\tfrac{e^2}{|\vec{r}_1-\vec{r}_2|}\right|c,d\right\rangle &= e^2\int dr_1\int dr_2 \textstyle\sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\left(\tfrac{4\pi}{(2l+1)}\right)\tfrac{r_<^l}{r_>^{l+1}}Y_l^{m^*}(\hat{r}_<)Y_l^m(\hat{r}_>)\\
\times\Big(&u_a(r_1)u_c(r_1)u_b(r_2)u_d(r_2)\chi_{\kappa_a}^{m_{ja}^\dagger}(\theta_1,\phi_1)\chi_{\kappa_c}^{m_{jc}}(\theta_1,\phi_1)\chi_{\kappa_b}^{m_{jb}^\dagger}(\theta_2,\phi_2)\chi_{\kappa_d}^{m_{jd}}(\theta_2,\phi_2)\\
&+u_a(r_1)u_c(r_1)v_b(r_2)v_d(r_2)\chi_{\kappa_a}^{m_{ja}^\dagger}(\theta_1,\phi_1)\chi_{\kappa_c}^{m_{jc}}(\theta_1,\phi_1)\chi_{-\kappa_a}^{m_{jb}^\dagger}(\theta_2,\phi_2)\chi_{-\kappa_d}^{m_{jd}}(\theta_2,\phi_2)\\
&+v_a(r_1)v_c(r_1)u_b(r_2)u_d(r_2)\chi_{-\kappa_a}^{m_{ja}^\dagger}(\theta_1,\phi_1)\chi_{-\kappa_c}^{m_{jc}}(\theta_1,\phi_1)\chi_{-\kappa_b}^{m_{jb}^\dagger}(\theta_2,\phi_2)\chi_{-\kappa_d}^{m_{jd}}(\theta_2,\phi_2)\\
&+v_a(r_1)v_c(r_1)v_b(r_2)v_d(r_2)\chi_{-\kappa_a}^{m_{ja}^\dagger}(\theta_1,\phi_1)\chi_{-\kappa_c}^{m_{jc}}(\theta_1,\phi_1)\chi_{-\kappa_b}^{m_{jb}^\dagger}(\theta_2,\phi_2)\chi_{-\kappa_d}^{m_{jd}}(\theta_2,\phi_2)
\end{aligned} \tag{3.37}$$

where $\chi_\kappa^{m_j}(\theta,\phi)$ is the spin-angular function, which when expanded is gives :

$$\chi_\kappa^{m_j}(\theta,\phi) = \sum_{m_s} c\left(l\frac{1}{2}j; m_j - m_s, m_s\right)Y_l^{m_j-m_s}(\theta,\phi)\chi^{m_s} \tag{3.38}$$

This is a complicated expression. Now let us rename radial wave functions as $u(r) = R_{(+1)}, v(r) = R_{(-1)}$, and define new quantities, [94]

$$\begin{gathered}
\beta_a = \pm 1, \beta_b = \pm 1\\
\kappa = -l-1 = -\left(j+\tfrac{1}{2}\right)\ ;\ j = l+\tfrac{1}{2}\\
\kappa = l = \left(j+\tfrac{1}{2}\right)\ ;\ j = l-\tfrac{1}{2}
\end{gathered} \tag{3.39}$$

and the quantum number $\bar{l}$ associated with $-\kappa$ as:

$$\begin{array}{ll} \bar{l} = l+1 = -\kappa & ,\kappa < 0 \\ \bar{l} = l-1 = \kappa - 1 & \kappa > 0 \end{array} \tag{3.40}$$

and new quantities [95]

$$\begin{array}{c} s_\kappa = \frac{\kappa}{|\kappa|} \\ s_\kappa = -1 \quad ; \quad j = l + \frac{1}{2} \\ s_\kappa = +1 \quad ; \quad j = l - \frac{1}{2} \\ s_\kappa = l - \bar{l} = 2\,(l-j) \end{array} \tag{3.41}$$

$$\begin{array}{l} \lambda_a = j_a + \frac{1}{2} s_{\kappa_a} \beta_a \\ \lambda_b = j_b + \frac{1}{2} s_{\kappa_b} \beta_b \\ \lambda_c = j_c + \frac{1}{2} s_{\kappa_c} \beta_c \\ \lambda_d = j_d + \frac{1}{2} s_{\kappa_d} \beta_d \end{array} \tag{3.42}$$

where j_i is the j quantum number associated with κ_i. Substituting Eq.(3.38), Eq. (3.39), Eq. (3.40), Eq.(3.41), and (3.42), into equation (3.37), we get

$$\begin{aligned} \left\langle a,b \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| c,d \right\rangle &= e^2 \int dr_1 \int dr_2 \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \left(\frac{4\pi}{(2l+1)} \right) \frac{r_<^l}{r_>^{l+1}} Y_l^{m^*}(\hat{r}_<) Y_l^m(\hat{r}_>) \\ &\times \sum_{\beta_a=\pm1} \sum_{\beta_b=\pm1} R_{a(\beta_a)}(r_1) R_{c(\beta_a)}(r_1) R_{b(\beta_b)}(r_2) R_{d(\beta_b)}(r_2) \\ &\times \Bigg(c(\lambda_a \frac{1}{2} j_a; m_{j_a} - \frac{1}{2}, \frac{1}{2} \Bigg) c \left(\lambda_c \frac{1}{2} j_c; m_{j_c} - \frac{1}{2}, \frac{1}{2} \right) Y_{\lambda_a}^{m_{j_a} - \frac{1}{2}^*}(r_1) Y_{\lambda_c}^{m_{j_c} - \frac{1}{2}}(r_1) \\ &+ \left(c \left(\lambda_a \frac{1}{2} j_a; m_{j_d} + \frac{1}{2}, -\frac{1}{2} \right) c \left(\lambda_c \frac{1}{2} j_c; m_{j_c} + \frac{1}{2}, \frac{1}{2} \right) Y_{\lambda_a}^{m_{j_a} + \frac{1}{2}^*}(r_1) Y_{\lambda_c}^{m_{j_c} + \frac{1}{2}}(r_1) \right) \\ &\times \left(c \left(\lambda_b \frac{1}{2} j_b; m_{j_b} - \frac{1}{2}, \frac{1}{2} \right) c \left(\lambda_d \frac{1}{2} j_d; m_{j_d} - \frac{1}{2}, \frac{1}{2} \right) Y_{\lambda_b}^{m_{j_b} - \frac{1}{2}^*}(r_2) Y_{\lambda_d}^{m_{j_d} - \frac{1}{2}}(r_2) \right. \\ &\left. + c \left(\lambda_b \frac{1}{2} j_b; m_{j_b} + \frac{1}{2}, \frac{1}{2} \right) c \left(\lambda_d \frac{1}{2} j_d; m_{j_d} + \frac{1}{2}, -\frac{1}{2} \right) Y_{\lambda_c}^{m_{j_c} + \frac{1}{2}^*}(r_2) Y_{\lambda_d}^{m_{j_d} + \frac{1}{2}}(r_2) \right) \end{aligned} \tag{3.43}$$

For more clear representation, we define new quantities $s_a = \pm\frac{1}{2}$, $s_b = \pm\frac{1}{2}$ and summing over these quantities and separating the radial and angular integrals, the equation (3.43) becomes

$$\left\langle a,b\left|\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\right|c,d\right\rangle=\sum_{\beta_a=\pm1}\sum_{\beta_b=\pm1}\sum_{s_a=\pm\frac{1}{2}}\sum_{s_b=\pm\frac{1}{2}}\sum_{l=0}^{\infty}\left(\frac{4\pi}{(2l+1)}\right)$$

$$\sum_{m=-l}^{+l}\left(c(\lambda_a\frac{1}{2}j_a;m_{j_a}-s_a,s_b)\right)c\left(\lambda_b\frac{1}{2}j_b;m_{j_b}-s_b,s_b\right)c\left(\lambda_c\frac{1}{2}j_c;m_{j_c}-s_a,s_b\right)$$

$$\int Y_{\lambda_a}^{m_{ja}-s_a^*}(r_1)Y_{\lambda_c}^{m_{jc}-s_a}(r_1)Y_l^{m^\star}(r_1)\,dr_1 c\left(\lambda_d\frac{1}{2}j_d;m_{j_d}-s_b,s_b\right)\int Y_l^m(r_2)Y_{\lambda_b}^{m_{j_b}-s_b^*}(r_2)$$

$$Y_{\lambda_d}^{m_{j_d}-s_b}(r_2)\,dr_2 e^2\int\int R_{a(\beta_a)}(r_1)R_{c(\beta_a)}(r_1)R_{b(\beta_b)}(r_2)R_{d(\beta_b)}(r_2)\frac{r_<^l}{r_>^{l+1}}dr_1dr_2 \tag{3.44}$$

To simplify equation (3.44) we let $c=a\,,d=b$, to obtain:

$$\left\langle a,b\left|\frac{e^2}{4\pi\varepsilon_\circ|r_1-r_2|}\right|a,b\right\rangle=\frac{e^2}{4\pi\varepsilon_\circ}\sum_{\beta_a=\pm1}\sum_{\beta_b=\pm1}\sum_{s_a=\pm\frac{1}{2}}\sum_{s_b=\pm\frac{1}{2}}\sum_{l=0}^{\infty}\left(\frac{4\pi}{(2l+1)}\right)$$

$$\sum_{m=-l}^{+l}\int\int R_{a(\beta_a)}^2(r_1)R_{b(\beta_b)}^2(r_2)\frac{r_<^l}{r_>^{l+1}}dr_1dr_2c^2(\lambda_a\frac{1}{2}j_a;m_{j_a}-s_a,s_a)$$

$$\int Y_{\lambda_a}^{m_{j_b}-s_a^*}(r_1)Y_{\lambda_a}^{m_{ja}-s_a}(r_1)Y_l^{m^\star}(r_1)\,dr_1c^2(\lambda_b\frac{1}{2}j_b;m_{j_b}-s_b,s_b)$$

$$\int Y_l^m(r_2)Y_{\lambda_b}^{m_{j_b}-s_b^*}(r_2)Y_{\lambda_b}^{m_{j_b}-s_b}(r_2)\,dr_2 \tag{3.45}$$

To simplify further, we introduce the spherical harmonics function as:

$$Y_l^{-m}(\theta,\phi)=(-1)Y_l^{m^*}(\theta,\phi) \tag{3.46}$$

The spherical harmonics are written in terms of Legendre functions as [96]:

$$Y_l^m(\theta,\phi)=(-1)^m\left(\frac{2l+1\;(l-m)!}{4\pi\;(l+m)!}\right)P_l^m(cos\theta)\,e^{im\phi} \tag{3.47}$$

The normalization condition is given as [97]

$$\int_0^{2\pi}d\phi\int_0^{\pi}sin\theta Y_l^{m^*}(\theta,\phi)Y_{l'}^{m'}(\theta,\phi)\,d\theta=\delta_{ll'}\delta_{mm\prime} \tag{3.48}$$

and

$$
\begin{aligned}
c_{lml'm'}^{l''m''} &= \int Y_{l''}^{*m''}(\Omega)\, Y_{l'}^{m'}(\Omega)\, Y_{l}^{m}(\Omega)\, d\Omega \\
&= \left(\frac{(2l+1)(2l'+1)}{4\pi(2l''+1)}\right) c\left(ll'l'';mm'\right) c\left(ll'l'';0,0\right) \delta_{m''m'+m}
\end{aligned}
\tag{3.49}
$$

and to add simplification, let $l'' = l$, $m'' = m$, we get to

$$
\int Y_{\lambda_a}^{m_{ja}-s_a^*}(r_1)\, Y_l^{m^*}(r_<)\, Y_{\lambda_a}^{m_{ja}-s_a}(r_1)\, dr_1 = \left(\frac{2l+1}{4\pi}\right)^{1/2} c\left(l_1ll_1;m_1m\right) c\left(l_1ll_1;0,0\right)
\tag{3.50}
$$

By using the triangle condition for Clebsh-Gordon coefficients as [98]

$$
j = |j_1 - j_2|;|j_1 - j_2|+1;|j_1 - j_2|+2,...,j_1+j_2-2,j_1+j_2-1,j_1+j_2
\tag{3.51}
$$

Eqn. (3.45) becomes

$$
\begin{aligned}
\left\langle a,b \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| a,b \right\rangle &= e^2 \sum_{\beta_a=\pm 1} \sum_{\beta_b=\pm 1} \sum_{s_a=\pm\frac{1}{2}} \sum_{s_b=\pm\frac{1}{2}} c^2(\lambda_a \tfrac{1}{2} j_a; m_{j_a} - s_a, s_a) \\
&\times c^2(\lambda_b \tfrac{1}{2} j_b; m_{j_b} - s_b, s_b) \int\!\!\int R_{a(\beta_a)}^2(r_1)\, R_{b(\beta_b)}^2(r_2)\, \frac{1}{r_>} dr_1 dr_2
\end{aligned}
\tag{3.52}
$$

where,

$$
c^2\left(l\frac{1}{2}j;m_j - \frac{1}{2},\frac{1}{2}\right) + c^2\left(l\frac{1}{2}j;m_j + \frac{1}{2},\frac{1}{2}\right) = 1
\tag{3.53}
$$

The summations over s_a and s_b in equation (3.52) can be re-expanded. Then using Eq. (3.53) we obtain :

$$
\left\langle a,b \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| a,b \right\rangle = e^2 \sum_{\beta_a=\pm 1} \sum_{\beta_b=\pm 1} \int\!\!\int R_{a(\beta_a)}^2(r_1)\, R_{b(\beta_b)}^2(r_2)\, \frac{1}{r_>} dr_1 dr_2
\tag{3.54}
$$

Eqn. (3.54) represents for the two particle integral which also called the direct integral or Coulomb integral (or direct Coulomb integral) denoted by J. We can also get rid of the summations in equation (3.54) over β_a and β_b, by putting $u(r)$ and $v(r)$ instead of $R^2_{a(\beta_a)}$ and $R^2_{b(\beta_b)}$ into equation (3.54), to obtain

$$J = e^2 \int \int \left(u_a^2(r_1) + v_a^2(r_1)\right)\left(u_b^2(r_2) + v_b^2(r_2)\right)\frac{1}{r_>}dr_1 dr_2 = F(a,b) \tag{3.55}$$

where $F_l(a,b)$ is the radial integral given [99]

$$F_l(a,b) = e^2 \int \int \left(u_a^2(r_1) + v_a^2(r_1)\right)\left(u_b^2(r_2) + v_b^2(r_2)\right)\frac{r_<^l}{r_>^{l+1}}dr_1 dr_2 \tag{3.56}$$

To find the total Coulomb average for all $N - electrons$ in the atom, we can write the equation (J) by another form as [100]:

$$J_T = \sum_a \left(\frac{1}{2}n_a(n_a - 1)F(a,a) + \frac{1}{2}\sum_{b \neq a} n_a n_b F(a,b)\right) \tag{3.57}$$

where the first term in Eqn. (3.57) represents the interaction of all electrons in $a - shell$ with all the other electrons in the same shell, $F(a,a)$ describes the interaction of one pairs of electrons, and $\frac{1}{2}n_a(n_a - 1)$ is the number of pairs in $a - shell$. The second term represents the interaction of all electrons in the $a - shell$ with all electrons in the $b - shell$. The factor $\frac{1}{2}$ outside the summation in second term avoids counting every pair of electrons twice. To obtain the exchange integral, recall equation (3.45). Then , using the same procedure used imperviously in the Coulomb integral, and letting $c = b, d = a$, equation (3.45) becomes :

$$\left\langle a,b \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| b,a \right\rangle = \sum_{\beta_a = \pm 1} \sum_{\beta_b = \pm 1} \sum_{s_a = \pm \frac{1}{2}} \sum_{s_b = \pm \frac{1}{2}} \sum_{l=0}^{\infty} \left(\frac{4\pi}{(2l+1)}\right)$$

$$\sum_{m=-l}^{+l} \left(c(\lambda_b \frac{1}{2} j_b; m_{j_b} - s_a, s_a)\right) c\left(\lambda_a \frac{1}{2} j_a; m_{j_a} - s_b, s_b\right)$$

$$c\left(\lambda_a \frac{1}{2} j_a; m_{j_a} - s_a, s_b\right) \int Y_{\lambda_a}^{m_{j_a} - s_a^*}(r_1) Y_{\lambda_b}^{m_{j_b} - s_a}(r_1) Y_l^{m^\star}(r_1) dr_1$$

$$c\left(\lambda_b \frac{1}{2} j_b; m_{j_b} - s_b, s_b\right) \int Y_l^m(r_2) Y_{\lambda_b}^{m_{j_b} - s_b^*}(r_2) Y_{\lambda_a}^{m_{j_a} - s_b}(r_2) d$$

$$re^2 \int \int R_{a(\beta_a)}(r_1) R_{b(\beta_a)}(r_1) R_{b(\beta_b)}(r_2) R_{a(\beta_b)}(r_2) \frac{r_<^l}{r_>^{l+1}} dr_1 dr_2 \tag{3.58}$$

The integral in equation (3.58) has three spherical harmonics, and will be zero unless [101]:

$$m = m_{j_a} - m_{j_b} \tag{3.59}$$

When removing the sum over m in eqn. (3.58) and replacing where ever it occurs using (3.59), and substituting into the angular integrals in eqn. (3.58) , yields:

$$\left\langle a,b \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| b,a \right\rangle = e^2 (-1)^{m_{ja}-m_{jb}} \sum_{\beta_a=\pm 1} \sum_{\beta_b=\pm 1} \sum_{l=0}^{\infty} c(\lambda_b l \lambda_a; 0,0)\, c(\lambda_a l \lambda_b; 0,0)$$

$$\int\int R_{a(\beta_a)}(r_1) R_{b(\beta_a)}(r_1) R_{b(\beta_b)}(r_2) R_{a(\beta_b)}(r_2) \frac{r_<^l}{r_>^{l+1}} dr_1 dr_2$$

$$\times I^{m_{ja},m_{j_b}}_{\lambda_a,\lambda_b,l}\, I^{m_{j_b},m_{ja}}_{\lambda_b,\lambda_a,l} \tag{3.60}$$

where :

$$I^{m_{j_2},m_{j_1}}_{\lambda_2,\lambda_1,l} = \sum_{s=\pm\frac{1}{2}} c\left(\lambda_2 \frac{1}{2} j_2; m_{j_2} - s, s\right) \times c\left(\lambda_1 \frac{1}{2} j_1; m_{j_1} - s, s\right) c\left(\lambda_1 l \lambda_2; m_{j_1} - s, m_{j_2} - m_{j_1}\right) \tag{3.61}$$

where Clebsh-Gordan symmetry relation was used. Then $I^{m_{j_2},m_{j_1}}_{\lambda_2,\lambda_1,l}$ can be written as [102]:

$$I^{m_{j_2},m_{j_1}}_{\lambda_2,\lambda_1,l} = (-1)^{\lambda_1+\lambda_2-l-j_2-m_{j_2}} \left(\frac{2j_1+1}{2l+1}\right)^{1/2} \times \sum_{s=\pm\frac{1}{2}} c\left(j_1 \frac{1}{2} \lambda_1; -m_{j_1}, s\right)$$

$$.c\left(\frac{1}{2}\lambda_2 j_2; s, m_{j_2} - s\right) c\left(\lambda_1 \lambda_2 l; s - m_{j_1}, m_{j_2} - s\right) \tag{3.62}$$

Using the symmetry relations for Racah coefficients, we get [103]

$$I^{m_{j_2},m_{j_1}}_{\lambda_2,\lambda_1,l} = (-1)^{\lambda_2 - m_{j_2} - \frac{1}{2}} \times \left(\frac{(2j_1+1)(2j_2+1)^{1/2}}{2l+1}\right) \times (2\lambda_1+1)^{1/2}$$

$$.W\left(\lambda_1 j_1 \lambda_2 j_2; \frac{1}{2} l\right) c\left(j_1 j_2 l; -m_{j_1}, m_{j_2}\right) \tag{3.63}$$

Now, putting Eq.(3.63) into (3.60), we get :

$$\left\langle a,b\left|\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\right|b,a\right\rangle = \sum_{l=0}^{\infty}(-1)^{m_{j_a}-m_{j_b}}\sum_{\beta_a=\pm1}\sum_{\beta_b=\pm1} d^l\left(j_a,m_{j_a},j_b,m_{j_b}\right)d^l$$

$$\left(j_b,m_{j_b},j_a,m_{j_a}\right)\times e^2\int\int R_{a(\beta_a)}(r_1)R_{b(\beta_a)}(r_1)R_{b(\beta_b)}(r_2)R_{a(\beta_b)}(r_2)$$

$$\frac{r_<^l}{r_>^{l+1}}dr_1dr_2 \tag{3.64}$$

where [104]

$$d^l\left(j_1,m_{j_1},j_2,m_{j_2}\right) = (-1)^{\lambda_1-m_{j_1}-\frac{1}{2}}\left(\frac{(2j_1+1)(2j_2+1)}{2l+1}\right)^{1/2}\times(2\lambda_1+1)^{1/2}$$

$$.c\left(j_1j_2l;-m_{j_1},m_{j_2}\right)W\left(\lambda_1j_1\lambda_2j_2;\frac{1}{2}l\right)c(\lambda_1l\lambda_2;0,0) \tag{3.65}$$

and the recoupling coefficients in the Clebsh-Gordan symmetry relations is [105]:

$$W\left(\lambda_1j_1\lambda_2j_2;\frac{1}{2}l\right)c(\lambda_1l\lambda_2;0,0) = (-1)^{\lambda_1}\left(\frac{(2\lambda_2+1)}{(2l+1)(2j_1+1)(2j_1+1)}\right)^{1/2}$$

$$\times\left(\frac{(2j_1+1)(2j_2+1)}{(2\lambda_1+1)(2\lambda_2+1)}\right)^{1/2}c\left(j_1j_2l;-\frac{1}{2},\frac{1}{2}\right) \tag{3.66}$$

Now substituting equations (3.66) into equation (3.65), yields

$$d^l\left(j_1,m_{j_1},j_2,m_{j_2}\right) = (-1)^{m_{j_1}+\frac{1}{2}}\times\frac{((2j_1+1)(2j_2+1))^{1/2}}{(2l+1)}$$

$$.c\left(j_1j_2l;-\frac{1}{2},\frac{1}{2}\right)c\left(j_1j_2l;-m_{j_1},m_{j_2}\right) \tag{3.67}$$

Rewritting equation (3.67) using simple expression [106]:

$$d^l\left(j_2,m_{j_2},j_1,m_{j_1}\right) = (-1)^{m_{j_2}-m_{j_1}}d^l\left(j_1,m_{j_1},j_2,m_{j_2}\right) \tag{3.68}$$

then the Clebsh-Gordon coefficients in equation (3.66) become independent of $\lambda_1$and λ_2. Therefore, we can go outside the summation over β_a and β_b in equation (3.64), and substituting (3.67) into (3.64), yields

$$\left\langle a,b\left|\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\right|b,a\right\rangle = e^2\sum_{l=0}^{\infty}\left(d^l\left(j_a,m_{j_a},j_b,m_{j_b}\right)\right)^2\sum_{\beta_a=\pm1}\sum_{\beta_b=\pm1}$$

$$\int\int R_{a(\beta_a)}(r_1)R_{b(\beta_a)}(r_1)R_{b(\beta_b)}(r_2)R_{a(\beta_b)}(r_2)\frac{r_<^l}{r_>^{l+1}}dr_1dr_2 \tag{3.69}$$

It is possibel to get rid of the summations over β_a and β_b in equation (3.69) by replacing $R_{i(\beta_i)}$ by $u(r)$ *and* $v(r)$, and introducing a new definition which has the compact expression :

$$b^l\left(j_a,m_{j_a},j_b,m_{j_b}\right)=\left(d^l\left(j_a,m_{j_a},j_b,m_{j_b}\right)\right)^2 \tag{3.70}$$

Substituting eqn. (3.70) into equation (3.69) and denoting exchange integrals by K, we get the expression of the exchange energy as:

$$K=\sum_{l=0}^{\infty}b^l\left(j_a,m_{j_a},j_b,m_{j_b}\right)\times G_l(a,b) \tag{3.71}$$

where $G_l(a,b)$is the radial integral given by [107]:

$$G_l(a,b)=\frac{e^2}{4\pi\varepsilon_\circ}\int\int\left(u_a(r_1)u_b(r_1)+v_a(r_1)v_b(r_1)\right)$$

$$\times\left(u_a(r_2)u_b(r_2)+v_a(r_2)v_b(r_2)\right)\frac{r_<^l}{r_>^{l+1}}dr_1dr_2 \tag{3.72}$$

Now simplify the term $b^l\left(j_a,m_{j_a},j_b,m_{j_b}\right)$ as

$$b^l\left(j_a,m_{j_a},j_b,m_{j_b}\right)=\left(\frac{2j_b+1}{2l+1}\right)c^2\left(j_aj_bl;-\frac{1}{2},\frac{1}{2}\right)c^2\left(j_blj_a;m_{j_b},m_{j_a}-m_{j_b}\right) \tag{3.73}$$

The exchange integral evaluated for $k_a-shell$ of an electron which has quantum numbers j_a,m_{j_a}interacting with the complete $k_b-shell$ electrons has quantum numbers j_b and all possible values of m_{j_b}, equation (3.73) becomes

$$\sum_{m_{j_b}=-j_b}^{j_b} b^l\left(j_a,m_{j_a},j_b,m_{j_b}\right)=\left(\frac{2j_b+1}{2l+1}\right)c^2\left(j_aj_bl;-\frac{1}{2},\frac{1}{2}\right)$$

$$\sum_{m_{j_b}=-j_b}^{j_b} c^2\left(j_blj_a;m_{j_b},m_{j_a}-m_{j_b}\right) \quad (3.74)$$

$$\sum_{m_{j_b}=-j_b}^{j_b} b^l\left(j_a,m_{j_a},j_b,m_{j_b}\right)=\frac{1}{2}\left(2j_b+1\right)\Gamma^l_{j_a,j_b} \quad (3.75)$$

where $(2j_b+1)$ is the number of electrons in the $b-shell$, and $\Gamma^l_{j_a,j_b}$ is given by :

$$\Gamma^l_{j_a,j_b}=\frac{2}{2l+1}c^2\left(j_aj_bl;-\frac{1}{2},\frac{1}{2}\right) \quad (3.76)$$

The exchange energy between an electron in the $k_a-shell$ and all the electrons in the $k_b-shell$, after substituting the equations (3.75) into equation (3.70), becomes

$$K=\sum_{l=0}^{\infty}\frac{1}{2}\left(2j_b+1\right)\Gamma^l_{j_a,j_b}G_l\left(a,b\right) \quad (3.77)$$

Eqn. (3.77) represents the exchange energy between one electron and the electrons in a different shell. The exchange energy between electrons in the same shell can be written as

$$K=\sum_{l=0}^{\infty}\frac{1}{2}\left(2j_b+1\right)\Gamma^l_{j_a,j_a}G_l\left(a,a\right) \quad (3.78)$$

The above equation when multiplied by factor $\frac{1}{2}n_a$ which gives the total exchange energy for one shell, and when multiplied eqn. (3.78) by factor $\frac{n_a-1}{2j}$ gives the total exchange energy between one electron and the electrons in different shell described by a Slater determinant wave function. The total exchange energy for an atom is given by [108]:

$$K_T=\sum_a\left(\frac{1}{2}n_a\frac{n_a-1}{2j_a}\sum_{l=0}^{\infty}\frac{1}{2}\left(2j_a+1\right)\Gamma^l_{j_a,j_a}G_l\left(a,a\right)\right.$$
$$\left.+\frac{1}{2}\sum_{b\neq a}n_a\sum_{l=0}^{\infty}\frac{1}{2}\left(2j_b+1\right)\Gamma^l_{j_a,j_b}G_l\left(a,b\right)\right) \tag{3.79}$$

This equation represents a final expression for the total exchange energy. The total energy expression for an atom, can be fond by combiningEqs. (3.37), (3.57), (3.79), to yield

$$E_T=\sum_a n_a\left(c\hbar\left(\int v_a\left(r\right)\left(\frac{\partial u_a\left(r\right)}{\partial r}+\frac{k_a}{r}u_a\left(r\right)\right)dr-\int u_a\left(r\right)\left(\frac{\partial v_a\left(r\right)}{\partial r}-\frac{k_a}{r}v_a\left(r\right)\right)dr\right)\right.$$
$$\left.-Ze^2\int\frac{1}{r}\left(u_a^2\left(r\right)+v_a^2\left(r\right)\right)dr+mc^2\int\left(u_a^2\left(r\right)-v_a^2\left(r\right)\right)dr\right)$$
$$-\sum_a\left(\frac{1}{2}n_a\frac{n_a-1}{2j_a}\sum_{l=0}^{\infty}\frac{1}{2}\left(2j_a+1\right)\Gamma^l_{j_a,j_a}F_l\left(a,a\right)-\sum_{b\neq a}n_a\sum_{l=0}^{\infty}\frac{1}{4}\left(2j_b+1\right)\right.$$
$$\left.\Gamma^l_{j_a,j_b}G_l\left(a,b\right)\right)+\sum_a\left(\frac{1}{2}n_a\left(n_a-1\right)F\left(a,a\right)+\frac{1}{2}\sum_{b\neq a}n_an_bF\left(a,b\right)\right) \tag{3.80}$$

3.6 Dirac-Hartree-Fock Equations for Atoms

The Dirac-Hartree-Fock (DHF) equations are derived by minimizing the expectation value of the total energy (3.80), with respect to variations in $u_a\left(r\right)$ and $v_a\left(r\right)$, subject to maintaining the normalization. Eqn. (3.80) has been set up for many-electron atoms. However, it's instructive to minimize it for a one-electron atom. In the one-electron limit, there is no exchange energy between electrons. The terms inside first summation in equation (3.80) represent the total energy for one electron in an atom as:

$$E_T^1=\sum_a n_a\left(c\hbar\left(\int v_a\left(r\right)\left(\frac{\partial u_a\left(r\right)}{\partial r}+\frac{k_a}{r}u_a\left(r\right)\right)dr-\int u_a\left(r\right)\left(\frac{\partial v_a\left(r\right)}{\partial r}-\frac{k_a}{r}v_a\left(r\right)\right)dr\right)\right.$$
$$\left.-Ze^2\int\frac{1}{r}\left(u_a^2\left(r\right)+v_a^2\left(r\right)\right)dr+mc^2\int\left(u_a^2\left(r\right)-v_a^2\left(r\right)\right)dr\right) \tag{3.81}$$

And a one electron has only one occupied shell, so the summation disappears. The equation (3.81) for one electron can be rearranged slightly to become

$$E_T^1 = \int v_k(r) \left(\left(\frac{\partial u_k(r)}{\partial r} + \frac{k}{r} u_k(r) \right) c\hbar - v_k(r) \left(mc^2 - V(r) \right) \right) dr$$
$$- \int u_k(r) \left(\left(\frac{\partial v_k(r)}{\partial r} - \frac{k}{r} v_k(r) \right) c\hbar - u_k(r) \left(mc^2 + V(r) \right) \right) dr \qquad (3.82)$$

where $V(r)$ is the nuclear Coulomb potential felt by the electron. When the wave functions are constrained to be normalized, such that $I_{a,b}$ is given by [109]

$$I_{a,b} = \int \left(u_a^*(r) u_b(r) + v_a^*(r) v_b(r) \right) dr = \delta_{a,b} \qquad (3.83)$$

the variation in the normalization is ΔI, where

$$\Delta I = 2 \int \left(\Delta u_k(r) u_k(r) + \Delta v_k(r) v_k(r) \right) dr \qquad (3.84)$$

If we vary $u(r)$,while everything else remains constant, the change in energy ΔE_T^1 for one electron is given by :

$$\Delta E_T^1 = \int v_k(r) \left(\left(\frac{\partial \Delta u_k(r)}{\partial r} + \frac{k}{r} \Delta u_k(r) \right) c\hbar \right) dr - \int \Delta u_k(r) \left(\left(\frac{\partial v_k(r)}{\partial r} - \frac{k}{r} v_k(r) \right) c\hbar \right)$$
$$-2u_k(r) \left(mc^2 + V(r) \right) dr \qquad (3.85)$$

The right way to minimize a quantity subject to a constraint for one electron, is to use the Lagrange multipliers method as given by [110]

$$\Delta E_T^1 - \varepsilon \Delta I = 0 \qquad (3.86)$$

where the first term in equation (3.85) that gives trouble, is the derivative of $\Delta u_k(r)$ and this problem can be solved by using integration by parts to obtain

$$\int v_k(r) \frac{\partial \Delta u_k(r)}{\partial r} dr = \left[v_k(r) \Delta u_k(r) \right]_0^\infty - \int \Delta u_k(r) \frac{\partial v_k(r)}{\partial r} dr \qquad (3.87)$$

The first term on the right hand side of equation (3.87) is zero, and $\Delta u_k(r)$ is zero at $r = 0$ and $r = \infty$. Substituting equation (3.87) into equation (3.85), and putting equations (3.84) and (3.85) into equations (3.86), yields

$$\int \Delta u_k(r)\left(2c\hbar\left(-\frac{\partial v_k(r)}{\partial r}+\frac{k}{r}v_k(r)\right)+2\left(mc^2+V(r)-\varepsilon\right)u_k(r)\right)dr=0 \tag{3.88}$$

This equation must be true for any variation function $\Delta u_k(r)$, and the quantity in square brackets is equal to zero, i.e.,

$$\frac{\partial v_k(r)}{\partial r}=\frac{k}{r}v_k(r)-\frac{1}{c\hbar}\left(\varepsilon-V(r)-mc^2\right)u_k(r) \tag{3.89}$$

By using a similar procedure in volving variation of $u(r)$and $v(r)$ in equation (3.82), we obtain

$$\frac{\partial u_k(r)}{\partial r}=-\frac{k}{r}u_k(r)-\frac{1}{c\hbar}\left(\varepsilon-V(r)+mc^2\right)v_k(r) \tag{3.90}$$

The equations (3.89) and (3.90) represent the single-particle radial Dirac equations. To find the variation energy for two electrons, the direct and the exchange Coulomb terms are add to the single-particle radial Dirac equations. The radial integral in equation (3.55) is

$$F_l(a,b)=e^2\int\int\left(u_a^2(r_1)+v_a^2(r_1)\right)\left(u_b^2(r_2)+v_b^2(r_2)\right)\frac{r_<^l}{r_>^{l+1}}dr_1dr_2 \tag{3.91}$$

and the radial integral in equation (3.79) is

$$G_l(a,b)=e^2\int\int\left(u_a(r_1)u_b(r_1)+v_a(r_1)v_b(r_1)\right)$$

$$\times\left(u_a(r_2)u_b(r_2)+v_a(r_2)v_b(r_2)\right)\frac{r_<^l}{r_>^{l+1}}dr_1dr_2 \tag{3.92}$$

The variations of the radial integrals $F_l(a,b)$ and $G_l(a,b)$ respectively, can be fond for small variations $\Delta u_a(r)$ in $u_a(r)$ and $\Delta v_a(r)$ in $v_a(r)$. First, start of the variations $\Delta u_a(r)$ in $u_a(r)$, and the variation radial integrals in direct Coulomb term $F_l(a,b)$ as:

$$\Delta F_l(a,b) = 2e^2 \int\int \left(u_a(r_1)\Delta u_a(r_1) + v_a(r_1)\Delta v_a(r_1)\right) \times \left(u_b^2(r_2) + v_b^2(r_2)\right) \frac{r_<^l}{r_>^{l+1}} dr_1 dr_2 \tag{3.93}$$

The variations of radial integrals in exchange Coulomb term $G_l(a,b)$ as :

$$\Delta G_l(a,b) = 2e^2 \int\int \left(u_b(r_1)\Delta u_a(r_1) + v_b(r_1)\Delta v_a(r_1)\right) \times \left(u_a(r_2)u_b(r_2) + v_a(r_2)v_b(r_2)\right) \frac{r_<^l}{r_>^{l+1}} dr_1 dr_2 \tag{3.94}$$

To simplify the radial integrals in equations (3.91) and (3.92), we need to introduce a new definition $Y_l(a,b,r)$ as [111]

$$Y_l(a,b,r) = \frac{e^2}{4\pi\varepsilon_\circ} r \int \left(u_a(r_2)u_b(r_2) + v_a(r_2)v_b(r_2)\right) \frac{r_<^l}{r_>^{l+1}} dr_2 \tag{3.95}$$

where $Y_l(a,b,r)$ represents the exchange energy produced from the interaction between the electron and the electrons in other shells. The variation in total energy ΔE_T in equation (3.80) can be written, after substituting Eq. (3.95) into Eq. (3.90) and (3.91), and putting these radial integrals equation in Eq.(3.80), we get

$$\begin{aligned}\Delta E_T = \; & \textstyle\sum_a n_a \Big(\int \Delta u_a(r_1) \Big(2c\hbar \Big(-\tfrac{\partial v_a(r_1)}{\partial r_1} + \tfrac{k_a}{r_1} v_a(r_1) \Big) + 2\left(mc^2 + V(r_1)\right) u_a(r_1) \\ & + \sum_b{}' 2n_b \frac{1}{r_1} Y_\circ(b,b,r_1) u_a(r_1) - \frac{n_a - 1}{2j_a} \sum_{l=0}^{\infty} (2j_a+1) \Gamma^l_{j_a,j_a} \frac{1}{r_1} Y_l(a,a,r_1) u_a(r_1) \\ & - \sum_{b\neq a}{}' (2j_b+1) \sum_{l=0}^{\infty} \Gamma^l_{j_a,j_b} \frac{1}{r_1} Y_l(a,b,r_1) u_b(r_1) \Big) dr_1 \Big)\end{aligned} \tag{3.96}$$

The symbol $\sum'$ means summation over pairs. Every pair is only summed once, not twice as the summations in equation (3.96). The first $\sum'$ in equation (3.96) includes $b = a$, and for that case $n_b = n_a - 1$, in equation (3.96). When using the Lagrange multipliers method with variational method it's possibel to find the minimum energy for more one electrons. The nature of the Lagrange multipliers requires some explanation. The Lagrange multipliers in Dirac-Hartree-Fock (DHF) approach, correspond to the energy eigenvalues of the electronic state. The Lagrange multipliers is given [112]:

$$\Delta E_T - \sum_a \varepsilon_{a,a}\Delta I_{a,a} - \sum_{a,b}\left(\varepsilon_{a,b}\Delta I_{a,b} + \varepsilon_{b,a}\Delta I_{b,a}\right) = 0 \tag{3.97}$$

The last two terms in Eqn. (3.97) are complex conjugates of each other, but the energy eigen value should be real, then $\varepsilon_{a,b} = \varepsilon^*_{b,a}$ in equation (3.97), so that the *Lagrange multipliers* must also be real. Substituting equations (3.96), into (3.97) to obtain the total minimum energy for an atom as:

$$\begin{aligned}
&\sum_a n_a \Bigg(\int \Delta u_a(r_1)\Bigg(2c\hbar\Bigg(-\frac{\partial v_a(r_1)}{\partial r_1} + \frac{k_a}{r_1}v_a(r_1)\Bigg) + 2\Big(mc^2 + V(r_1) - \varepsilon_{a,a}\Big)u_a(r_1) \\
&+\sum_b{}' 2n_b\frac{1}{r_1}Y_\circ(b,b,r_1)\,u_a(r_1) - \frac{n_a-1}{2j_a}\sum_{l=0}^{\infty}(2j_a+1)\,\Gamma^l_{j_a,j_a}\frac{1}{r_1}Y_l(a,a,r_1)\,u_a(r_1) \\
&-\sum_{b\neq a}{}'(2j_b+1)\sum_{l=0}^{\infty}\Gamma^l_{j_a,j_b}\frac{1}{r_1}Y_l(a,b,r_1)\,u_b(r_1) - \sum_{b\neq a}{}'\varepsilon_{a,b}u_b(r_1)\Bigg)\,dr_1\Bigg) = 0
\end{aligned} \tag{3.98}$$

To simplify these expressions, we introduce a new definition as :

$$U_a(r) = Ze^2 - \sum_b{}' n_b\frac{1}{r_1}Y_\circ(b,b,r_1) + \frac{1}{2}\frac{n_a-1}{2j_a}\sum_{l=0}^{\infty}(2j_a+1)\,\Gamma^l_{j_a,j_a}\frac{1}{r_1}Y_l(a,a,r_1) \tag{3.99}$$

This equation represents the potential felt by an electron in $a-shell$. The first term in equation (3.99) represents the nuclear potential, and the second term represents the direct Coulomb interaction due to all other electrons, and the last term represents an effective exchange potential due to all other electrons in the $a-shell$. Substituting equation (3.99) into equation (3.98), yields

$$c\hbar\left(-\frac{\partial v_a(r)}{\partial r}+\frac{k_a}{r}v_a(r)\right)+\left(\varepsilon_{a,a}+U_a(r)-mc^2\right)u_a(r)+\frac{1}{2}\sum_{b\neq a}^{\prime}\sum_{l=0}^{\infty}(2j_b+1)$$

$$\Gamma^l_{j_a,j_b}\frac{1}{r}Y_l(a,b,r)\,u_b(r)+\sum_{b\neq a}^{\prime}\varepsilon_{a,b}u_b(r)\,\delta_{k_ak_b}=0 \qquad (3.100)$$

The variation $\Delta v_a(r)$ in $v_a(r)$, can be found by using same procedure with variation $\Delta u_a(r)$ in $u_a(r)$.

$$c\hbar\left(-\frac{\partial u_a(r)}{\partial r}+\frac{k_a}{r}u_a(r)\right)+\left(\varepsilon_{a,a}+U_a(r)-mc^2\right)v_a(r)-\frac{1}{2}\sum_{b\neq a}^{\prime}\sum_{l=0}^{\infty}(2j_b+1)$$

$$\Gamma^l_{j_a,j_b}\frac{1}{r}Y_l(a,b,r)\,v_b(r)-\sum_{b\neq a}^{\prime}\varepsilon_{a,b}v_b(r)\,\delta_{k_ak_b}=0 \qquad (3.101)$$

The two equations (3.100) and (3.101), represent the Dirac-Hartree-Fock (DHF) equations for the electronic structure of many-electrons atoms. Where $U_a(r)$ is potential for each electron shell which differs for each electron and $\varepsilon_{a,a}$, $\varepsilon_{a,b}$, represent the diagonal and off diagonal energies respectively. The term $Y_l(a,b,r)$ is derived from the exchange energy between the electron and the other electrons in all other shells. The Kronecker $\delta-function$ in the final term is non-zero, if the angular momentum quantum numbers differ. To find $\varepsilon_{a,a}$, equation (3.100) is multipled by $u_a(r)$ and equation (3.101) is multiplied by $-v_a(r)$. Then, adding the resulting equations and integrating the sum over r, yields [113]

$$\varepsilon_{a,a}=c\hbar\int\left(v_a(r)\left[\frac{\partial u_a(r)}{\partial r}+\frac{k_a}{r}u_a(r)\right]-u_a(r)\left[\frac{\partial v_a(r)}{\partial r}-\frac{k_a}{r}v_a(r)\right]\right)dr$$

$$-\frac{1}{2}\left(\frac{n_a-1}{2j_a}\right)(2j_a+1)\sum_{l=0}^{\infty}\Gamma^l_{j_a,j_a}F_l(a,a)+\sum_{b\neq a}^{\prime}n_bF_\circ(a,b)$$

$$-\frac{1}{2}\sum_{b\neq a}^{\prime}\sum_{l=0}^{\infty}(2j_b+1)\,\Gamma^l_{j_a,j_b}G_l(a,b) \qquad (3.102)$$

The first four terms of equation (3.102) represent the one-particle energy of an electron in state a. To find the $off-digonal\ Lagrange\ multipliiers$, equation (3.100) is multiplied by $u_c(r)$ and equation (3.72) is multiplied by$-v_c(r)$, where $c \neq a$, then adding the two equations and integrating over all space, yields

$$\begin{aligned}
\varepsilon_{a,c} = & mc^2 \int \left[u_a(r)\,u_c(r) - v_a(r)\,v_c(r)\right] dr - Ze^2 \int \left[u_a(r)\,u_c(r) + v_a(r)\,v_c(r)\right] drdr \\
& + c\hbar \int \left(v_a(r) \left[\frac{\partial u_a(r)}{\partial r} + \frac{k_a}{r} u_a(r) \right] - u_a(r) \left[\frac{\partial v_a(r)}{\partial r} - \frac{k_a}{r} v_a(r) \right] \right) \\
& + \sum^{\prime}_{b \neq a,c} n_b R^{\circ}(babc) + (n_a - 1) R^{\circ}(a,a,a,c) + n_c \frac{2j_c}{2j_c + 1} R(c,a,c,c) \\
& - \frac{1}{2} \left(\frac{n_a - 1}{2j_a} \right) (2j_a + 1) \sum_{l=0}^{\infty} \Gamma^{l}_{j_a,j_a} R^{l}(a,a,a,c) - \frac{1}{2} \sum_{l=0}^{\infty} \left(\sum^{\prime}_{b \neq a,c} (2j_b + 1) \Gamma^{l}_{j_a,j_b} \right. \\
& \left. R^{l}(a,b,b,c) - (2j_c + 1) \Gamma^{l}_{j_a,j_c} R^{l}(a,c,c,c) \right) \qquad (3.103)
\end{aligned}$$

where $R^l(a,c,c,c)$ is the Slater integrals, defined as:

$$\begin{aligned}
R^{l}(a,c,c,c) = & e^2 \int \int \left(u_a(r_1)\,u_c(r_1) + v_a(r_1)\,v_c(r_1) \right) \\
& \times \left(u_b(r_2)\,u_d(r_2) + v_b(r_2)\,v_d(r_2) \right) \frac{r_<^{l}}{r_>^{l+1}} dr_1 dr_2 \qquad (3.104)
\end{aligned}$$

Part Two

Relativistic Hartree-Fock for Molecular Structure

3.7 The Basic Theory

This section highlights the study of the systems having many-particle (electrons), moving in the field of nuclei. A correct description of these systems should be based on relativistic quantum molecules, to introduce in a natural way spin of the electrons, and takes into account the effects that occur, when particles move at velocities close to the speed of light (electron in 1s orbital). This theory is based on Dirac equation, which combines together quantum mechanics and principles of the special relativity [114]. To derive the Dirac equation, one must start with the idea of preserving the relativistic equivalence between space and time coordinates. The Schrödinger equation does not conform to this requirement, because it's first order in time derivatives and second order in space derivative [115]. Dirac argued that it is necessary for the time coordinate to appear as a first derivative, and, in order to preserve this condition, the space coordinate should appear as first derivative as well. The time-dependent Dirac equation for an electron moving in electromagnetic field described by the scalar potential ϕ and the vector potential $\left(\vec{A}_x,\vec{A}_y,\vec{A}_z\right)$, has the following form [116,117]

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\Psi\left(\vec{r},t\right) = \Big[& c\hat{\vec{\alpha}}_x\left(\hat{p}_x+\frac{e}{c}A_x\right)+c\hat{\vec{\alpha}}_y\left(\hat{\vec{p}}_y+\frac{e}{c}\vec{A}_y\right)+c\hat{\vec{\alpha}}_z\left(\hat{\vec{p}}_z+\frac{e}{c}\vec{A}_z\right) \\ & +\left(-e\phi+\hat{\beta}mc^2\right)I_4\Psi\left(\vec{r},t\right)\Big] \end{aligned} \tag{3.105}$$

where $\hat{\vec{\alpha}}$and $\hat{\beta}$ are 4×4 matrices called Dirac matrices given as [118]

$$\begin{aligned} \hat{\alpha}_x &= \begin{pmatrix} 0&0&0&1\\ 0&0&1&0\\ 0&1&0&0\\ 1&0&0&0 \end{pmatrix} \quad \hat{\alpha}_y = \begin{pmatrix} 0&0&0&-i\\ 0&0&i&0\\ 0&-i&0&0\\ i&0&0&0 \end{pmatrix} \\ \hat{\alpha}_z &= \begin{pmatrix} 0&0&1&0\\ 0&0&0&-1\\ 1&0&0&0\\ 0&-1&0&0 \end{pmatrix} \quad \hat{\beta} = \begin{pmatrix} 1&0&0&0\\ 0&1&0&0\\ 0&0&-1&0\\ 0&0&0&-1 \end{pmatrix} \end{aligned} \tag{3.106}$$

$\hat{\vec{\alpha}}$ and $\hat{\beta}$ matrices can be written more compactly in 2-component form as[119]

$$\hat{\alpha}_x = \begin{pmatrix} 0_2 & \hat{\sigma}_x \\ \hat{\sigma}_x & 0_2 \end{pmatrix}; \hat{\alpha}_y = \begin{pmatrix} 0_2 & \hat{\sigma}_y \\ \hat{\sigma}_y & 0_2 \end{pmatrix}; \hat{\alpha}_z = \begin{pmatrix} 0_2 & \hat{\sigma}_z \\ \hat{\sigma}_z & 0_2 \end{pmatrix}; \hat{\beta} = \begin{pmatrix} I_2 & 0_2 \\ 0_2 & -I_2 \end{pmatrix} \tag{3.107}$$

where I_2 and 0_2 are the 2-dimensional identity and null matrices, respectively, $\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$ are the Pauli spin matrices and $\hat{\vec{p}}$ is the vector of the momentum operator $(\hat{p}_x, \hat{p}_y, \hat{p}_z)$. The time-dependent Dirac equation (3.105) is Lorentz invariant and its wave function $\Psi(\vec{r},t)$ is not a scalar quantity, but rather a 4-component vector, referred as a spinor

$$\Psi(\vec{r},t) = \begin{pmatrix} \psi_\uparrow^L(\vec{r},t) \\ \psi_\downarrow^L(\vec{r},t) \\ \psi_\uparrow^S(\vec{r},t) \\ \psi_\downarrow^S(\vec{r},t) \end{pmatrix} \tag{3.108}$$

In this case $\uparrow$ and $\downarrow$ represent the degree of freedom of the electron spin, where L and S are the large and small components, respectively of the wave function. The wave function of Eqn. (3.105) can be written as a product of spatial and temporal parts, as[120]

$$\Psi(\vec{r},t) = \Psi(\vec{r})\,\Theta(t) \tag{3.109}$$

where $\Psi(\vec{r})$ is the spatial part and $\Theta(t)$ is the temporal part. The Hamiltonian in Dirac equation is independent of time. When substituting equation (3.109) into Dirac equation (3.105), yields, the right hand side which is a function of r only and the left side a function of t only. Since the two side are equale, they must be equal to a constant, which is the total energy E. The solution of the temporal part is easily obtained as a simple exponential, $\Theta(t) = e^{Et/i\hbar}$. The spatial part is the time-independent Dirac equation for a charged particle. which can be written in a more compact form using the 2-component Pauli matrices as:

$$\begin{pmatrix} mc^2 - e\phi & c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) + e\hat{\vec{\sigma}}.\vec{A} \\ c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) + e\hat{\vec{\sigma}}.\vec{A} & -mc^2 - e\phi \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = E \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} \qquad (3.110)$$

Here $\hat{\vec{\sigma}}.\hat{\vec{p}}$ and $\hat{\vec{\sigma}}.\vec{A}$ represent the inner product of a vector of three Pauli spin matrices $(\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$ with the vector of the momentum operator $(\hat{p}_x, \hat{p}_y, \hat{p}_z)$ and the vector of the vector potential $(\hat{A}_x, \hat{A}_y, \hat{A}_z)$ respectively. This form of the time-independent Dirac Hamiltonian is used widely for computational purposes. We will first discuss some aspects of the one-electron Dirac Hamiltonian.

3.7.1 The One-Electron Equation

The Dirac equation for a free particle in the two-component notation reduces to

$$\begin{pmatrix} mc^2 - E & c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) \\ c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) & -mc^2 - E \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = 0 \qquad (3.111)$$

The Born-Oppenheimer approximation field in which the electron moves is represented by a static potential ϕ of the nuclear framework

$$\begin{pmatrix} mc^2 - e\phi & c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) \\ c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) & -mc^2 - e\phi \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = E \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} \qquad (3.112)$$

The nuclei are considered to be fixed in space and may have either a finite or a point charge distribution. Properties of this relativistic one-electron Hamiltonian are well known and can be found in standard textbooks [121,122].

3.7.2 The Many-Electron Approach

The free particle Dirac equation (3.112) can be extended to a particle in an external electromagnetic field. The Hamiltonian for interaction of an electron with an external field has form :

$$\hat{h}_D = c\hat{\vec{\alpha}}.\hat{\vec{p}} + mc^2\hat{\beta} + ec\hat{\vec{\alpha}}.\vec{A} - e\phi \tag{3.113}$$

where ϕ is the external scalar potential and $\vec{A}$ is the vector potential. The relativistic one-electron Hamiltonian in the presence of the static potential in the Born-Oppenheimer reference frame of nuclei is

$$\hat{h}_D = c\hat{\vec{\alpha}}.\hat{\vec{p}} + mc^2\hat{\beta} + \hat{V}_N(\vec{r}) \tag{3.114}$$

In our project we are interested in many-body Hamiltonian, and not just a single particle in an electric field. The extension from one to many particles is describes by the Dirac-Coulomb Hamiltonian for a molecular system of an electron in the field of $N - nuclei$ which has the form :

$$\hat{H} = \sum_{I}^{M} \frac{\hat{\vec{P}}_I^2}{2m_I} + \sum_{i=1}^{N} \hat{h}_D + \sum_{i<j}^{N} \hat{g}(i,j) + \hat{V}_{N-N} \tag{3.115}$$

The second term is a sum over one electron Dirac operators in the molecular field defined in equation (3.114), while the third term describes the electron-electron interaction in terms of the instantaneous Coulomb interaction given as

$$\hat{g}(i,j) \equiv V_c(i,j) = \frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} \tag{3.116}$$

The last term represents the Coulomb interaction of nuclei and is given by :

$$\hat{V}_{N-N} = \sum_{A<B}^{N} \frac{Z_A Z_B}{R_{AB}} \tag{3.117}$$

where Z_A and Z_B are the nuclear charges A,B respectively. In all our calculations, we will consider the Born-Oppenheimer approximation (BOA) [123]. The electrons are considered to be moving in the field of fixed nuclei. The Born-Oppenheimer approximation is inherently incompatible with the theory of special relativity, since it singles out a preferred reference frame. The frame in which nuclei can be treated as stationary source of external field. Relativistic correction to the nuclear motion is expected to be small [124]. The advantage of the Born-Oppenheimer approximation is that it reduces the complexity of the molecular description, and allows us to focus our attention on the electronic degree of freedom, hence it freezes the nuclear motion, and neglects the kinetic energy operator for the nuclei. In this clamped-nuclei approximation, the remaining electronic Hamiltonian is

$$\hat{H}'_{el} = \sum_{i}^{N} \hat{h}_D + \sum_{i<j}^{N} \hat{g}(i,j) + V_{N-N} \tag{3.118}$$

where N is the total number of electrons, $\hat{h}_D$ is the one-electron Hamiltonian. The repulsive energy operator of the clamped nuclei, V_{N-N} is added to the electronic Hamiltonian. The eigenfunction of the many-electron Hamiltonian $\hat{H}'_{el}$ is

$$\hat{H}'_{el}\Psi_{el,A} = E'_{el,A}\Psi_{el,A} \tag{3.119}$$

where $\Psi_{el,A} = \Psi_{el,A}(\{\vec{r}_i\})$ is the electronic wave function of the $A-th$ electronic state. Since the nucleus-nucleus interaction energy operator V_{N-N} is a multiplicative constant with respect to integration over electronic coordinate, it can thus simply be subtracted from the Hamiltonian

$$\hat{H}_{el} = \hat{H}'_{el} + V_{N-N} \tag{3.120}$$

and, hence, from the electronic energy eigenvalue $E'_{el,A}$. The total state electronic wave function can be expanded in a product basis as:

$$\Psi\left(\{\vec{r}_i\},\left\{\vec{R}_I\right\}\right) = \sum_{A} \chi_A\left(\{R_I\}\Psi_{el,A}(\{\vec{r}_i\},\{R_I\})\right) \tag{3.121}$$

The eigenvalues of the electronic Hamiltonian defined by the Born-Oppenheimer approximation are assumed to vary smoothly as function of nuclear coordinates. The eigenvalue $E_{el,A}$ is called the electronic energy. The electronic wave functions represent the set of basis functions, and the nuclear wave functions χ_A, appear as coordinate dependent expansion coefficients,$\chi_A = \chi_A(\{R_I\})$. Substituting Eq. (3.115), Eq.(3.118), and Eq.(3.120) in equation (3.121), we obtain

$$\left[\sum_{I}^{M}\frac{\hat{P}_I^2}{2m_I}+\hat{H}'_{el}\right]\sum_{A}\chi_A\Psi_{el,A}=E\sum_{A}\chi_A\Psi_{el,A} \tag{3.122}$$

Multiplication Eq. (3.123) from the left with $\langle\Psi_{el,B}|$, yields

$$\left\langle\Psi_{el,B}\left|-\sum_{I}^{M}\frac{\hat{P}_I^2}{2m_I}\right|\sum_{A}\Psi_{el,A}\chi_A\right\rangle+\left\langle\Psi_{el,B}\left|\hat{H}'_{el}\right|\sum_{A}\Psi_{el,A}\chi_A\right\rangle=E\left\langle\Psi_{el,B}\right|\sum_{A}\Psi_{el,A}\chi_A\right\rangle \tag{3.123}$$

It must be emphasized that integration in equation (3.124) is over all electronic coordinates. The nuclear coordinates remain untouched, and appling the orthonormal condition on the eigenfunction in equation (3.124),$\langle\Psi_{el,B}|\Psi_{el,A}\rangle=\delta_{BA}$, yields

$$\sum_{A}\left\langle\Psi_{el,B}\left|-\sum_{I}^{M}\frac{\hbar^2\triangle_I}{2m_I}\right|\Psi_{el,A}\chi_A\right\rangle+E'_{el,B}\chi_B=E\chi_B \tag{3.124}$$

where $\left(\hbar^2\triangle_I\right)$ is the square of the momentum operator $\hat{P}_I^2$ of the nucleus I. For the remaining bracket on the left hand side of above equation, the product rule needs to be applied twice, hence

$$\begin{aligned}\triangle_I\Psi_{el,A}\chi_A&=\nabla_I\left[\chi_A\nabla_I\Psi_{el,A}+\Psi_{el,A}\nabla_I\chi_A\right]\\&=\chi_A\nabla_I\Psi_{el,A}+2\left(\nabla_I\chi_A\right)\left(\nabla_I\Psi_{el,A}\right)+\Psi_{el,A}\nabla_I\chi_A\end{aligned} \tag{3.125}$$

Substituting equation (3.126) into equation (3.125), we get

$$\begin{aligned}-\sum_{I}^{M}\frac{\hbar^2\triangle_I}{2m_I}\chi_B+\left(E'_{el,B}-E\right)\chi_B=\sum_{A}\chi_A&\left[\left\langle\Psi_{el,B}\left|\sum_{I}^{M}\frac{\hbar^2\triangle_I}{2m_I}\right|\Psi_{el,A}\right\rangle\right.\\&\left.+\sum_{I}^{M}\left(\nabla_I\chi_A\right).\left\langle\Psi_{el,B}\left|\frac{\hbar^2\nabla_I}{m_I}\right|\Psi_{el,A}\right\rangle\right]\end{aligned} \tag{3.126}$$

If we neglect the so-called non-adiabatic terms on the right hand side, we arrive at an eigenvalue equation,

$$\left[-\sum_{I}^{M}\frac{\hbar^2\triangle_I}{2m_I}+E'_{el,B}\left(\{R_I\}\right)\right]\chi_B\left(\{R_I\}\right)=E\chi_B\left(\{R_I\}\right) \tag{3.127}$$

3.8 The Dirac-Hartree-Fock Approach for Molecules

In many areas of physics many-particle problems are solved by generating a basis- set of suitable single-particle solutions, and then by using this basis to obtain approximate solutions for the full many-particle problem. This is also the approach that will be used to solve the Dirac-Coulomb equation for molecular systems.

3.8.1 The Energy Expression for Molecules

The exact total electronic wave function is obtained by expansion into the complete set of CSFs constructed from a completes set of electron spinors

$$\Psi_A=\sum_{I=0}^{\infty}C_{IA}\Phi_I \tag{3.128}$$

$$\Phi_I=\sum_{K}\Theta_K B_{KI} \tag{3.129}$$

The electronic energy $E_{el,A}$can then be written as

$$E_{el,A}=\left\langle\Psi_{el,A}\left|\hat{H}_{el}\right|\Psi_{el,A}\right\rangle$$

$$=\sum_{IJ}C^*_{IA}C_{JA}\sum_{KL}B^*_{KI}B_{LJ}\left\langle\Theta_K\left|\hat{H}_{el}\right|\Theta_L\right\rangle \tag{3.130}$$

where Θ_K is the Slater determinant given by :

$$\Theta_K\left(1,...,N\right)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_{k_1}(\vec{r}_1) & \psi_{k_1}(\vec{r}_2) & \cdots & \psi_{k_1}(\vec{r}_N)\\ \psi_{k_2}(\vec{r}_1) & \psi_{k_2}(\vec{r}_2) & .... & \psi_{k_2}(\vec{r}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \psi_{k_N}(\vec{r}_1) & \psi_{k_N}(\vec{r}_2) & \cdots & \psi_{K_N}(\vec{r}_N)\end{vmatrix} \tag{3.131}$$

The equation (3.132) represents the Slater determinant of the simplest approximation to an electronic ground state. The Slater determinant satisfies

Pauli exclusion principle, and when actting with the antisymmetric operator on equation (3.132), It this equation can be written as:

$$\Theta_K = \hat{A}\Theta_{k_1,k_2,...,k_N}(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) \tag{3.132}$$

where $\hat{A}$ is the antisymmetrization operator

$$\hat{A} = \frac{1}{\sqrt{N!}}\sum_{p=1}^{N!}(-1)^p P_p \tag{3.133}$$

and k denotes the specific set $\{k_1,k_2,...,k_N\}$ of one electron spinor in the Slater determinant, so we can write equation (3.131) as

$$E_{el,A} = \sum_{IJ} C^*_{IA}C_{JA}\sum_{KL} B^*_{KI}B_{LJ}\left\langle A\Theta_K\left|\hat{H}_{el}\right|A\Theta_L\right\rangle \tag{3.134}$$

$$= \sum_{IJ} C^*_{IA}C_{JA}\sum_{KL} B^*_{KI}B_{LJ}\left\langle \Theta_K\left|A^{\dagger}\hat{H}_{el,A}A\right|\Theta_L\right\rangle$$

$$= \sum_{IJ} C^*_{IA}C_{JA}\sum_{KL} B^*_{KI}B_{LJ}\sum_{p}(-1)^p\left\langle \Theta_K\left|\hat{H}_{el}\right|P_p\Theta_L\right\rangle$$

$$= \sum_{IJ} C^*_{IA}C_{JA}\sum_{KL} B^*_{KI}B_{LJ}\sum_{p}(-1)^p\times\left[\left\langle \Theta_K\left|\sum_{i=1}^{N}\hat{h}(i)\right|P_p\Theta_L\right\rangle + \left\langle \Theta_K\left|\frac{1}{2}\sum_{i\neq j}^{N}\hat{g}(i,j)\right|P_p\Theta_L\right\rangle\right]$$

$$= \sum_{IJ} C^*_{IA}C_{JA}\sum_{KL} B^*_{KI}B_{LJ}\left[\left\langle \Theta_K\left|\sum_{i=1}^{N}\hat{h}(i)\right|\Theta_L\right\rangle + \left\langle \Theta_K\left|\frac{1}{2}\sum_{i\neq j}^{N}\hat{g}(i,j)\{1-P_{ij}\}\right|\Theta_L\right\rangle\right] \tag{3.135}$$

The total integral in the second term separates into products of integrals over individual electronic coordinates

$$\left\langle \Theta_K\left|\sum_{i_1,i_2,...,i_N}^{N}\hat{g}(i_1,i_2,...,i_N)\right|\Theta_L\right\rangle = N(N-1)...(N-n+1)$$

$$\times\left\langle \psi_{k_1}(1)\,\psi_{k_2}(2)...\psi_{k_N}(N)\left|\hat{g}(1,2,...,N)\right|\psi_{l_1}(1)\,\psi_{l_1}(2)...\psi_{l_N}(N)\right\rangle$$

$$\times\left\langle \psi_{k_{n+1}}|\psi_{l_{n+1}}\right\rangle\times...\times\left\langle \psi_{k_N}|\psi_{l_N}\right\rangle \tag{3.136}$$

The same procedure can be used in the non-relativistic HF approach to solve equation (3.136). The energy given in a compact form is

$$E_{el,A}^{DHF} = \sum_{i=1}^{N} \hat{h}_i + \frac{1}{2}\sum_{ij}^{N}\left(\hat{J}_{ij} - \hat{K}_{ij}\right) \tag{3.137}$$

The superscript DHF stands for Dirac-Hartree-Fock which denotes the fact that the Hartree-Fock expression utilizes the Dirac one electron Hamiltonian, and $\hat{h}_i$ is the one-electron integral given by

$$\hat{h}_i = \left\langle \Psi_i(1) \left| \hat{h}_D(1) \right| \Psi_i(1) \right\rangle \tag{3.138}$$

where $\hat{J}_{ij}$ is the two-electron Coulomb integral, given by

$$\hat{J}_{ij} = \left\langle \Psi_i(1)\Psi_j(2) \left| \hat{g}(1,2) \right| \Psi_i(1)\Psi_j(2) \right\rangle \tag{3.139}$$

and K_{ij} is the exchange integral given by

$$\hat{K}_{ij} = \left\langle \Psi_i(1)\Psi_j(2) \left| \hat{g}(1,2) \right| \Psi_j(1)\Psi_i(2) \right\rangle \tag{3.140}$$

With the generalized one-electron integrals and two electron integrals in Eqs.(3.139), (3.140) and (3.141) respectively, these equations can be weitten in compact form as:

$$\hat{h}_{ij} = \left\langle \Psi_i(1) \left| \hat{h}_D(1) \right| \Psi_j(1) \right\rangle \tag{3.141}$$

$$\hat{g}_{ijkl} = \left\langle \Psi_i(1)\Psi_j(2) \left| \hat{g}(1,2) \right| \Psi_k(1)\Psi_l(2) \right\rangle \tag{3.142}$$

Substituting equation (3.142), (3.143) into equation (3.138), we get the total energy expression as:

$$E_{el,A}^{DHF} = \sum_{ij}^{N} \hat{h}_{ij} + \frac{1}{2}\sum_{ijkl}^{N} \hat{g}_{ijkl} \tag{3.143}$$

The equation (3.144) can be conveniently simplified by defining γ_{ij}^{A}, Γ_{ijkl}^{A}[125]

$$\gamma_{ij}^{A} = \sum_{IJ} C_{IA}^{*} C_{JA} \sum_{KL} B_{KI}^{*} B_{LJ} \hat{h}_{ij}^{KL} \tag{3.144}$$

and

$$\Gamma_{ijkl}^{A} = \sum_{IJ} C_{IA}^{*} C_{JA} \sum_{KL} B_{KI}^{*} B_{LJ} \hat{g}_{ijkl}^{KL} \tag{3.145}$$

where γ_{ij}^{A} *and* Γ_{ijkl}^{A} are called structure factors or coupling coefficients. So, the electronic energy expression can be written as [126].

$$E_{el,A} = \sum_{ij}^{n'} \gamma_{ij}^{A} \hat{h}_{ij} + \frac{1}{2} \sum_{ijkl}^{n'} \Gamma_{ijkl}^{A} \hat{g}_{ijkl} \tag{3.146}$$

where n'denotes the total number of one electron states. The last equation represents the most general expression for the electron energy of many electron system with a given total number of electrons.

3.8.2 Dirac-Hartree-Fock Equation for Molecules

Approximate solutions to the Dirac-Coulomb equation can be obtained by variational method. The basic idea of this method is to introduce a trial function furnished with parameters that can be varied, so as to obtain the best possible approximate solution within parameter space. The parametrization of trial function, leads to a parametrization of its energy, known as the expectation value of the Dirac-Coulomb Hamiltonian. Approximations to exact eigenfunction of the Hamiltonian are found as stationary values of the energy in the parameters space [127]. Note that, if the variational parameters are introduced in a non-linear manner, the reciprocal relation would not hold true therefore a stationary value of the energy may correspond to a physically unacceptable solution of the Dirac-Coulomb equation [123]. Let us consider the general form of the trial function in molecular electronic structure theory. The basic building blocks for approximative wave functions are Molecular Orbital “MOs” and electronic configurations. They can be introduced by turninig off the electron-electron interaction, then the electronic Hamiltonian reduces to a sum of one-electron Dirac equations. The wave function may be written as a Hartree-product of one electron molecular 4-spinors :

$$\Phi = \prod_{i=1}^{n} \psi_i(r_i) \tag{3.147}$$

The spinors are chosen from the complete set $\{\psi_i\}$of orthonormal solutions to the corresponding Dirac equation in the molecular field. We shall refer to any set of one electron functions as our 1-particle basis and denote the individual one-electron functions molecular orbitals "MOs". Physically, the equation (3.148) is not an acceptable many-electron wave function, since it dos not obey the Pauli-principle, which states that the many-electron wave function should change sign under the permutation of any pair of electrons (fermions). We can remedy the situation by antisymmetrizing the wave function, therefore, the wave function has the form of equation (3.132), represents slater-determinant, of orthonormal molecular orbitals, $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. The Slater-determinant represents a particular electronic configuration, namely the set of molecular orbitals appearing in the determinant. When the electron-electron interaction is turned on, it is no longer possible to separate the electronic degree of freedom, and the exact electronic wave function can no longer be expressed in terms of a single slater-determinant. It can be expanded in all possible Slater-determinants and generated from the complete 1-particle basis is given by.

$$\psi = \sum_i c_i \Phi_i \tag{3.148}$$

The exact solution, is therefore obtained in terms of complete 1-particle and n-particle bases, where the set $\{\Phi_i\}$ of Slater determinants in equation (3.132) constitutes the n-particle basis. Therefore we may seek an approximate solution of the Dirac-Coulomb equation in the space of truncated 1-particle and n-particle basis. The search for stationary energies then corresponds to separate rotations within the 1-particle and n-particle basies. The simplest variational approach is to choose a single Slater-determinant equation (3.132) as the trial function. This forms the basis for the HF method in non-relativistic theory and the DHF method in relativistic theory. These are independent particle models which view the electron as moving independently in the field of nuclei and the average field of the other electrons. The independent particle model, usually, provides an adequate description of molecular structure at the equilibrium geometry, but fails in situations, where degeneracies or near-degeneracies of configuration occur. Near-degeneracies, typically, arise in bond breaking and bond formation, in open shell and excited state. In relativistic molecules, additional near-degeneracies may be introduced by the fine structure of the spin-orbit splitting. Such systems require a multi-configuration approach. In relativistic quantum molecule, variational method is very important, so the starting point from the total electronic energy $E_{el,A}$ is given by:

$$E_{el,A}[\Psi_A] = E_{el,A}\left[\left\{c_{i\mu}\right\},\{\psi_i\}\right] = \left\langle \Psi_A \left| \hat{H}_{el} \right| \Psi_A \right\rangle \tag{3.149}$$

where

$$\psi_i(\vec{r}) = \begin{pmatrix} \sum_{\mu}^{L} c_{i\mu}\phi_{\mu}^{L}(\vec{r}_A) \\ \sum_{\mu}^{S} c_{i\mu}\phi_{\mu}^{S}(\vec{r}_B) \end{pmatrix} \tag{3.150}$$

where $\psi_i(\vec{r})$ is a molecular spinor and $c_{i\mu}$ is a molecular spinor coefficient, and $c_{i\mu}$are unknown which are determined by, using variational condition. The variational condition is given as follows :

$$\delta E[\Psi_A] = \left\langle \Psi_A \left| \hat{H}_{el} \right| \Psi_A \right\rangle + \left\langle \Psi_A \left| \hat{H}_{el} \right| \delta\Psi_A \right\rangle = 0 \tag{3.151}$$

$$\frac{\partial E_{el,A}\left[\left\{c_{i\mu}\right\},\{\Psi_A\}\right]}{\partial c_{i\mu}} = 0 \tag{3.152}$$

$$\frac{\partial E_{el,A}\left[\left\{c_{i\mu}\right\},\{\Psi_A\}\right]}{\delta \psi_i} = 0 \tag{3.153}$$

where we have a set of coefficient $\left\{c_{i\mu}\right\}$and orbitals $\{\Psi_A\}$. To determine a set of spinors ψ_i, for a given expression of the total electronic energy, the energy as functional of the spinors $E_{el,A}[\{\Psi_A\}]$ is minimized. This variation must be carried out under the constraint that the orbitals remain orthonormal. Therefore we define a Lagrange functional L as :

$$L\left[\left\{\psi_i^L,\psi_i^S\right\}\right] = E\left[\left\{\psi_i^L,\psi_i^S\right\}\right] - \sum_{ij}^{N} \varepsilon_{ij}\left[\left\langle \psi_i^L|\psi_j^L\right\rangle + \left\langle \psi_i^S|\psi_j^S\right\rangle - \delta_{ij}\right] \tag{3.154}$$

where ε_{ij} are the *Lagrangian multipliers*. For stationarity, the variation δL

with respect to all parameters must equal zero, and thus we determine

$$\delta_{\psi_i} L\left[\{\psi_i\},\{\varepsilon_{ij}\}\right] = \delta_{\psi_i} E_{el,A} - \sum_{j}^{N} \varepsilon_{ij}\left(\langle\delta\psi_i|\psi_i\rangle + \langle\psi_j|\delta\psi_i\rangle\right) = 0 \quad (3.155)$$

and

$$\frac{\partial L\left[\{\psi_i\},\{\varepsilon_{ij}\}\right]}{\partial\varepsilon_{ij}} = \langle\psi_i|\psi_j\rangle - \delta_{ij} = 0 \quad (3.156)$$

To obtain the basis set expansion for the spinor of Linear Combination of Atomic Orbital "*LCAO*" type we could differential the *Lagrange functional* directly and would obtain equations in matrix form. In this way we can proceed in more general way with the method of variation. The variation of any the matrix element over an operator $\hat{H}_{el}$containing $\psi_i$in $L\left[\{\psi_i\},\{\varepsilon_{ij}\}\right]$ may be written as the limit for infinitely small variations of a given orbital ψ_i as:

$$\delta\left[\langle\psi_i|\hat{H}_{el}|\psi_j\rangle + \langle\psi_j|\hat{H}_{el}|\psi_i\rangle + \langle\psi_i|\hat{H}_{el}|\psi_i\rangle\right] =$$

$$\lim_{\delta\psi_i\to 0}\left[\frac{\langle\psi_i+\delta\psi_i|\hat{H}_{el}|\psi_j\rangle + \langle\psi_j|\hat{H}_{el}|\psi_i+\delta\psi_i\rangle + \langle\psi_i+\delta\psi_i|\hat{H}_{el}|\psi_i+\delta\psi_i\rangle}{(\psi_i+\delta\psi_i)-\psi_i}\right.$$

$$\left. - \frac{\langle\psi_i|\hat{H}_{el}|\psi_j\rangle + \langle\psi_j|\hat{H}_{el}|\psi_i\rangle + \langle\psi_i|\hat{H}_{el}|\psi_i\rangle}{(\psi_i+\delta\psi_i)-\psi_i}\right] \quad (3.157)$$

Resolving the term in brackets in equation (3.152) allows us to write this limit as

$$= \lim_{\delta\psi_i\to 0}\frac{\langle\delta\psi_i|\hat{H}_{el}|\psi_j\rangle + \langle\psi_j|\hat{H}_{el}|\delta\psi_i\rangle + \langle\delta\psi_i|\hat{H}_{el}|\psi_i\rangle + \langle\psi_i|\hat{H}_{el}|\delta\psi_i\rangle + \langle\delta\psi_i|\hat{H}_{el}|\delta\psi}{\delta\psi_i} \quad (3.158)$$

$$= \lim_{\delta\psi_i\to 0}\frac{\langle\delta\psi_i|\hat{H}_{el}|\psi_j\rangle + \langle\psi_j|\hat{H}_{el}|\delta\psi_i\rangle + \langle\delta\psi_i|\hat{H}_{el}|\psi_i\rangle + \langle\psi_i|\hat{H}_{el}|\delta\psi_i\rangle}{\delta\psi_i} \quad (3.159)$$

Abbreviating the complex conjugate terms as "c.c", we finally obtain the variational of matrix element of the operator $\hat{H}_{el}$, that contains ψ_i. And substituting equations (3.160) into equation (3.158) , we get

$$\delta\left[\left\langle \psi_i \left|\hat{H}_{el}\right| \psi_j\right\rangle + \left\langle \psi_j \left|\hat{H}_{el}\right| \psi_i\right\rangle + \left\langle \psi_i \left|\hat{H}_{el}\right| \psi_i\right\rangle\right] =$$

$$\lim_{\delta\psi_i\to 0} \frac{\left\langle \delta\psi_i \left|\hat{H}_{el}\right| \psi_j\right\rangle + \left\langle \delta\psi_i \left|\hat{H}_{el}\right| \psi_i\right\rangle}{\delta\psi_i} + c.c = 0 \tag{3.160}$$

The variation of the Lagrangian functional $\delta L\left[\{\psi_i\}\right]$ with respect to the spinors can now be written as :

$$\delta L\left[\{\psi_i\}\right] = \sum_{j}^{N} \gamma_{ij} \left\langle \delta\psi_i \left|\hat{h}_D\right| \psi_j\right\rangle + \frac{1}{2}\sum_{jkl}^{N} \Gamma_{ijkl} \times \left[\left\langle \delta\psi_i(1)\left|\hat{g}(1,2)\left(1-P_{12}\right)\right| \psi_k(1)\,\psi_l(2)\right\rangle\right.$$

$$+ \left\langle \psi_j(1)\,\delta\psi_i(2)\left|\hat{g}(1,2)\left(1-P_{12}\right)\right| \psi_k(1)\,\psi_l(2)\right\rangle - \sum_{j}^{N} \varepsilon_{ij} \left\langle \delta\psi_i | \psi_j\right\rangle + c.c = 0 \tag{3.161}$$

After rearranging and adjusting the summation indices of equation (3.162), we obtain

$$\delta L\left[\{\psi_i\}\right] = \sum_{j}^{N} \left[\gamma_{ij} \left\langle \delta\psi_i \left|\hat{h}_D\right| \psi_j\right\rangle + \sum_{kl}^{N} \Gamma_{ikjl} \left\langle \delta\psi_i(1)\,\psi_k(2)\left|\hat{g}(1,2)\left(1-P_{12}\right)\right| \psi_j(1)\,\psi_l(2)\right\rangle\right.$$

$$\left. -\varepsilon_{ij} \left\langle \delta\psi_i | \psi_j\right\rangle\right] + c.c = 0 \tag{3.162}$$

This equation holds for any variation of $\delta\psi_i$, so that we may require the remaining integrand to be zero

$$\sum_{j}^{N} \left[\gamma_{ij}\hat{h}_D\psi_j + \sum_{kl}^{N} \Gamma_{ikjl} \left\langle \psi_k(2)\left|\hat{g}(1,2)\left(1-P_{12}\right)\right| \psi_j(1)\,\psi_l(2)\right\rangle - \varepsilon_{ij}\psi_j\right] = 0 \tag{3.163}$$

It is convenient to introduce the Fock operator f_{ij} given by

$$\hat{f}_{ij}(r) = \gamma_{ij}\hat{h}_D(r) + \sum_{kl}^{N} \Gamma_{ikjl} \left[\hat{J}_{kl}(r) - \hat{K}_{kl}(r)\right] \tag{3.164}$$

where $\hat{J}_{kl}$ is the Coulomb operator given by

$$\hat{J}_{kl}\psi_j = \left\langle \psi_k(2)\left|\hat{g}(1,2)\right| \psi_l(2)\right\rangle \psi_j(1) \tag{3.165}$$

and the $\hat{K}_{kl}$ in equation (3.165) is the exchange operator having the form

$$\hat{K}_{kl}\psi_j = \left\langle \psi_k(2)\left|\hat{g}(1,2)\right|\psi_j(2)\right\rangle \psi_l(1) \tag{3.166}$$

So, equation (3.164) can be written the stationary condition form as

$$\sum_{j}^{N} f_{ij}\psi_j = \sum_{j}^{N} \varepsilon_{ij}\psi_j \tag{3.167}$$

Re arranging equation (3.168) for spinor ψ_i, it becomes:

$$\left[f_{ii} - \varepsilon_{ii}\right]\psi_i = \sum_{j,j\neq i}^{N} \left[\varepsilon_{ij} - f_{ij}\right]\psi_j \tag{3.168}$$

For the approximation of the electronic state Ψ_A, all f_{ij} for $i \neq j$ vanish and the above equation can be simplified to become:

$$f_{ii}\psi_i = \sum_{i}^{N} \varepsilon_{ij}\psi_j \tag{3.169}$$

The equation (3.170) is called Dirac-Hartree-Fock equation, where $\hat{f}_{ii}$ is the Fock operator given by:

$$\hat{f}_{ii} = \hat{h}_D + \sum_{k}^{N}\left[\hat{J}_{kk} + \hat{K}_{kk}\right] \tag{3.170}$$

3.9 Basis Set Expansion of Molecular Spinors

In quantum mechanics, the molecular system wave functions are represented by a basis expansion of infinite dimension. For the study of isolated molecular systems, it can be very convenient to use the Linear Combination of Atomic Orbitals “LCAO” as:

$$\Phi^{MO}(\vec{r}) = \sum_{i}^{N_{atom}} b_i\psi_i\left(\vec{r},\vec{R}_A\right) \tag{3.171}$$

Then one forms a number of molecular spinors equal to the number of atomic spinor, where each molecular spinor Φ^{MO} in equation (3.172) is a linear combination of atomic spinor ψ_i centered in its own nucleus at the position R_A. Atomic spinor components are indicated by the superscript i in $\psi_k^{(i)}$, which represent the single-particle 4-spinors that are expanded scalar function basis set for the large component $\left\{\phi^L\right\}$and small $\left\{\phi^S\right\}$component parts

$$\psi_k^{(i)} = \begin{pmatrix} \psi_k^{L^\alpha} \\ \psi_k^{L^\beta} \\ \psi_k^{L^\alpha} \\ \psi_k^{L^\beta} \end{pmatrix} = \begin{pmatrix} \sum_\mu \phi_\mu^L c_{\mu k}^{L^\alpha} \\ \sum_\mu \phi_\mu^L c_{\mu k}^{L^\beta} \\ \sum_\mu \phi_\nu^S c_{\nu k}^{S^\alpha} \\ \sum_\mu \phi_\nu^S c_{\nu k}^{S^\beta} \end{pmatrix} \tag{3.172}$$

These basis in above equation can be represented by Gaussian functions or atomic centered Cartesian Gaussian given by :

$$G_{ijk}^{\alpha}(\vec{r}_A) = N x_A^i y_A^j z_A^k exp\left(-\xi r_A^2\right) \tag{3.173}$$

where ,$i+j+k=l$,is the angular quantum number, A refers to the nuclear center, and N is a normalization constant. For a given quantum number l, there are $\frac{1}{2}(l+1)(l+2)$ Cartesian Gaussians. This basis set for a given l value may be transformed to a set of $(2l+1)$ spherical Gaussians given by

$$G_{nlm}^{\alpha}(\vec{r}_A) = N r_A^{n-1} exp\left(-\xi r_A^2\right) Y_{lm}(\theta_A, \phi_A) \tag{3.174}$$

with the restriction $n=l+1$,where $Y_{lm}(\theta_A, \phi_A)$ are spherical harmonics. It is also possible to form terms , directly from the set of 2-spinor Gaussian of the form :

$$G_{nkm}^{\alpha}(\vec{r}_A) = N r_A^{n-1} exp\left(-\xi r_A^2\right) \chi_{k,m}(\theta_A, \phi_A) \tag{3.175}$$

where $\chi_{k,m}(\theta_A, \phi_A)$ is the angular part of the Dirac equation. A basis set contains several Gaussian functions for each considered value of the angular momentum $l\,(s,p,d,...)$. The large exponent describes, predominantly, the core orbitals, close to the nucleus. The very low-value exponents describe the diffuse orbitals. To construct a basis set, each Gaussian exponent is optimized separately with the self-consistent field method [128]. In general manner, the more basis functions is contained in the basis set, the better will be the description, in order to describe the one-electron spinors of molecules that enter the Slater determinants to approximate the total electronic wave function. It is natural to be inspired by the fact that molecules are composed of atoms. The relativistic description of molecules means that each molecular spinor $\psi_i(\vec{r})$ entering a Slater determinant must be expanded in a set of four-component atomic spinors $\psi_k^{atom}(\vec{r})$

$$\psi_i(\vec{r}) = \sum_k^{m'} d_{ik}\psi_k^{atom}(\vec{r}) \tag{3.176}$$

Each atomic spinor $\psi_k^{atom}(\vec{r}) = \psi_k^{atom}\left(\vec{r},\vec{R}_A\right)$ has its center at the position of the nucleus $R_A$of some atom A. As a first step, we include only those atomic spinors $\psi_k^{atom}(\vec{r})$ which would be considered in an atomic Dirac–Hartree–Fock calculation on every atom of the molecule. The number of basis spinors "m'" is then smallest for such a minimal basis set. In this case, it can be calculated as the number of shells "s" per atom times the degeneracy "d" of these shells times the number of atoms "M" in the molecule,

$$m = s(A) \times d(s) \times M \tag{3.177}$$

In practice, the number of basis spinors m increases even further for a minimal basis set because we have no analytic expression for the atomic spinors of a many-electron atom available. Hence, the atomic spinors themselves need to be expanded in terms of known basis functions $\phi_\mu^a(\vec{r},R_A)$ given by

$$\psi_k^{atom}(\vec{r},R_A) = \sum_\mu^{m'_k} \begin{pmatrix} b_{k\mu}^{(1)}\phi_\mu^{(1)}\left(\vec{r},\vec{R}_A\right) \\ b_{k\mu}^{(2)}\phi_\mu^{(2)}\left(\vec{r},\vec{R}_A\right) \\ b_{k\mu}^{(3)}\phi_\mu^{(3)}\left(\vec{r},\vec{R}_A\right) \\ b_{k\mu}^{(4)}\phi_\mu^{(4)}\left(\vec{r},\vec{R}_A\right) \end{pmatrix} \tag{3.178}$$

where $b_{k\mu}$ represents the set of contraction coefficients. When substituting equation (3.179) into equation (3.177), the final basis set expansion for a molecular spinor can then be written as,

$$\psi_i(\vec{r}) = \sum_k^{m'} \sum_\mu^{m'_k} d_{ik} \begin{pmatrix} b_{k\mu}^{(1)} \phi_\mu^{(1)} \left(\vec{r}, \vec{R}_A\right) \\ b_{k\mu}^{(2)} \phi_\mu^{(2)} \left(\vec{r}, \vec{R}_A\right) \\ b_{k\mu}^{(3)} \phi_\mu^{(3)} \left(\vec{r}, \vec{R}_A\right) \\ b_{k\mu}^{(4)} \phi_\mu^{(4)} \left(\vec{r}, \vec{R}_A\right) \end{pmatrix} \equiv \sum_\mu^{m} \begin{pmatrix} c_{i\mu}^{(1)} \phi_\mu^{(1)} \left(\vec{r}, \vec{R}_A\right) \\ c_{i\mu}^{(2)} \phi_\mu^{(2)} \left(\vec{r}, \vec{R}_A\right) \\ c_{i\mu}^{(3)} \phi_\mu^{(3)} \left(\vec{r}, \vec{R}_A\right) \\ c_{i\mu}^{(4)} \phi_\mu^{(4)} \left(\vec{r}, \vec{R}_A\right) \end{pmatrix} \tag{3.179}$$

Accordingly, the total number of basis functions are $4 \times m$ with $m = m \times m_k$. In principle, the number of basis spinors m needs to be infinitely large complete basis for an exact representation of a molecular spinor in this basis. For practical reasons, however, it must be as small as possible in order to keep the computational effort as low as possible. The basis set size should thus be small but still allow for sufficiently accurate calculations. In order to achieve this, we need to exploit the physics of the problem to the largest extent, a procedure in which the LCAO idea is the first step. Hence, we emphasize that the expansion of Eq. (3.150) provides an optimum description of an atomic spinor. To obtain a minimal basis set constructed of atomic spinors, we may well freeze the coefficients $b_{k\mu}^{(a)}$ and thus reduce the number m back to the smaller number m'. Then, only the m' coefficients d_{ik} are to be determined rather than the $4m c_{i\mu}$ coefficients. To use fixed $b_{k\mu}^{(a)}$ in a molecular calculation is known as using a '*contracted*' basis set. Various variants of such contractions are known but we shall not delve deeper into such purely technical issues. Basis functions that have not been contracted are called primitives or primitive basis functions. The molecular spinors can also be expressed in terms of 2-spinor expansions these expansions $\psi_i(r)$ of 2-spinor basis functions are given by [130]

$$\psi_i(\vec{r}) = \begin{pmatrix} \sum_\mu c_{i\mu}^L \phi_\mu^L(\vec{r}_A) \\ \sum_\mu c_{i\mu}^S \phi_\mu^S(\vec{r}_A) \end{pmatrix} \tag{3.180}$$

with the spherical two-component basis functions $\phi_\mu^L(\vec{r}_A)$ and $\phi_\mu^S(\vec{r}_A)$ given by :

$$\phi_\mu^L(\vec{r}_A) = \frac{P_\mu(\vec{r}_A)}{r_A} \chi_{\kappa_\mu m_\mu(\theta_A, \phi_A)} \tag{3.181}$$

$$\phi_{\mu}^{S}(\vec{r}_A) = i\frac{Q_{\mu}(\vec{r}_A)}{r_A}\chi_{-\kappa_{\mu}m_{\mu}(\theta_A,\phi_A)} \tag{3.182}$$

The subscript A, denotes that the electronic coordinate is to taken relative to atomic nucleus A at which it is centered,$r_A = \vec{r} - \vec{R}_A$, and $\chi_{\kappa_{\mu}m_{\mu}(\theta_A,\phi_A)}$ are two-component spherical spinors.We can write the radial parts $P_{\mu}^{GTF}(r_A)$ and $Q_{\mu}^{GTF}(r_A)$ using the Gaussian type radial basis functions given by :

$$P_{\mu}^{GTF}(\vec{r}_A) = N_{\mu}^{L} r_A^{l_{\mu}+1} exp\left(-\xi_{\mu} r_A^2\right) \tag{3.183}$$

$$Q_{\mu}^{GTF}(\vec{r}_A) = N_{\mu}^{S}\left[\left(\kappa_{\mu} + l_{\mu} + 1\right) - \xi_{\mu} r_A\right] r_A^{l_{\mu}} exp\left(-\xi_{\mu} r_A^2\right) \tag{3.184}$$

Hence, the factors ξ_{μ} in the exponents are only adjustable parameters of these basis functions and this parameter ξ_{μ} is usually called the ‘exponents’ of the basis functions. The spherical Gaussian basis sets introduced so far can be written as Cartesian Gaussian functions,

$$\phi_{\mu}^{L}(\vec{r}_A) = N_{\mu}^{L} x^{\alpha_{\mu}} y^{\beta_{\mu}} z^{\gamma_{\mu}} exp\left(-\xi_{\mu}^{L} r_A^2\right) \tag{3.185}$$

$$\phi_{\mu}^{S}(\vec{r}_A) = N_{\mu}^{S} x^{\alpha_{\mu}} y^{\beta_{\mu}} z^{\gamma_{\mu}} exp\left(-\xi_{\mu}^{S} r_A^2\right) \tag{3.186}$$

The sum of the exponents $\alpha_{\mu}, \beta_{\mu}, and \gamma_{\mu}$ is related to the angular momentum quantum number, and we generate one-electron atomic functions from the basis set. The Gaussian combination, fits as best as possible the analytical radial wave function. The use of four components wave function required an additional condition, to have stable results. This has been shown that the expansion for the large and small component should be performed in a balanced way. The solution for this problem is called the $kinetic - balance$ [131].

3.10 Kinetic Balance

Since all basis sets contain a large component (L) and small component (S) set, It is possible to establish the relation between the large and small component parts of the four-component spinor at Dirac-Hartree-Fock level. The time-independent Dirac equation for one electron in the form of two coupled equations is given by,

$$\left(V_N - E\right)\psi^L + c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right)\psi^S = 0 \tag{3.187}$$

$$c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right)\psi^L + \left(V_N - E - 2m_ec^2\right)\psi^S = 0 \tag{3.188}$$

Equation (3.189), can be rewritten as

$$2m_ec^2\psi^S = c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right)\psi^L + V_N\psi^S - E\psi^S \tag{3.189}$$

so that, the small component can be expressed as a function of the large component [132]

$$\psi^S = \frac{c}{2m_ec^2 - V_N + E}\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right)\psi^L \tag{3.190}$$

$$\psi^S = \frac{1}{2m_ec}B\left(E\right)\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) \tag{3.191}$$

$$B\left(E\right) = \left[1 + \frac{E - V_N}{2m_ec^2}\right]^{-1} \tag{3.192}$$

In case of $2mc^2 \gg -V_N + E$ in equation (3.191), we get

$$\psi^S \approx \frac{\hat{\vec{\sigma}}.\hat{\vec{p}}}{2m_ec}\psi^L \tag{3.193}$$

The equation (3.194) is called $kinetic-balance$ condition [133,134]. It shows that the lower component of the spinor ψ^S is by a factor of $\frac{1}{c}$ smaller than ψ^L (for small linear momenta). This is the reason why $\psi^L$is also called the large component, and ψ^S the small component. We may instantaneously write the kinetic balance condition for the molecular spinors $\psi_i^{\prime}s$ [135]

$$\psi_i^S = \frac{c}{2m_ec^2 - W + \varepsilon_i}\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right)\psi_i^L \tag{3.194}$$

where ε_i is the orbital energy and W is the total interaction potential of the Fock operator. The potential contains the electron–nucleus and electron–electron mean-field interaction(W contains V_N and the electron–electron mean-field potential energy). In the limit $c \to \infty$, the small component vanish, and now a days *kinetic-balanc* is used for building relativistic small component basis set, starting from the large component counter parts. From Eq.(3.194), we can see that the small component function depends on the operator $\hat{\vec{\sigma}}.\hat{\vec{p}}$, which is a partial derivative along the x, y, z coordinates. Applying this derivative to equation (3.186), we obtain a dependence of the small component on $l-1$ and $l+1$. This means that in the design of the basis set higher angular momenta are included by increasing the number of primitive small component functions with respect to the number of primitives of the large component. The approximate kinetic-balance condition after acting on Cartesian Gaussian functions primitive Gaussian in Eq.(3.186), gives [133]

$$\frac{\partial}{\partial x} x^{\alpha_\mu} exp\left(-\xi_\mu r_A^2\right) = \left[\alpha_\mu x^{\alpha_\mu - 1} - 2\xi_\mu x^{\alpha_\mu + 1}\right] exp\left(-\xi_\mu r_A^2\right) \qquad (3.195)$$

It's clear that the Eq.(3.195) is a linear combination of two functions with the same value of ξ. But different values of α aris , which have to be evaluated to associate the exponentsξ_μ for small component with those of the large component ξ_μ . Because of the derivative operator $\hat{p} = -i\hbar\nabla$ every large component Gaussian basis spinor ϕ_i^L gives rise to two small-component basis functions with the same exponent, That is, starting from a $p_x - type$ Gaussian basis function for the large component, for example, the kinetic balance requirement produces an $s - type$ and a $d - type$ basis function for the small component. Therefore, the small-component basis has to comprise at least all spinors originating by differentiation of the large-component basis. As a consequence, the small- component basis will contain functions with higher angular momentum than the large-component basis in order to represent both upper and lower parts of the Dirac Hamiltonian with equal quality for electronic solutions. Thus the small-component basis can become twice as large as the large-component basis, as sketched in Figure (3.1) [136]. To fulfill the kinetic-balance condition, these functions have to be contained in the small component basis. The connection of the large component function to a small component function with the same exponential parameter,but with its 1-value shifted up or down by one, is typical for the kinetic-balance operator and is retained if the relations are further worked out for the four-component functions.

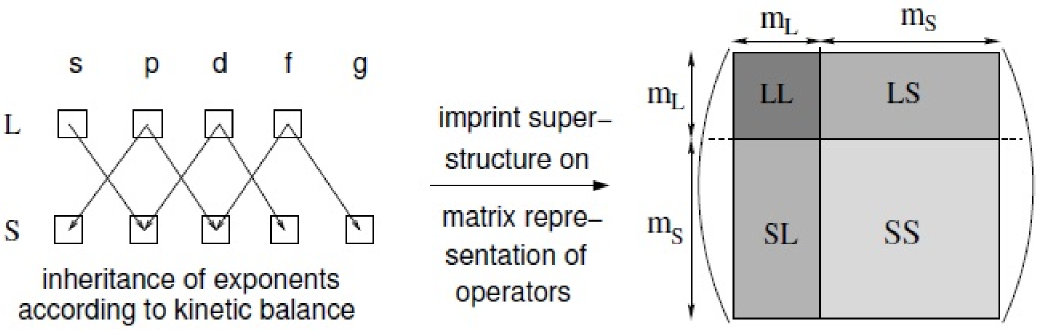


Figure 3.1: **Generation of small components exponents from large components exponents through kinetic balance** [136]

3.11 Dirac-Hartree-Fock Energy With Basis Set

The starting point in the discussion of this section is the Dirac-Hartree-Fock energy, which can be written as:

$$E_{el,A}^{DHF} = \sum_{i}^{N} \left\langle \Psi_i(1) \left| \hat{h}_D(1) \right| \Psi_i(1) \right\rangle + \frac{1}{2} \sum_{ij}^{N} \left[\left\langle \Psi_i(1) \Psi_j(2) \left| \hat{g}(1,2) \right| \Psi_i(1) \Psi_j(2) \right\rangle \right.$$

$$\left. - \left\langle \Psi_i(1) \Psi_j(2) \left| \hat{g}(1,2) \right| \Psi_j(1) \Psi_i(2) \right\rangle \right] \tag{3.196}$$

The four-component basis-set expansion for a molecular spinor is given by Eq. (3.180) in section (3.9)

$$\psi_i(\vec{r}) = \sum_{k}^{m'} \sum_{\mu}^{m'_k} d_{ik} \begin{pmatrix} b_{k\mu}^{(1)} \phi_\mu^{(1)} \left(\vec{r}, \vec{R}_A\right) \\ b_{k\mu}^{(2)} \phi_\mu^{(2)} \left(\vec{r}, \vec{R}_A\right) \\ b_{k\mu}^{(3)} \phi_\mu^{(3)} \left(\vec{r}, \vec{R}_A\right) \\ b_{k\mu}^{(4)} \phi_\mu^{(4)} \left(\vec{r}, \vec{R}_A\right) \end{pmatrix} \equiv \sum_{\mu}^{m} \begin{pmatrix} c_{i\mu}^{(1)} \phi_\mu^{(1)} \left(\vec{r}, \vec{R}_A\right) \\ c_{i\mu}^{(2)} \phi_\mu^{(2)} \left(\vec{r}, \vec{R}_A\right) \\ c_{i\mu}^{(3)} \phi_\mu^{(3)} \left(\vec{r}, \vec{R}_A\right) \\ c_{i\mu}^{(4)} \phi_\mu^{(4)} \left(\vec{r}, \vec{R}_A\right) \end{pmatrix} \tag{3.197}$$

and the Dirac Hamiltonian can be written in the 4-component form given by :

$$\hat{h}_{D=}\begin{pmatrix} V_N & 0 & c\hat{\vec{p}}_z & c\left(\hat{\vec{p}}_x-i\hat{\vec{p}}_y\right) \\ 0 & V_N & c\left(\hat{\vec{p}}_x+i\hat{\vec{p}}_y\right) & c\hat{\vec{p}}_z \\ c\hat{\vec{p}}_z & c\left(\hat{\vec{p}}_x-i\hat{\vec{p}}_y\right) & \left(V_N-2mc^2\right) & 0 \\ c\left(\hat{\vec{p}}_x+i\hat{\vec{p}}_y\right) & c\hat{\vec{p}}_z & 0 & V_N-2mc^2 \end{pmatrix} \qquad (3.198)$$

Substitute Eqs. (3.198) and (3.196), in Eq. (3.197). we get

$$\begin{aligned} E_{el,0}^{DHF} = & \sum_{i}^{N}\sum_{\mu\nu}^{m}\left[c_{i\mu}^{(1)^*}c_{i\nu}^{(1)}\left\langle\phi_\mu^{(1)}\left|V_N\right|\phi_\nu^{(1)}\right\rangle+c_{i\mu}^{(2)^*}c_{i\nu}^{(2)}\left\langle\phi_\mu^{(2)}\left|V_N\right|\phi_\nu^{(2)}\right\rangle\right. \\ & +c_{i\mu}^{(3)^*}c_{i\nu}^{(3)}\left\langle\phi_\mu^{(3)}\left|V_N-2m_ec^2\right|\phi_\nu^{(3)}\right\rangle+c_{i\mu}^{(4)^*}c_{i\nu}^{(4)}\left\langle\phi_\mu^{(4)}\left|V_N-2m_ec^2\right|\phi_\nu^{(4)}\right\rangle \\ & +c_{i\mu}^{(1)^*}c_{i\nu}^{(3)}\left\langle\phi_\mu^{(1)}\left|c\hat{\vec{p}}_z\right|\phi_\nu^{(3)}\right\rangle+c_{i\mu}^{(1)^*}c_{i\nu}^{(4)}\left\langle\phi_\mu^{(1)}\left|c\left(\hat{\vec{p}}_x-i\hat{\vec{p}}_y\right)\right|\phi_\nu^{(4)}\right\rangle \\ & +c_{i\mu}^{(2)^*}c_{i\nu}^{(3)}\left\langle\phi_\mu^{(2)}\left|c\left(\hat{\vec{p}}_x+i\hat{\vec{p}}_y\right)\right|\phi_\nu^{(3)}\right\rangle+c_{i\mu}^{(2)^*}c_{i\nu}^{(4)}\left\langle\phi_\mu^{(2)}\left|c\hat{\vec{p}}_z\right|\phi_\nu^{(4)}\right\rangle \\ & +c_{i\mu}^{(3)^*}c_{i\nu}^{(1)}\left\langle\phi_\mu^{(3)}\left|c\hat{\vec{p}}_z\right|\phi_\nu^{(1)}\right\rangle+c_{i\mu}^{(3)^*}c_{i\nu}^{(2)}\left\langle\phi_\mu^{(3)}\left|c\left(\hat{\vec{p}}_x-i\hat{\vec{p}}_y\right)\right|\phi_\nu^{(2)}\right\rangle \\ & +c_{i\mu}^{(4)^*}c_{i\nu}^{(1)}\left\langle\phi_\mu^{(4)}\left|c\left(\hat{\vec{p}}_x+i\hat{\vec{p}}_y\right)\right|\phi_\nu^{(1)}\right\rangle+c_{i\mu}^{(4)^*}c_{i\nu}^{(2)}\left\langle\phi_\mu^{(4)}\left|c\hat{\vec{p}}_z\right|\phi_\nu^{(2)}\right\rangle \\ & +\frac{1}{2}\sum_{ij}^{N}\sum_{\mu\nu}^{m}\sum_{ab}^{4}\left\{\left[c_{i\mu}^{(a)^*}c_{i\lambda}^{(a)}c_{j\mu}^{(b)^*}c_{jk}^{(b)}-c_{i\mu}^{(a)^*}c_{j\lambda}^{(a)}c_{j\nu}^{(b)^*}c_{ik}^{(b)}\right]\right. \\ & \left.\times\left\langle\phi_\mu^{(a)}(1)\,\phi_\nu^{(b)}(2)\left|\frac{1}{r_{12}}\right|\phi_\lambda^{(a)}(1)\,\phi_k^{(b)}(2)\right\rangle\right\} \end{aligned} \qquad (3.199)$$

The pair exchange that differentiates Coulomb and exchange integrals is transferred into the molecular spinor coefficients in Eq. (3.200), to be multiplied with the corresponding two-electron integral over four basis functions each. Thus this type of basis-set expansion leads to 16 different pairs of molecular spinor coefficient product to be multiplied with two-electron integrals per Coulomb and per exchange integral. To simply equation (3.200), we use the expansion in terms of 2-spinor basis functions in Eq.(3.181)

$$\psi_i(\vec{r}) = \begin{pmatrix} \sum_\mu c^L_{i\mu}\phi^L_\mu(\vec{r}_A) \\ \sum_\mu c^S_{i\mu}\phi^S_\mu(\vec{r}_A) \end{pmatrix} \tag{3.200}$$

where $\psi_i(\vec{r})$ represent the molecular spinor, and $c'_{i\mu}s$ represent the coefficients of molecular spinor and the Dirac Hamiltonian in (2×2) super-structure form of the one electron, given by:

$$h_D = \begin{pmatrix} V_N & c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) \\ c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) & V_N - 2mc^2 \end{pmatrix} \tag{3.201}$$

Now, substituting Eqs. (3.202) and (3.201) into (3.200), we get

$$\begin{aligned}
E^{DHF}_{el,0} = &\sum_i^N \sum_{\mu\nu}^m \Big[c^{(L)^*}_{i\mu} c^{(L)}_{i\nu} \left\langle \phi^{(L)}_\mu \left| V_N \right| \phi^{(L)}_\nu \right\rangle + c^{(S)^*}_{i\mu} c^{(S)}_{i\nu} \left\langle \phi^{(S)}_\mu \left| V_N - 2m_e c^2 \right| \phi^{(S)}_\nu \right\rangle \\
&+ c^{(L)^*}_{i\mu} c^{(S)}_{i\nu} \left\langle \phi^{(L)}_\mu \left| c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) \right| \phi^{(S)}_\nu \right\rangle + c^{(S)^*}_{i\mu} c^{(L)}_{i\nu} \left\langle \phi^{(S)}_\mu \left| c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) \right| \phi^{(L)}_\nu \right\rangle \Big] \\
&+ \frac{1}{2} \sum_{ij}^N \sum_{\mu\nu\lambda k}^m \Big[c^{(L)^*}_{i\mu} c^{(L)}_{i\lambda} c^{(L)^*}_{j\mu} c^{(L)}_{jk} \left\langle \phi^{(L)}_\mu(1)\,\phi^{(L)}_\nu(2) \left| \frac{1}{r_{12}} \right| \phi^{(L)}_\lambda(1)\,\phi^{(L)}_k(2) \right\rangle \\
&+ c^{(L)^*}_{i\mu} c^{(L)}_{i\lambda} c^{(S)^*}_{j\nu} c^{(S)}_{jk} \left\langle \phi^{(L)}_\mu(1)\,\phi^{(S)}_\nu(2) \left| \frac{1}{r_{12}} \right| \phi^{(L)}_\lambda(1)\,\phi^{(S)}_k(2) \right\rangle \\
&+ c^{(S)^*}_{i\mu} c^{(S)}_{i\lambda} c^{(L)^*}_{j\nu} c^{(L)}_{jk} \left\langle \phi^{(S)}_\mu(1)\,\phi^{(L)}_\nu(2) \left| \frac{1}{r_{12}} \right| \phi^{(S)}_\lambda(1)\,\phi^{(L)}_k(2) \right\rangle \\
&+ c^{(S)^*}_{i\mu} c^{(S)}_{i\lambda} c^{(S)^*}_{j\nu} c^{(S)}_{jk} \left\langle \phi^{(S)}_\mu(1)\,\phi^{(S)}_\nu(2) \left| \frac{1}{r_{12}} \right| \phi^{(S)}_\lambda(1)\,\phi^{(S)}_k(2) \right\rangle \\
&- c^{(L)^*}_{i\mu} c^{(L)}_{j\lambda} c^{(L)^*}_{j\mu} c^{(L)}_{ik} \left\langle \phi^{(L)}_\mu(1)\,\phi^{(L)}_\nu(2) \left| \frac{1}{r_{12}} \right| \phi^{(L)}_\lambda(1)\,\phi^{(L)}_k(2) \right\rangle \\
&- c^{(L)^*}_{i\mu} c^{(L)}_{j\lambda} c^{(S)^*}_{j\nu} c^{(S)}_{ik} \left\langle \phi^{(L)}_\mu(1)\,\phi^{(S)}_\nu(2) \left| \frac{1}{r_{12}} \right| \phi^{(L)}_\lambda(1)\,\phi^{(S)}_k(2) \right\rangle \\
&- c^{(S)^*}_{i\mu} c^{(S)}_{j\lambda} c^{(L)^*}_{j\nu} c^{(L)}_{jk} \left\langle \phi^{(S)}_\mu(1)\,\phi^{(L)}_\nu(2) \left| \frac{1}{r_{12}} \right| \phi^{(S)}_\lambda(1)\,\phi^{(L)}_k(2) \right\rangle \\
&- c^{(S)^*}_{j\mu} c^{(S)}_{j\lambda} c^{(S)^*}_{j\nu} c^{(S)}_{ik} \left\langle \phi^{(S)}_\mu(1)\,\phi^{(S)}_\nu(2) \left| \frac{1}{r_{12}} \right| \phi^{(S)}_\lambda(1)\,\phi^{(S)}_k(2) \right\rangle
\end{aligned} \tag{3.202}$$

For more simplification, we introduce a new definition of the elements of the m-dimensional relativistic density matrix $D = \left\{D_{\mu\nu}\right\}$ with an (LL), (LS), (SL) and (SS) super-structure,

$$D_{\mu\nu}^{(XY)} = \sum_{i}^{N} c_{i\mu}^{(X)^*} c_{i\nu}^{(Y)}\,, \quad and \quad X,Y \in \{L,S\} \tag{3.203}$$

So, the Dirac-Hartree-Fock energy can be written in a more compact way as

$$\begin{aligned}
E_{el,0}^{DHF} = \sum_{\mu\nu}^{m} \Big[& D_{\mu\nu}^{(LL)} \left\langle \phi_\mu^L \left| V_N \right| \phi_\nu^L \right\rangle + D_{\mu\nu}^{(SS)} \left\langle \phi_\mu^{(S)} \left| V_N - 2m_e c^2 \right| \phi_\nu^{(S)} \right\rangle \\
& + D_{\mu\nu}^{(LS)} \left\langle \phi_\mu^{(L)} \left| c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) \right| \phi_\nu^{(S)} \right\rangle + D_{\mu\nu}^{(SL)} \left\langle \phi_\mu^{(S)} \left| c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) \right| \phi_\nu^{(L)} \right\rangle \Big] \\
+ \frac{1}{2} \sum_{\mu\nu\lambda k}^{m} \Big\{ & \left[D_{\mu\lambda}^{(LL)} D_{\nu k}^{(LL)} - D_{\mu k}^{(LL)} D_{\nu\lambda}^{(LL)} \right] \left\langle \phi_\mu^{(L)}(1)\, \phi_\nu^{(L)}(2) \left| \frac{1}{r_{12}} \right| \phi_\lambda^{(L)}(1)\, \phi_k^{(L)}(2) \right\rangle \\
& + \left[D_{\mu\lambda}^{(LL)} D_{\nu k}^{(SS)} - D_{\mu k}^{(LS)} D_{\nu\lambda}^{(SL)} \right] \left\langle \phi_\mu^{(L)}(1)\, \phi_\nu^{(S)}(2) \left| \frac{1}{r_{12}} \right| \phi_\lambda^{(L)}(1)\, \phi_k^{(S)}(2) \right\rangle \\
& \left[D_{\mu\lambda}^{(SS)} D_{\nu k}^{(LL)} - D_{\mu k}^{(SL)} D_{\nu\lambda}^{(LS)} \right] \left\langle \phi_\mu^{(S)}(1)\, \phi_\nu^{(L)}(2) \left| \frac{1}{r_{12}} \right| \phi_\lambda^{(S)}(1)\, \phi_k^{(L)}(2) \right\rangle \\
& \left[D_{\mu\lambda}^{(SS)} D_{\nu k}^{(SS)} - D_{\mu k}^{(SS)} D_{\nu\lambda}^{(SS)} \right] \left\langle \phi_\mu^{(S)}(1)\, \phi_\nu^{(S)}(2) \left| \frac{1}{r_{12}} \right| \phi_\lambda^{(S)}(1)\, \phi_k^{(S)}(2) \right\rangle
\end{aligned} \tag{3.204}$$

The Dirac Hamiltonian in (2×2) super-structure form equation (3.202) can be written in a matrix form of an $(m_L + m_S) - dimensional$ matrix, i.e. $\hat{h}_D = \left\{\hat{h}_{\mu\nu}^D\right\}$, and the elements are still in the (2×2) super-structure, given by

$$\hat{h}_{\mu\nu}^D = \begin{pmatrix} \hat{h}_{\mu\nu}^{D(LL)} & \hat{h}_{\mu\nu}^{D(LL)} \\ \hat{h}_{\mu\nu}^{D(SL)} & \hat{h}_{\mu\nu}^{D(SS)} \end{pmatrix} = \begin{pmatrix} V_{\mu\nu}^{LL} & c\left[\hat{\vec{\sigma}}.\hat{\vec{p}}\right]_{\mu\nu}^{(LS)} \\ c\left[\hat{\vec{\sigma}}.\hat{\vec{p}}\right]_{\mu\nu}^{(SL)} & V_{\mu\nu}^{(SS)} - 2m_e c^2 S_{\mu\nu}^{(SS)} \end{pmatrix} \tag{3.205}$$

where the matrix elements in Eq. (3.206) are defined as

$$V_{\mu\nu}^{LL} = \left\langle \phi_{\mu}^{L} \left| V_N \right| \phi_{\nu}^{L} \right\rangle \tag{3.206}$$

$$c\left[\hat{\vec{\sigma}}.\hat{\vec{p}}\right]_{\mu\nu}^{(LS)} = \left\langle \phi_{\mu}^{(L)} \left| c\left(\hat{\vec{\sigma}}.\hat{\vec{p}}\right) \right| \phi_{\nu}^{(S)} \right\rangle \tag{3.207}$$

$$S_{\mu\nu}^{(SS)} = \left\langle \phi_{\mu}^{(S)} | \phi_{\nu}^{(S)} \right\rangle \tag{3.208}$$

The two electron terms in Eq.(3.205) represent the Coulomb and exchange energy, we can introduce a new definition of the Coulomb matrix $J_{\mu\lambda}^{(XX)}$ given by :

$$\begin{aligned}\hat{J}_{\mu\lambda}^{(XX)} = \sum_{\nu k} \Bigg[& D_{\nu k}^{(LL)} \left\langle \phi_{\mu}^{(X)}(1)\,\phi_{\nu}^{(L)}(2) \left| \frac{1}{r_{12}} \right| \phi_{\lambda}^{(X)}(1)\,\phi_{k}^{(L)}(2) \right\rangle \\ & + D_{\nu k}^{(SS)} \left\langle \phi_{\mu}^{(X)}(1)\,\phi_{\nu}^{(S)}(2) \left| \frac{1}{r_{12}} \right| \phi_{\lambda}^{(X)}(1)\,\phi_{k}^{(S)}(2) \right\rangle \Bigg] \; ; X \in \{L,S\}\end{aligned} \tag{3.209}$$

$$\hat{J}_{\mu\lambda}^{(LS)} = \hat{J}_{\mu\lambda}^{(SL)} = 0 \tag{3.210}$$

Hence, the Coulomb matrix $\hat{J}$ has a block-diagonal form, given by

$$\hat{J} = \begin{pmatrix} \hat{J}^{(LL)} & \hat{J}^{(LS)} \\ \hat{J}^{(SL)} & \hat{J}^{(SS)} \end{pmatrix} = \begin{pmatrix} \hat{J}^{(LL)} & 0 \\ 0 & \hat{J}^{(SS)} \end{pmatrix} \tag{3.211}$$

The exchange terms in Eq (3.205) can be defined in terms of the exchange matrix $K_{\mu\lambda}^{(XY)}$ given by:

$$\hat{K}_{\mu k}^{(LL)} = \sum_{\nu\lambda} D_{\nu\lambda}^{(LL)} \left\langle \phi_{\mu}^{(L)}(1)\,\phi_{\nu}^{(L)}(2) \left| \frac{1}{r_{12}} \right| \phi_{\lambda}^{(L)}(1)\,\phi_{k}^{(L)}(2) \right\rangle \tag{3.212}$$

$$\hat{K}_{\mu k}^{(SL)} = \sum_{\nu\lambda} D_{\nu\lambda}^{(LS)} \left\langle \phi_{\mu}^{(L)}(1)\,\phi_{\nu}^{(S)}(2) \left| \frac{1}{r_{12}} \right| \phi_{\lambda}^{(L)}(1)\,\phi_{k}^{(S)}(2) \right\rangle \tag{3.213}$$

$$\hat{K}_{\mu k}^{(LS)} = \sum_{\nu\lambda} D_{\nu\lambda}^{(LS)} \left\langle \phi_{\mu}^{(S)}(1)\,\phi_{\nu}^{(L)}(2) \left| \frac{1}{r_{12}} \right| \phi_{\lambda}^{(S)}(1)\,\phi_{k}^{(L)}(2) \right\rangle \tag{3.214}$$

$$\hat{K}_{\mu k}^{(SS)} = \sum_{\nu\lambda} D_{\nu\lambda}^{(SS)} \left\langle \phi_{\mu}^{(S)}(1)\,\phi_{\nu}^{(S)}(2) \left| \frac{1}{r_{12}} \right| \phi_{\lambda}^{(S)}(1)\,\phi_{k}^{(S)}(2) \right\rangle \tag{3.215}$$

And the exchange matrix K can be written as

$$\hat{K} = \begin{pmatrix} \hat{K}^{(LL)} & \hat{K}^{(LS)} \\ \hat{K}^{(SL)} & \hat{K}^{(SS)} \end{pmatrix} \tag{3.216}$$

Finally, we can write the energy in matrix form, given by

$$E_{el,0}^{DHF}\left[\{c_{i\mu}\}\right] =$$

$$\sum_{i=1}^{n} \left(c_i^{(L)}, c_i^{(S)}\right) \cdot \begin{pmatrix} V^{(LL)} + \hat{J}^{(LL)} - \hat{K}^{(LL)} & c\left[\hat{\vec{\sigma}}.\hat{\vec{p}}\right]^{(LS)} - \hat{K}^{(LS)} \\ c\left[\hat{\vec{\sigma}}.\hat{\vec{p}}\right]^{(SL)} - \hat{K}^{(SL)} & V^{(SS)} - 2m_e c^2 S^{(SS)} + \hat{J}^{(SS)} - \hat{K}^{(SS)} \end{pmatrix} \cdot \begin{pmatrix} c_i^{(L)} \\ c_i^{(S)} \end{pmatrix} \tag{3.217}$$

The Dirac–Hartree–Fock energy depends on the molecular spinor coefficients $c_{i\mu}$

Chapter 4

Results and Discussion

Results and Discussion

The electronic properties of atoms and molecules are studied by theoretical methods with in non-relativistic and relativistic framework. The results of this study has been achieved by using a modified GRASP1.0.0 program which is an acronym for the General-purpose Relativistic Atomic structure Program, designed for atoms [137]. The accuracy in GRASP1.0.0 program is 1.000×10^{-09}. In our work we have takein atoms in group15 from periodic table. The results for diatomic molecules Li_2, N_2, $F_2, and\, Se_2$ are obtain by using DIRAC14.2 program which is an acronym for the Direct Iterative Relativistic All-electron Calculations, designed for atoms and molecules 138]. The results obtained in our work for atoms are compared with C.F.Fischer in case of non-relativistic treatment [46], and Visscher in case of relativistic treatment [139] of the ground state. This chapter shows the analysis of the results and figures achieved in this project.

4.1 The Configuration Energy for Natural Atoms

In the present work we find the energy of the ground state configuration and excited state configuration for each atom in group15 of block P in periodic table. All elements in this group have the same valance-shell configuration, type np^3. Table (4.1) represents the energy configuration of the natural atoms (group15). Comparison between our results with experimental results, for two cases, non-relativistic and relativistic calculations for group15. The electron configuration np^3 for each atom in the group15 gives rise to three atomic terms ${}^2D, {}^4S, \quad and\ {}^2P$ in case of non-relativistic treatment by using Dunning basis sets type cc-pVDZ. But for the relativistic case the configuration np^3 for each atom in the same group we have different terms because of the spin-orbit coupling, they are split into five states ${}^4S_{3/2}, {}^2D_{5/2}, {}^2D_{3/2}, {}^2P_{3/2}$ and $, {}^2P_{1/2}$ by using Dyall basis set type dyall-2zp. The number of Slater determinants or so-called micro-configuration for each element in this group is the number of ways to distribute 3-electrons over 6 spin-orbitals. This is $\begin{pmatrix} 6 \\ 3 \end{pmatrix} = \frac{6!}{3!3!} = 20$ number of Slater determinants. This means that the electronic configuration for each element really indicates 20 different quantum states. However, we can write each state as a linear combination of the 20 possible Slater determinants for each element $\Psi_\alpha = \sum_{k=1}^{20} c_{k\alpha}\Phi_k$. To solve the hardest problem in case multi Slater determinants ,we used Configuration Interaction method to obtain results in table (4.1). The state ${}^4S_{3/2}$ has 4 determinants representing the ground state, state ${}^2D_{5/2}$ has 6 determinants, state ${}^2D_{3/2}$ has 4 determinants representing the first excite state, state ${}^2P_{1/2}$ has 2 determinants, and state ${}^2P_{3/2}$ have 4 determinants representing second excite state. The energy configurations for natural atoms in non-relativistic case and relativistic case have been calculated by using modified GRASP1.0.0 code.

Table 4.1: **Comparison of experimental energy levels of neutral atoms with our results**

Natural Atom	Term	J	Energy level [exp] cm^{-1}	Energy level [Relativistic-calculi-Ourwork]cm^{-1}	Energy level [non-relativistic calculus-Our work]cm^{-1}
$_7N$	^4S	3/2	0.000 [140,141]	0.000	0.000
	^2D	5/2	-19224.464 [140,141]	-22636.036246	-22642.624859
		3/2	-19233.177 [40,141]	-22638.137931	
	^2P	1/2	-28838.920 [40,141]	-37726.047203	-37737.708098
		3/2	-28839.306[40,141]	-37731.457672	
$_{15}P$	^4S	3/2	0.000[142,141]	0.000	0.000
	^2D	3/2	-11361.02 [142,141]	-15123.922999	-15139.400026
		5/2	-11376.63 [142,141]	-15139.325896	
	^2P	1/2	-18722.71 [142,141]	-25212.124156	-25232.333377
		3/2	-18748.01 [142,141]	-25244.700967	
$_{33}As$	^4S	3/2	0.000[143,141]	0.000	0.000
	^2D	3/2	-10592.666 [143,141]	-14378.80179	-14399.596246
		5/2	-10914.866 [143,141]	-14628.029343	
	^2P	1/2	-18186.328 [143,141]	-24257.337035	-23999.327077
		3/2	-18647.663 [143,141]	-24651.208818	
$_{51}Sb$	^4S	3/2	0.000[143,141]	0.000	0.000
	^2D	3/2	-8512.125 [144,141]	-12132.102745	-12809.252581
		5/2	-9854.018 [144,141]	-13295.592133	
	^2P	1/2	-16395.359 [144,141]	-21707.388802	-21348.754301
		3/2	-18464.202 [144,141]	-23528.134251	
$_{83}Bi$	^4S	3/2	0.000[145,140]	0.000	0.000
	^2D	3/2	-11419.039 [145,141]	-12536.828371	-12188.664764
		5/2	-15437.501[145,141]	-17316.263029	
	^2P	1/2	-21660.914[145,141]	-25144.185126	-20314.441273
		3/2	-33164.805[145,140]	-36341.493487	
$_{115}Uup$	^4S	3/2	-	0.000	0.000
	^2D	3/2	-	-37179.611441	-11270.711484
		5/2	-	-42317.771157	
	^2P	1/2	-	-49494.048252	-18759.570083
		3/2	-	-93970.244144	

The experimental energies of the ground state ${}^4S_{3/2}$ for N, P, As, Sb, Bi respectively, are given by $117225.7cm^{-1}$ [139], $84580.83cm^{-1}$ [141], $78950cm^{-1}$[146], $69431.34cm^{-1}$ [147], $58762.0cm^{-1}$[148] . The last element (Z=115) in group 15 has no experimental value as yet, but in our work, we can calculate ground state energy for state ${}^4S_{3/2}$ as $95648.6cm^{-1}$ and find energies for all states.

4.2 Spin-Orbit Mixing (State Interaction)

The effect due to spin–orbit coupling is considered the main reason for the splitting of the p shell into $p_{1/2}$ and $p_{3/2}$, the d shells into $d_{3/2}$ and $d_{5/2}$ and so on. The np^3electron configuration for each element in group15 gives rise to three $LS-states$, ${}^4S, {}^2D$ and ${}^2P$. The effect of spin-orbit coupling of these states will lead to splitting into, ${}^4S_{3/2}, {}^2D_{5/2}, {}^2D_{3/2}, {}^2P_{3/2}$ $, {}^2P_{1/2}$. Some states that have the same total angular momentum J may interact and mix. This means the states ${}^4S_{3/2}, {}^2D_{3/2}$, and ${}^2P_{3/2}$ interact, leading to doublet-quadruplet mixing, but this interaction is forbidden in a non-relativistic framework. The symbol es for the terms in relativistic cas are different notation the first configurations $nP^1_{1/2}, nP^2_{3/2}\ for\, J = 5/2$ have 6 determinants, the second configurations $nP^2_{1/2}, nP^1_{3/2}$ for $J = 3/2$ have 4 determinants, the third configurations $nP^1_{1/2}, nP^2_{3/2}$for$J = 3/2$ have 4 determinants, the fourth configurations $nP^3_{3/2}\ for\, J = 3/2$ have 4 determinants, and the fifth configurations $nP^1_{1/2}, nP^2_{3/2}\ for\ j = 1/2$ have 2 determinants. The second, third, and fourth configurations have the same $J = 3/2$. Each configuration of these states is called Configuration State Functions $CSFs$. The linear combination of configuration state functions $CSFs$ called Atomic State Functions $ASFs$ has the form $\Psi_i = \sum_{m=1}^{5} CSF_m\rangle\, c_{mi}$, where m is the number of $CSFs$, and where the $c_i^{\prime}s$ are the configuration mixing coefficients for state Ψ, and $\sum_{i=1}^{m}\left|c_i^2\right| = 1$ represents the weight of configuration state functions $CSFs$. The average occupation of $P_{3/2}$ in atomic state function has the form $\left\langle occ\left(P_{3/2}\right)\right\rangle = \sum_m CSF_{occ}\left(P_{3/2}\right).\left|c_i^2\right|$. Each atom in group15 has five configuration state functions as explained in previous section. Table (4.2) gives the contribution weight interaction of the atomic state function (ASF) for three configuration state functions (CSF) that have the same total angular momentum J of each atom in group15 in relativistic framework. The effective occupation weight number as function of the atomic number(Z) of the $np_{3/2}$ orbital for each state given in Fig (4.1)

Table 4.2: The contribution of weight states that have the same total angular momentum for group15

Z	Contribution of weight states that have same $J = 3/2$		
	$nP^1_{3/2}$	$nP^2_{3/2}$	$nP^3_{3/2}$
7	0.2825	0.4444	0.2731
15	0.2996	0.4446	0.2559
33	0.0002	0.9776	0.0222
51	0.4628	0.4777	0.0595
83	0.2090	0.7901	0.0008
115	0.0095	0.9881	0.0025

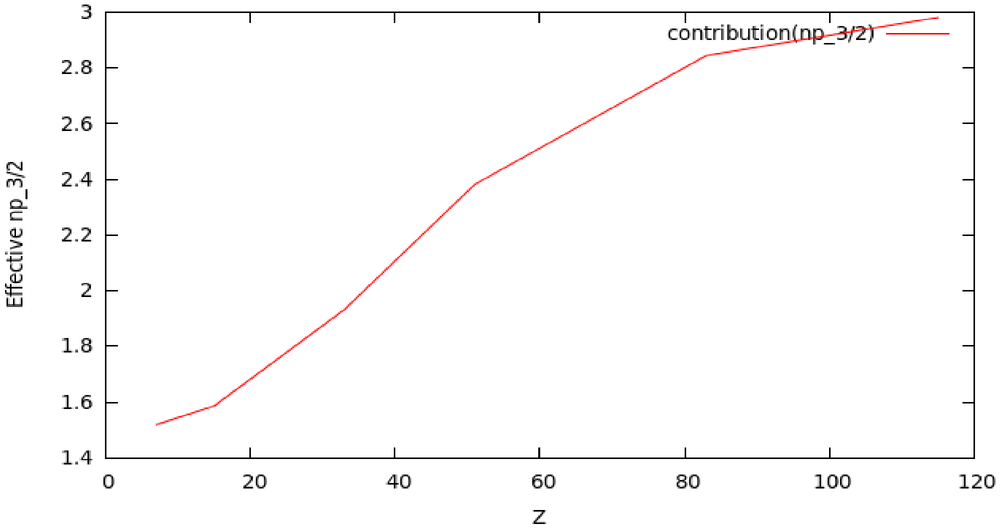


Figure 4.1: **Effective occupation weight number of the $np_{3/2}$orbital as function of the atomic number(Z)**

4.3 Non-relativistic Hartree-Fock for Atoms

Table (4.3) gives the the non-relativistic orbital energies in Hartree-Fock level for the nitrogen atom in atomic units, obtained by using Gaussian basis-set type *Dunning* $(cc-pVDZ)$ with two model nuclear charge distributions. The first model is point charge and the second is Gaussian charge distribution model. The basis-set *cc-pVDZ* has [3s2p1d] contractive functions for nitrogen atom, and has (9s4p1d) primitive functions for nitrogen atom. Our results are compared with those of C.F. Fischer [46] in table (4.3).

Table 4.3: **Hartree-Fock spinor energy for different nuclear models for N-atom with basis set**

The ground state Hartree-Fock energy with *Dunning basis set cc-pVDZ* for nitrogen atom			
Spinor	Our work/HF-energy (a.u.)-point model	Our work/HF-energy (a.u.)-Gaussian model	C.F.Fischer/HF-energy (a.u.)using Grid Technique
1s	15.66639161100	15.66638860079	15.6290595
2s	0.9636702700312	0.9636701067407	0.9453236
2p	0.5086548640255	0.5086549107696	0.56758885

Table (4.4) gives the the non-relativistic orbital energies in Hartree-Fock level for phosphorus atom in atomic units, obtained by using Gaussian basis-set type *Dunning* $(cc-pVDZ)$ with two model nuclear charge distributions. The basis-set *cc-pVDZ* has [4s3p1d] contractive functions for phosphorus atom, and has (12s8p1d) primitive functions for phosphorus atom. Our results are compared with those of C.F. Fischer [46] in table (4.4).

Table 4.4: **Hartree-Fock spinor energy for different nuclear models for P-atom with basis set**

The ground state Hartree-Fock energy with Dunning basis set cc-pVDZ for phosphorus atom			
Spinor	Our work/HF-energy (a.u.)-point model	Our work/HF-energy (a.u.)-Gaussian model	C.F.Fischer/HF-energy (a.u.)using Grid Technique
1s	79.98906454033	79.98896408548	79.96912
2s	7.528773798541	7.528766526948	7.5110935
2p	5.418450867141	5.418452223616	5.400955
3s	0.7063628418693	0.7063622517076	0.69641485
3p	0.3505641350000	0.3505642812601	0.3917082

Table (4.5) gives the non-relativistic orbital energies in Hartree-Fock level for the arsenic atom in atomic units, obtained by using Gaussian basis-set type *Dunning* $(cc-pVDZ)$ with two model nuclear charge distributions. The basis-set *cc-pVDZ* has [5s4p2d] contractive functions for arsenic atom, and has (14s11p6d) primitive functions for arsenic atom, and comparing our results with C.F.Fischer results [46].

Table 4.5: **Hartree-Fock spinor energy for different nuclear models for As-atom with basis set**

The ground state Hartree-Fock energy with Dunning basis set cc-pVDZ for Arsenic atom

Spinor	Our work/HF-energy (a.u.)-point model	Our work/HF-energy (a.u.)-Gaussian model	C.F.Fischer/HF-energy (a.u.)using Grid Technique
1s	432.6020902090	432.5976700577	432.58619
2s	56.32520354201	56.32477746980	56.30982
2p	50.16912209304	50.16915761056	50.153735
3s	8.044609904424	8.044544513191	8.029619
3p	5.895508632684	5.895515598165	5.8806905
4s	0.6951367708357	0.6951316213837	0.6858967
3d	2.127599622272	2.127604898083	2.112655555
4p	0.3301361963250	0.3301372428760	0.36948255

Table (4.6) gives the the non-relativistic orbital energies in Hartree-Fock level for the antimony atom in atomic units, obtained by using Gaussian basis-set type $Dyall$ $(dyall-2zp)$ with two model nuclear charge distributions. The basis-set $dyall-2zp$ has [21s15p11d1f] contractive functions for antimony atom, and has (21s15p11d1f) primitive functions for antimony atom, and comparing our results with C.F.Fischer results [46].

Table 4.6: **Hartree-Fock spinor energy for different nuclear models for Sb-atom with basis set**

The ground state Hartree-Fock energy with Dyall basis set dyall-2zp for Antimony atom

Spinor	Our work/HF-energy (a.u.)-point model	Our work/HF-energy (a.u.)-Gaussian model	Charlotte Froese Fischer/HF-energy (a.u.)using Grid Technique
1s	1085.601391167	1085.567407612	1085.58905
2s	164.7700678882	164.7665463130	164.75797
2p	154.0159042754	154.0161140794	154.0038
3s	33.64818691602	33.64750141569	33.636223
3p	29.11807061409	29.11812444522	29.106151
4s	6.074808510639	6.074675454163	6.0631855
3d	20.81006314552	20.81011174023	20.798079
4p	4.456219707509	4.456234533260	4.44471865
5s	0.5889413634203	0.5889279394407	0.5817731
4d	1.699371666838	1.699383261431	1.68786555
5p	0.2992468300293	0.2992495888001	0.33471125

Table (4.7) gives the the non-relativistic orbital energies in Hartree-Fock level for the bismuth atom in atomic units, obtained by using Gaussian basis-set $Dyall$ type $(dyall-2zp)$ with two model nuclear charge distributions. The basis-set $dyall-2zp$ has [24s20p14d9f] contractive functions for bismuth atom, and has (24s20p14d9f) primitive functions for bismuth atom, and comparing our results with C.F.Fischer results [46].

Table 4.7: **Hartree-Fock spinor energy for different nuclear models for Bi-atom with basis set**

The ground state Hartree-Fock energy with Dyall basis set dyall-2zp for bismuth atom

Spinor	Our work/HF-energy (a.u.)-point model	Our work/HF-energy (a.u.)-Gaussian model	Charlotte Froese Fischer/HF-energy (a.u.)using Grid Technique
1s	3000.163735658	2999.832734383	3000.15275
2s	512.8526043069	512.8160575933	512.84175
2p	493.4598678575	493.4612612584	493.44903
3s	125.4157312057	125.4074441361	125.40496
3p	116.1448735417	116.1452732285	116.13412
4s	29.59821136067	29.59610802740	29.5875005
3d	99.06717042097	99.06755218046	99.05639
4p	25.44835367523	25.44848334851	25.4376765
5s	5.508208214800	5.507791445388	5.4977845
4d	17.82889617363	17.82901514152	17.8181785
5p	4.005043283896	4.005087313235	3.99471445
6s	0.5581695152534	0.5581226782181	0.55169005
4f	7.419412602500	7.419505303731	7.4087005
5d	1.487435388793	1.487470378546	1.47715695
6p	0.2861884819993	0.2861977082341	0.32010435

Table (4.8) gives the the non-relativistic orbital energies in Hartree-Fock level for the ununpentium atom [149] in atomic units, obtained by using Gaussian basis-set *Dyall* type $(dyall-2zp)$ with two model nuclear charge distributions. The first model is point charge and the second is Gaussian charge distribution model. The basis-set $dyall-2zp$ has contractive functions [26s23p16d12f] and has (26s23p16d12f) primitive functions for ununpentium atom. and comparing our results with C.F.Fischer results [46].

Table 4.8: **Hartree-Fock spinor energy for different nuclear models for Uup-atom with basis set**

The ground state Hartree-Fock energy with Dyall basis set dyall-2zp for Ununpentium atom			
Spinor	Our work/HF-energy (a.u.)-point model	Our work/HF-energy (a.u.)-Gaussian model	Our work/HF-energy (a.u.)-point-without basis set using Grid Technique
1s	5899.960411720	5898.482551546	5898.054648730
2s	1079.936867394	1079.768754103	1079.349997789
2p	1051.175392391	1051.180199446	1051.041606519
3s	297.7647459564	297.7242654790	297.3758347434
3p	282.7704018980	282.7719200088	282.8360680359
4s	87.67056102714	87.65858721745	87.42038472118
3d	255.2005386354	255.2020160433	255.8994294738
4p	80.06665921454	80.06721596819	80.11951894910
5s	23.49327940830	23.48975962008	23.35853851884
4d	66.01239474752	66.01292748307	66.47149052178
5p	19.99082418540	19.99103875354	20.03523474467
6s	4.681054317942	4.680273601348	4.636655382532
4f	46.69217630000	46.69264536664	47.24147816556
5d	13.71540018451	13.71559905830	13.95772054556
6p	3.387790427697	3.387873251973	3.404411318790
7s	0.5065770006769	0.5064801107768	0.4997786128369
5f	5.703220283898	5.703376220399	5.947219211560
6d	1.276019899695	1.276087072882	1.346060246721
7p	0.2568643350823	0.2568832386987	0.2684413074059

4.4 Total Electronic Hartree Fock Energy for Atoms of Group15

As was discussed in more detail in chapter two part one, we can find the total electronic HF energy for ground state by using GRASP1.0.0 modified program in case of non-relativistic treatment. Table (4.9) gives comparison of the total HF electronic energies for group15-atoms, using two different nuclear charge distribution model with two types of Gaussian Basis-set; Dunning type $cc-pVDZ$ and Dyall type $dyall-2zp$ in case of non-relativistic treatment. From the table it is clear that the Gaussian nucleus model gives a smaller total energy than the point charge model.

Table 4.9: **Total electronic energies for the different nuclear models with Gaussian basis set**

Z	Electronic configu-ration	Total electronic energy (a.u)-point model /Our work	Total electronic energy (a.u)-Gauss model /Our work	Total electronic energy (a.u) by C.F.Fischer[46] using Grid Technique	$P.E = \frac{\begin{matrix} point \\ (Fischer) \end{matrix} - \begin{matrix} Gauss \\ model \end{matrix}}{point(Fischer)} \times 100\%$
7	$2s^2 2p^3$	-54.28929125000	-54.28928404265	-54.400934	0.20%
15	$3s^2 3p^3$	-340.6442717812	-340.6440398301	-340.71878	0.02%
33	$4p^3$	-2234.167785734	-2234.157611288	-2234.2386	0.003%
51	$5s^2 5p^3$	-6313.422328672	-6313.343782906	-6313.4853	0.002%
83	$6p^3$	-20095.52650467	-20094.75773532	-20095.586	0.004%
115	$7p^3$	-43584.10822144	-43580.66196908	-43584.14349336 our work	0.007%

4.5 Effect of The Nuclear Charge Distribution on Spinor Energies

The effect of nuclear charge distribution on the total energy and spinor energy are notable when switching from the singular potential of point nucleus to a Gaussian nucleus potential. The most important is the effect on relative energies. Here we may note that the effect is observable, but small for moderate nuclear charge it becomes larger for super heavy atoms. The spinor energies and total ground state energies are given in tables below for atoms group 15 from periodic table, in Hartree atomic units.

4.5.1 The Dirac-Hartree-Fock Spinor Energy for Group15 Atoms

To obtain results of the orbital energies in Dirac-Hartree-Fock level for atoms in group 15, two different model nuclear charge distributions where used . The first model is point charge and the second model is Gaussian charge distribution. Table (4.10) compares our results with Visscher [139], results of the relativistic orbital energies for the nitrogen atom in atomic units, obtained by using Gaussian basis-set Dyall type $(dyall.2zp)$. The $dyall-2zp$ large components basis-set has [10s6p1d] contractive functions and (10s6p1d) primitive functions for nitrogen atom. The $dyall-v2z$ small component basis-set has

[6s11p6d1f] contractive functions and (6s11p6d1f) primitive functions for nitrogen atom.

Table 4.10: **Relativistic spinor energies using different nuclear charge models for N-atom**

The ground state Dirac-Hartree-Fock energy with Dyall basis set *dyall.2zp* for nitrogen atom

Spinor	Our work/DHF-energy(a.u.)-point model	Our work/DHF-energy(a.u.)-Gaussian model	Visscher /DHF-energy(a.u.) using Grid Technique[139]
$1s_{1/2}$	15.67641393998	15.67641086411	15.676414
$2s_{1/2}$	0.9647881086797	0.9647879414597	0.96478811
$2p_{1/2}$	0.5088816659328	0.5088817137571	0.50888167
$2p_{3/2}$	0.5081840426397	0.5081840904034	0.50818404

Table (4.11) gives comparison of our results with Visscher [139], results of the relativistic orbital energies in Dirac-Hartree-Fock level for the phosphorus atom in atomic units. The results are obtained by using Gaussian basis-set Dyall type $(dyall.2zp)$. The large components basis-set type $dyall-2zp$ has [12s8p2d] contractive functions and (12s8p2d) primitive functions for phosphorus atom. Small components basis-set type $dyall-2zp$ has [8s16p8d1f] contractive functions and has (8s16p8d1f) primitive functions for phosphorus atom.

Table 4.11: **Relativistic spinor energies using different nuclear charge models for P-atom**

The ground state Dirac-Hartree-Fock energy with Dyall basis set dyall.2zp for phosphorus atom

Spinor	Our work/DHF-energy (a.u.)-point model	Ourwork/DHF-energy (a.u.)-Gaussian model	Visscher /DHF-energy (a.u.) using Grid Technique[139]
$1s_{1/2}$	80.23031525695	80.23020545473	80.230315
$2s_{1/2}$	7.566465817966	7.566457790623	7.5664658
$2p_{1/2}$	5.441233165503	5.441234655682	5.4412332
$2p_{3/2}$	5.405918929562	5.405920420815	5.4059189
$3s_{1/2}$	0.7094589099354	0.7094582579317	0.70945891
$3p_{1/2}$	0.3514633487919	0.3514635094280	0.35146335
$3p_{3/2}$	0.3493907143972	0.3493908748457	0.34939071

Table (4.12) gives comparison of our results with Visscher [139], results of the relativistic orbital energies in Dirac-Hartree-Fock level for arsenic atom in atomic units. The obtained results by using Gaussian basis-set Dyall type

$(dyall.2zp)$. The large components basis-set type $dyall-2zp$ has [15s11p7d1f] contractive functions and has (15s11p7d1f) primitive functions for arsenic atom. Small components basis-set type $dyall-2zp$ has [11s22p12d7f1g] contractive functions and has (11s22p12d7f1g) primitive functions for arsenic atom.

Table 4.12: **Relativistic spinor energies using different nuclear charge models for As-atom**

The ground state Dirac-Hartree-Fock energy with Dyall basis set dyall.v2z for Arsenic atom

Spinor	Ourwork/DHF-energy (a.u.)-point model	Ourwork/DHF-energy (a.u.)-Gaussian model	Visscher /DHF-energy (a.u.) using Grid Technique[139]
$1s_{1/2}$	439.2247311001	439.2183037329	439.22473
$2s_{1/2}$	57.81549006985	57.81483873461	57.81549
$2p_{1/2}$	51.42597182112	51.42602153862	51.425972
$2p_{3/2}$	50.06813273071	50.06818657561	50.068133
$3s_{1/2}$	8.292958907325	8.292858200028	8.2929589
$3p_{1/2}$	6.081267398763D+00	6.081277254166D+00	6.0812674
$3p_{3/2}$	5.885302590048	5.885313145586	5.8853026
$4s_{1/2}$	0.7128161556667	0.7128081265659	0.71281616
$3d_{3/2}$	2.099912013124	2.099919925352	2.099912
$3d_{5/2}$	2.070458146139	2.070465983591	2.0704581
$4p_{1/2}$	0.3359837734273	0.3359853238800	0.33598377
$4p_{3/2}$	0.3255323076120	0.3255338785350	0.32553231

Table (4.13) gives comparison of our results with Visscher [139], results of the relativistic orbital energies in Dirac-Hartree-Fock level for the antimony atom in atomic units. To obtained results by using Gaussian basis-set Dyall type $(dyall-2zp)$. The large components basis-set type $dyall-2zp$ has [21s15p11d1f] contractive functions and has (21s15p11d1f) primitive functions for antimony atom. Small components basis-set type $dyall-v2z$ has [15s32p16d11f1g] contractive functions and has (15s32p16d11f1g) primitive functions for antimony atom.

Table 4.13: **Relativistic spinor energies using different nuclear charge models for Sb-atom**

The ground state Dirac-Hartree-Fock energy with Dyall basis set dyall.2zp for antimony atom

Spinor	Ourwork/DHF-energy (a.u.)-point model	Ourwork/DHF-energy (a.u.)-Gaussian model	Visscher /DHF-energy (a.u.)using Grid Technique[139]
$1s_{1/2}$	1127.119473109	1127.041546454	1127.1195
$2s_{1/2}$	174.9685171413	174.9593874499	174.96852
$2p_{1/2}$	163.1951791397	163.1955322116	163.19518
$2p_{3/2}$	153.9015321395	153.9020702545	153.90153
$3s_{1/2}$	35.80588275517	35.80409121650	35.805883
$3p_{1/2}$	30.95326573690	30.95336312051	30.953266
$3p_{3/2}$	29.18918436071	29.18932304145	29.189184
$4s_{1/2}$	6.490168786914	6.489819993540	6.4901688
$3d_{3/2}$	20.72511640126	20.72524037880	20.725116
$3d_{5/2}$	20.36366220033	20.36378359542	20.363662
$4p_{1/2}$	4.769274183204	4.769304463568	4.7692742
$4p_{3/2}$	4.440117314199	4.440155399446	4.4401173
$5s_{1/2}$	0.6273484565397	0.6273113409773	0.62734846
$4d_{3/2}$	1.655236554788	1.655265599716	1.6552366
$4d_{5/2}$	1.605707409992	1.605735903253	1.6057074
$5p_{1/2}$	0.3136375235310	0.3136440321581	0.31363752
$5p_{3/2}$	0.2900003330087	0.2900073000793	0.29000033

Table (4.14) gives comparison of our results with Visscher [139], results of the relativistic orbital energies in Dirac-Hartree-Fock level for the bismuth atom in atomic units. To obtained results by using Gaussian basis-set Dyall type $(dyall-2zp)$. The large components basis-set type $dyall-2zp$ has [24s20p14d9f] contractive functions and has (24s20p14d9f) primitive functions for bismuth atom. Small components basis-set type $dyall-2zp$ has [20s38p29d14f9g] contractive functions and has (20s38p29d14f9g) primitive functions for bismuth atom.

Table 4.14: **Relativistic spinor energies using different nuclear charge models for Bi-atom**

The ground state Dirac-Hartree-Fock energy with Dyall basis set dyall-2zp for Bismuth atom-

Spinor	Ourwork/DHF-energy (a.u.)-point model	Ourwork/DHF-energy (a.u.)-Gaussian model	Visscher /DHF-energy (a.u.)using Grid Technique[139]
$1s_{1/2}$	3352.039076443	3349.426060889	3352.0391
$2s_{1/2}$	607.7970911034	607.3929225354	607.79709
$2p_{1/2}$	582.4967817486	582.4827155162	582.49678
$2p_{3/2}$	497.0931648138	497.1084526627	497.09316
$3s_{1/2}$	149.3877267202	149.2941325671	149.38773
$3p_{1/2}$	138.1044219131	138.1010029562	138.10442
$3p_{3/2}$	118.7419926655	118.7464701558	118.74199
$4s_{1/2}$	35.75784510191	35.73385000036	35.757845
$3d_{3/2}$	100.6180719438	100.6222678433	100.61807
$3d_{5/2}$	96.55142237998	96.55537283099	96.551422
$4p_{1/2}$	30.83293247254	30.83232473061	30.832932
$4p_{3/2}$	25.99901422753	26.00045681049	25.999014
$5s_{1/2}$	6.691186092642	6.686253607900	6.6911861
$4d_{3/2}$	18.02529423455	18.02656353821	18.025294
$4d_{5/2}$	17.11319409309	17.11440129796	17.113194
$5p_{1/2}$	4.909505586620	4.909584733623	4.9095056
$5p_{3/2}$	3.976443466448	3.976926293748	3.9764435
$6s_{1/2}$	0.6868478253917	0.6861931922182	0.68684783
$4f_{5/2}$	6.703886554846	6.704797943718	6.7038866
$4f_{7/2}$	6.495226320245	6.496119123073	6.4952263
$5d_{3/2}$	1.389084536207	1.389435763865	1.3890845
$5d_{5/2}$	1.270617290964	1.270949267762	1.2706173
$6p_{1/2}$	0.3384213555385	0.3384834872791	0.33842136
$6p_{3/2}$	0.2610826852490	0.2611778720615	0.26108269

Table (4.15) gives comparison of our results using Gaussian basis-set and without Gaussian basis-set of the relativistic orbital energies in Dirac-Hartree-Fock level for ununpentium atom in atomic units. To obtained results by using Gaussian basis-set Dyall type $(dyall-2zp)$. The large components basis-set type $dyall-2zp$ has [26s23p16d12f] contractive functions and has (26s23p16d12f) primitive functions for ununpentium atom. Small components basis-set type $dyall-2zp$ has [23s42p35d16f12g] contractive functions and has (23s42p35d16f12g) primitive functions for ununpentium atom.

Table 4.15: **Relativistic spinor energies using different nuclear charge models for Uup-atom**

The ground state Dirac-Hartree-Fock energy with Dyall basis set dyall.2zp for Ununpentium atom

Spinor	Ourwork/DHF-energy(a.u.)-point model	Ourwork/DHF-energy(a.u.)-Gaussian model	Ourwork/DHF-energy(a.u.) with out basis-set using Grid Technique -point model
$1s_{1/2}$	7692.743279688	7608.831870440	7692.743279693
$2s_{1/2}$	1594.729544466	1575.873224054	1594.729544470
$2p_{1/2}$	1540.288405602	1536.827733074	1540.288405607
$2p_{3/2}$	1071.193542304	1071.725443621	1071.193542305
$3s_{1/2}$	433.9396492659	429.2857713086	433.9396492696
$3p_{1/2}$	410.8960726388	409.9316778840	410.8960726433
$3p_{3/2}$	296.0324677059	296.2084651931	296.0324677082
$4s_{1/2}$	127.9634222334	126.6080139819	127.9634222370
$3d_{3/2}$	265.6623689875	265.8271544004	265.6623689914
$3d_{5/2}$	247.0539097751	247.2007559732	247.0539097764
$4p_{1/2}$	117.2484671125	116.9727943473	117.2484671162
$4p_{3/2}$	83.93976753015	84.00409862472	83.93976753252
$5s_{1/2}$	35.14524950375	34.74139069872	35.14524950487
$4d_{3/2}$	63.75079989965	63.80278971574	68.92886631433
$4d_{5/2}$	68.92886631151	68.98636539870	63.75079990293
$5p_{1/2}$	30.36977682437	30.29379931806	30.36977682533
$5p_{3/2}$	20.72638477718	20.75055873844	20.72638477776
$6s_{1/2}$	7.365786673419	7.259823178097	7.365786673723
$4f_{5/2}$	44.11737616348	44.16188325562	44.11737616470
$4f_{7/2}$	42.59909669208	42.64185249661	42.59909669323
$5d_{3/2}$	14.16365861571	14.18360112888	14.16365861700
$5d_{5/2}$	12.81098539738	12.82905899428	12.81098539739
$6p_{1/2}$	5.542250520871	5.525680464906	5.542250520728
$6p_{3/2}$	3.298719414074	3.307294525163	3.298719414351
$7s_{1/2}$	0.8772251063641	0.8583728431790	0.8772251066735
$5f_{5/2}$	4.851061396679	4.864141861758	4.851061396897
$5f_{7/2}$	4.549872603143	4.562437818085	4.549872603197
$6d_{3/2}$	1.146712647361	1.152217380975	1.146712647902
$6d_{5/2}$	0.9593721407993	0.9640033146962	0.9593721413814
$7p_{1/2}$	0.4474219455236	0.4458895150570	0.4474219460526
$7p_{3/2}$	0.2139921453225	0.2155264592600	0.2139921452578

4.5.2 The Total Dirac-Hartree-Fock Electronic Energy for Atoms

The total DHF electronic energies for group15-atoms in periodic table, are obtaing by using two different nuclear charge distribution models with Dyall Basis set type $dyall-2zp$. Table (4.16) shows the Gaussian model giving a higher total energy than the point charge model.

Table 4.16: **Total DHF electronic energies using different nuclear models with basis-set dyall-2zp**

Z	Electronic configu-ration	Total electronic energy (a.u)-point model /present work	Total electronic energy (a.u)-Gaussian model /present work	Total electronic energy (a.u)- by Visscher using Grid Technique[138]	$P.E=\frac{\begin{matrix}point\\(visscher)\end{matrix}-\begin{matrix}Gauss\\model\end{matrix}}{point(visscher)}\times 100\%$
7	$2s^2 2p^3$	-54.32085443665	-54.32084706926	-54.3277292629	0.01%
15	$3s^2 3p^3$	-341.4903528722	-341.4900989335	-341.4949424692	0.001%
33	$4p^3$	-2259.452500113	-2259.437579618	-2259.456841457	0.0008%
51	$5s^2 5p^3$	-6480.698339178	-6480.514171242	-6480.702171855	0.002%
83	$6p^3$	-21572.23237662	-21565.70280668	-21572.23594272	0.03%
115	$7p^3$	-51189.80613005	-50951.45542798	-51189.80613005 ourwork	0.46%

4.6 The Radial Expectation Value

The mean values of r^n for non-relativistic treatment is $\langle r^n \rangle_{i,j}^{l} = \int_0^\infty \left[P_i P_j\right] r^n dr$, where P_i is the radial wave function described by Dunning basis set type cc-pVDZ. The mean value for relativistic treatment is $\langle r^n \rangle_{i,j}^{l} = \int_0^\infty \left[P_i P_j + Q_i Q_j\right] r^n dr$ [136], where P_i, Q_i are the large and small radial wave functions, respectively, describe by Dyall basis set type dyall-2zp. In the present work we find the radial expectation value $\langle r \rangle$ for different nuclear charges distribution models. First one point charge distribution model and second one Gaussian charge distribution model are used. Comparison between $\langle r \rangle$ in HF level, and $\langle r \rangle$ in DHF level for group 15 in periodic table is given in table (4.17). We see that the mean radius of spinors decreases due to relativistic effects. Table (4.17) and Table (4.18) show the comparison for the radial expectation values between HF level and DHF level for nitrogen atom and phosphorus atom using different nuclear charge distribution models for our results and Charlotte's results [46].

Table 4.17: **Comparison between HF and DHF of $\langle r \rangle$ using different nuclear distribution charge for N-atom**

The radial expectation value $\langle r \rangle$ (a.u.) using different basis set in HF and DHF for nitrogen atom

Spinor	$\langle r \rangle$ (a.u) by Charlott	$\langle r \rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.22829	0.22825983	0.22825986	0.22807568	0.22807571
$2s_{1/2}$	1.332277	1.3263232	1.3263234	1.3252661	1.3252662
$2p_{1/2}$				1.4458042	1.4458041
$2p_{3/2}$	1.409632	1.4466234	1.4466233	1.4471153	1.4471152

Table 4.18: **Comparison between HF and DHF results for $\langle r \rangle$ using different nuclear distribution charge for P-atom**

The radial expectation value $\langle r \rangle$ using different Basis set in HF and DHF for phosphors atom

Spinor	$\langle r \rangle$ (a.u) by Charlott	$\langle r \rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.111431	0.10380412	0.10380423	0.10340521	0.10340532
$2s_{1/2}$	0.562941	0.51561199	0.51561229	0.5136256	0.51362594
$2p_{1/2}$				0.48158216	0.48158211
$2p_{3/2}$	0.535408	0.48354809	0.48354804	0.48369061	0.48369057
$3s_{1/2}$	2.207087	1.9277923	1.9277932	1.9223661	1.9223671
$3p_{1/2}$				2.3635647	2.3635643
$3p_{3/2}$	2.752211	2.36881	2.3688096	2.3717095	2.371709

Table (4.19) and Table (4.20) respectively, shows comparison for the radial expectation values between HF level and DHF level for arsenic atom and antimony atom. Using different nuclear charge distribution models. The results from our obtained comparing with Charlotte, results [46].

Table 4.19: **Comparison between HF and DHF results for $\langle r \rangle$ using different nuclear distribution charge for As-atom**

The radial expectation value $\langle r \rangle$ using different Basis set in HF and DHF for arsenic atom					
Spinor	$\langle r \rangle$ (a.u) by Charlott	$\langle r \rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.046363	0.046363469	0.046363874	0.045475919	0.045476506
$2s_{1/2}$	0.205963	0.20596288	0.20596387	0.20178263	0.20178409
$2p_{1/2}$				0.17464139	0.17464133
$2p_{3/2}$	0.178758	0.17875807	0.17875802	0.17827902	0.17827895
$3s_{1/2}$	0.605963	0.60595127	0.60595373	0.59557442	0.59557804
$3p_{1/2}$				0.60925059	0.60925033
$3p_{3/2}$	0.620229	0.62038075	0.62038055	0.61910609	0.61910578
$4s_{1/2}$	2.029707	2.0252903	2.0252988	1.9925168	1.9925295
$3d_{3/2}$				0.66741283	0.66741217
$3d_{5/2}$	0.667451	0.66730005	0.66729962	0.67197603	0.67197537
$4p_{1/2}$				2.5242016	2.5241977
$4p_{3/2}$	2.512258	2.5611016	2.5610988	2.5696461	2.5696417

Table 4.20: **Comparison between HF and DHF results for $\langle r \rangle$ using different nuclear distribution charge for Sb-atom**

The radial expectation value $\langle r \rangle$ using different Basis set in HF and DHF for antimony atom					
Spinor	$\langle r \rangle$ $(a.u)$ by Charlotte	$\langle r \rangle$ $(a.u)$ -Ourwork-HF-point model using Dunning basis set	$\langle r \rangle$ $(a.u)$ -Ourwork-HF-Gaussain model using Dunning basis set	$\langle r \rangle$ $(a.u)$ -Ourwork-DHF-point model using Dyall basis set	$\langle r \rangle$ $(a.u)$ -Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.28816	0.029815912	0.029816733	0.028413134	0.028414991
$2s_{1/2}$	0.128494	0.12849379	0.1284957	0.12203233	0.1220369
$2p_{1/2}$				0.10336125	0.10336123
$2p_{3/2}$	0.109749	0.10974911	0.10974905	0.10879436	0.1087942
$3s_{1/2}$	0.342004	0.34200314	0.34200702	0.32854881	0.3285581
$3p_{1/2}$				0.31973849	0.31973826
$3p_{3/2}$	0.333323	0.33332336	0.33332315	0.33068608	0.33068554
$4s_{1/2}$	0.821515	0.82150245	0.82151084	0.79325324	0.7932734
$3d_{3/2}$				0.30234486	0.30234423
$3d_{5/2}$	0.304568	0.30456666	0.30456642	0.30586094	0.30586032
$4p_{1/2}$				0.83674705	0.83674608
$4p_{3/2}$	0.867077	0.8673444	0.86734372	0.86368613	0.86368432
$5s_{1/2}$	2.390167	2.3858973	2.3859274	2.2928933	2.292968
$4d_{3/2}$				1.0165963	1.016592
$4d_{5/2}$	1.016401	1.0161527	1.0161511	1.0297216	1.0297172
$5p_{1/2}$				2.8456867	2.8456708
$5p_{3/2}$	2.901138	2.9518812	2.9518731	2.9688872	2.9688645

Table (4.21) shows comparison for the radial expectation value $\langle r \rangle$ between HF level and DHF level for bismuth. Using two different nuclear charge distribution models. The results our obtained comparing with Charlotte, results [46].

Table 4.21: **Comparison between HF and DHF results for$\langle r \rangle$ using different nuclear distribution charge for Bi-atom**

The radial expectation value $\langle r \rangle$ using different Basis set in HF and DHF for bismuth atom					
Spinor	$\langle r \rangle$ (a.u) by Charlott	$\langle r \rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.018233	0.018232761	0.018234574	0.015780291	0.015793731
$2s_{1/2}$	0.076596	0.076595502	0.076599516	0.065716919	0.065752034
$2p_{1/2}$				0.053955292	0.0539579
$2p_{3/2}$	0.064750	0.064750493	0.064750414	0.062962803	0.062961921
$3s_{1/2}$	0.192187	0.19218713	0.19219464	0.17067767	0.17074399
$3p_{1/2}$				0.16151088	0.16151529
$3p_{3/2}$	0.183033	0.1830335	0.18303326	0.17783421	0.17783158
$4s_{1/2}$	0.417902	0.41790175	0.41791632	0.053955292	0.37675449
$3d_{3/2}$				0.015780291	0.15463153
$3d_{5/2}$	0.159629	0.15962895	0.15962871	0.065716919	0.15957658
$4p_{1/2}$				0.062962803	0.37801084
$4p_{3/2}$	0.420547	0.42054786	0.42054728	0.17067767	0.41100553
$5s_{1/2}$	0.930093	0.93008302	0.93011516	0.84039171	0.84068511
$4d_{3/2}$				0.16151088	0.41503495
$4d_{5/2}$	0.423968	0.42396749	0.42396669	0.17783421	0.42583227
$5p_{1/2}$				0.89564719	0.89566224
$5p_{3/2}$	0.994107	0.99443621	0.99443415	0.98011627	0.98008874
$6s_{1/2}$	2.543441	2.5393481	2.539464	2.2417491	2.2428653
$4f_{5/2}$				0.43646733	0.4364543
$4f_{7/2}$	0.430420	0.43041781	0.43041664	0.4424149	0.44240174
$5d_{3/2}$				1.2012479	1.2011784
$5d_{5/2}$	1.204947	1.2046218	1.2046158	1.2439741	1.2438985
$6p_{1/2}$				2.7802113	2.7801622
$6p_{3/2}$	3.084795	3.1365459	3.1365184	3.1865734	3.1861687

Table (4.22) shows comparison for the radial expectation value between HF level and DHF level for ununipentum atom.

Table 4.22: **Comparison between HF and DHF results for $\langle r \rangle$ using different nuclear distribution charge for Uup-atom**

The radial expectation value $\langle r \rangle$ using different Basis set in HF and DHF for ununipentum atom				
Spinor	$\langle r \rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\langle r \rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.013129526	0.013132536	0.0091796002	0.0093155189
$2s_{1/2}$	0.054498294	0.054504804	0.037747737	0.038157168
$2p_{1/2}$			0.029233786	0.029334117
$2p_{3/2}$	0.045866295	0.045866203	0.043274943	0.043264269
$3s_{1/2}$	0.13335673	0.13336837	0.10087824	0.10164956
$3p_{1/2}$			0.093496607	0.09368931
$3p_{3/2}$	0.12589836	0.1258981	0.11847085	0.11843944
$4s_{1/2}$	0.27329761	0.2733178	0.21699424	0.21834565
$3d_{3/2}$			0.10094203	0.10091404
$3d_{5/2}$	0.10828753	0.10828728	0.1075556	0.10752876
$4p_{1/2}$			0.21325374	0.21358501
$4p_{3/2}$	0.27027642	0.27027582	0.2576934	0.25761618
$5s_{1/2}$	0.53007501	0.5301112	0.43002503	0.43251093
$4d_{3/2}$			0.2489391	0.24886099
$4d_{5/2}$	0.26141193	0.26141122	0.26052017	0.26044253
$5p_{1/2}$			0.43789333	0.43850097
$5p_{3/2}$	0.54167863	0.54167725	0.52270075	0.52249432
$6s_{1/2}$	1.090516	1.0905968	0.86744182	0.87326472
$4f_{5/2}$			0.23962001	0.23954063
$4f_{7/2}$	0.23975801	0.23975727	0.24497671	0.24489774
$5d_{3/2}$			0.54992911	0.54968884
$5d_{5/2}$	0.56897578	0.56897368	0.57443725	0.57419332
$6p_{1/2}$			0.92297806	0.92450201
$6p_{3/2}$	1.169189	1.1691844	1.145176	1.1442491
$7s_{1/2}$	2.8006744	2.8009612	2.0712314	2.0919357
$5f_{5/2}$			0.65073705	0.65035196
$5f_{7/2}$	0.63480692	0.63480344	0.66557784	0.66518347
$6d_{3/2}$			1.4147888	1.4129862
$6d_{5/2}$	1.4243698	1.4243548	1.5111582	1.509236
$7p_{1/2}$			2.4979793	2.5041922
$7p_{3/2}$	3.4448006	3.4447367	3.6225641	3.6095804

Table (4.23) explain comparison for the radial expectation values $\langle r^2 \rangle$ between HF level and DHF level for nitrogen atom . Using different nuclear charge distribution models. The results from our obtained comparing with Charlotte, results [46]. We can see, the mean radius of a spinors decreased due to relativistic effects.

Table 4.23: **Comparison between HF and DHF results for $\langle r^2 \rangle$ using different nuclear distribution charge for N-atom**

The radial expectation value $\langle r^2 \rangle$(a.u.) using different basis set in HF and DHF for nitrogen atom

Spinor	$\langle r^2 \rangle$ (a.u) by Charlott [46]	$\langle r^2 \rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\langle r^2 \rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\langle r^2 \rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\langle r^2 \rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.070265	0.070235735	0.070235755	0.070137107	0.070137128
$2s_{1/2}$	2.149438	2.1294117	2.1294121	2.1261908	2.1261912
$2p_{1/2}$				2.7044179	2.7044177
$2p_{3/2}$	2.547658	2.7071583	2.707158	2.7091717	2.7091715

Table (4.24) shows comparison of the radial expectation values $\langle r^2 \rangle$ between HF level and DHF level for phosphorus atom . Using different nuclear charge distribution models. The results from our obtained comparing with Charlotte, results [46].

Table 4.24: **Comparison between HF and DHF results for $\langle r^2 \rangle$ for different nuclear distribution charge for P-atom**

The radial expectation value $\langle r^2 \rangle$ using different Basis set in HF and DHF for phosphors atom

Spinor	$\langle r^2 \rangle$ (a.u) by Charlott	$\langle r^2 \rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\langle r^2 \rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\langle r^2 \rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\langle r^2 \rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.014488	0.014488142	0.014488169	0.014391216	0.014391246
$2s_{1/2}$	0.315921	0.31585463	0.315855	0.31358086	0.31358126
$2p_{1/2}$				0.28990962	0.28990956
$2p_{3/2}$	0.291798	0.29206497	0.29206492	0.29230493	0.29230487
$3s_{1/2}$	4.347115	4.3249126	4.3249166	4.3012872	4.3012916
$3p_{1/2}$				6.6659403	6.6659377
$3p_{3/2}$	6.389641	6.6944134	6.694411	6.7119714	6.7119688

Table (4.25) and Table (4.26) shows comparison of the radial expectation values $\left\langle r^2 \right\rangle$ between HF level and DHF level for arsenic and antimony atoms respectively. The results from our obtained comparing with Charlotte, results [46].

Table 4.25: **Comparison between HF and DHF results for $\left\langle r^2 \right\rangle$ using different nuclear distribution charge for As-atom**

The radial expectation value $\left\langle r^2 \right\rangle$ using different basis set in HF and DHF for arsenic atom					
Spinor	$\left\langle r^2 \right\rangle$ (a.u) by Charlott	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.002879	0.002879472	0.0028795184	0.0027840833	0.0027841489
$2s_{1/2}$	0.049964	0.049963604	0.049964076	0.048088887	0.04808957
$2p_{1/2}$				0.037449585	0.037449559
$2p_{3/2}$	0.039071	0.039071229	0.039071206	0.038899067	0.038899033
$3s_{1/2}$	0.422160	0.4221415	0.42214489	0.40814975	0.40815467
$3p_{1/2}$				0.43545812	0.43545773
$3p_{3/2}$	0.450758	0.45105381	0.4510535	0.44951933	0.44951886
$4s_{1/2}$	4.747515	4.7266865	4.7267256	4.5780971	4.5781547
$3d_{3/2}$				0.55724402	0.55724284
$3d_{5/2}$	0.556645	0.55630501	0.55630424	0.5649068	0.5649056
$4p_{1/2}$				7.5012469	7.5012219
$4p_{3/2}$	7.371548	7.7156661	7.7156481	7.7753666	7.7753384

Table 4.26: **Comparison between HF and DHF results for $\left\langle r^2 \right\rangle$ using different nuclear distribution charge for Sb-atom**

The radial expectation value $\left\langle r^2 \right\rangle$ using different basis set in HF and DHF for antimony atom					
Spinor	$\left\langle r^2 \right\rangle$ (a.u) by Charlott [46]	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.001189	0.0011891717	0.0011892319	0.0010934519	0.0010935805
$2s_{1/2}$	0.019398	0.019397915	0.01939848	0.017625108	0.017626388
$2p_{1/2}$				0.013139265	0.013139256
$2p_{3/2}$	0.014649	0.01464897	0.014648953	0.014429038	0.014428995
$3s_{1/2}$	0.133489	0.13348854	0.13349155	0.12350818	0.12351509
$3p_{1/2}$				0.11878488	0.1187847
$3p_{3/2}$	0.128664	0.12866391	0.12866375	0.12686495	0.12686453
$4s_{1/2}$	0.761324	0.76129722	0.76131272	0.71050186	0.71053781
$3d_{3/2}$				0.10830341	0.10830296
$3d_{5/2}$	0.109644	0.10964274	0.10964256	0.11069274	0.11069229
$4p_{1/2}$				0.79808446	0.79808242
$4p_{3/2}$	0.855986	0.8566607	0.85665928	0.8503251	0.85032131
$5s_{1/2}$	6.507030	6.4841073	6.4842685	5.9970549	5.9974401
$4d_{3/2}$				1.2149269	1.214916
$4d_{5/2}$	1.212440	1.2116961	1.2116919	1.246746	1.2467346
$5p_{1/2}$				9.3767464	9.3766313
$5p_{3/2}$	9.668054	10.073235	10.073176	10.213168	10.213

Table (4.27) shows comparison between of the radial expectation values $\left\langle r^2 \right\rangle$ between HF level and DHF level for bismuth atom. The results from our obtained comparing with Charlotte, results [46].

Table 4.27: **Comparison between HF and DHF results for $\left\langle r^2 \right\rangle$ using different nuclear distribution charge for Bi-atom**

The radial expectation value $\left\langle r^2 \right\rangle$ using different basis set in HF and DHF for bismuth atom					
Spinor	$\left\langle r^2 \right\rangle$ (a.u) by Charlott [46]	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.000444	0.00044418449	0.00044426559	0.00034580865	0.00034632056
$2s_{1/2}$	0.006876	0.0068755206	0.0068762256	0.0051797701	0.0051850201
$2p_{1/2}$				0.0036527604	0.0036530563
$2p_{3/2}$	0.005075	0.0050747218	0.0050747093	0.0048293534	0.0048292177
$3s_{1/2}$	0.042089	0.042089014	0.042092278	0.033480075	0.033505608
$3p_{1/2}$				0.030491001	0.030492531
$3p_{3/2}$	0.038725	0.03872463	0.038724531	0.036755386	0.036754287
$4s_{1/2}$	0.196495	0.19649417	0.19650786	0.16015019	0.16025817
$3d_{3/2}$				0.028076555	0.028075616
$3d_{5/2}$	0.029725	0.029725049	0.029724962	0.029773422	0.029772471
$4p_{1/2}$				0.16260403	0.1626103
$4p_{3/2}$	0.200415	0.20041587	0.2004153	0.19196789	0.19196126
$5s_{1/2}$	0.966119	0.96609629	0.96616283	0.79055793	0.79110502
$4d_{3/2}$				0.19885232	0.19884376
$4d_{5/2}$	0.206808	0.20680654	0.20680574	0.20909878	0.20908989
$5p_{1/2}$				0.90361369	0.90364078
$5p_{3/2}$	1.110609	1.1115343	1.1115293	1.0824889	1.0824228
$6s_{1/2}$	7.330088	7.3070578	7.3077156	5.7125757	5.7182223
$4f_{5/2}$				0.22683601	0.22682178
$4f_{7/2}$	0.219561	0.21955829	0.21955704	0.23295964	0.23294505
$5d_{3/2}$				1.6655842	1.6653779
$5d_{5/2}$	1.668392	1.6672832	1.6672654	1.7877966	1.7875647
$6p_{1/2}$				8.907309	8.9068736
$6p_{3/2}$	10.859224	11.295326	11.29511	11.742169	11.738941

Table (4.28) shows comparison between of the radial expectation values $\left\langle r^2 \right\rangle$ between HF level and DHF level for uniunpentum atom. The results from our obtained comparing with Charlotte, results [46].

Table 4.28: **Comparison between HF and DHF results for $\left\langle r^2 \right\rangle$ using different nuclear distribution charge for Uup-atom**

The radial expectation value $\left\langle r^2 \right\rangle$ using different basis set in HF and DHF for uniunpentum atom				
Spinor	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-HF-point model using Dyall basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-HF-Gaussain model using Dyall basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\left\langle r^2 \right\rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	0.00023020982	0.00023030672	0.00012476292	0.00012783119
$2s_{1/2}$	0.0034767675	0.0034775796	0.0017686493	0.0018041273
$2p_{1/2}$			0.0011379202	0.0011444508
$2p_{3/2}$	0.0025407228	0.0025407125	0.0022913302	0.0022902044
$3s_{1/2}$	0.020244866	0.020248369	0.01184166	0.012017581
$3p_{1/2}$			0.010392578	0.010432377
$3p_{3/2}$	0.018300174	0.018300097	0.016395209	0.016386507
$4s_{1/2}$	0.08392963	0.083941997	0.053417037	0.05407387
$3d_{3/2}$			0.011986442	0.011979822
$3d_{5/2}$	0.013603444	0.013603381	0.013480584	0.013473829
$4p_{1/2}$			0.052060599	0.052216883
$4p_{3/2}$	0.082637528	0.082637152	0.075588958	0.07554326
$5s_{1/2}$	0.31302626	0.31306911	0.20703427	0.20940676
$4d_{3/2}$			0.071455093	0.071410127
$4d_{5/2}$	0.078226681	0.078226255	0.078027519	0.077980942
$5p_{1/2}$			0.21563379	0.21621871
$5p_{3/2}$	0.3281479	0.32814616	0.3065967	0.30635
$6s_{1/2}$	1.3189869	1.3191812	0.83941396	0.85059181
$4f_{5/2}$			0.066131272	0.066086842
$4f_{7/2}$	0.065867882	0.065867471	0.068968106	0.068922924
$5d_{3/2}$			0.34245775	0.34215549
$5d_{5/2}$	0.36521874	0.36521599	0.37328571	0.37296746
$6p_{1/2}$			0.95426788	0.95734182
$6p_{3/2}$	1.5228587	1.5228453	1.4694408	1.4669412
$7s_{1/2}$	8.8340659	8.8358513	4.8446051	4.9425795
$5f_{5/2}$			0.4894226	0.48882957
$5f_{7/2}$	0.46358199	0.46357677	0.51197351	0.51134987
$6d_{3/2}$			2.2863833	2.2802817
$6d_{5/2}$	2.2988022	2.2987503	2.6131314	2.6061828
$7p_{1/2}$			7.1249429	7.1600044
$7p_{3/2}$	13.538533	13.537982	15.191185	15.077022

Table(4.29) and Table (4.30) shows comparison between of the radial expectation values $\left\langle r^{-1} \right\rangle$ between HF level and DHF level for nitrogen and phosphorus atoms, respectively. The results from our obtained comparing with Charlotte, results [46].

Table 4.29: **Comparison between HF and DHF results for $\langle r^{-1}\rangle$ using different nuclear distribution charge for N-atom**

The radial expectation value $\langle r^{-1}\rangle$ (a.u) using different basis set in HF and DHF for nitrogen atom

Spinor	$\langle r^{-1}\rangle$ (a.u) Charlotte[46]	$\langle r^{-1}\rangle$ (a.u)-Ourwork-HF-point model/ Dunning basis set	$\langle r^{-1}\rangle$ (a.u)-Ourwork-HF-Gaussain model/ Dunning basis set	$\langle r^{-1}\rangle$ (a.u)-Ourwork-DHF-point model/ Dyall basis set	$\langle r^{-1}\rangle$ (a.u)-Ourwork-DHF-Gaussain mode/ Dyall basis set
$1s_{1/2}$	6.65324	6.6538794	6.6538779	6.6621081	6.6621065
$2s_{1/2}$	1.07818	1.0831782	1.083178	1.0845192	1.0845191
$2p_{1/2}$				0.94287863	0.94287867
$2p_{3/2}$	0.95769	0.94207685	0.94207689	0.94184289	0.94184293

Table 4.30: **Comparison between HF and DHF results for $\langle r^{-1}\rangle$ using different nuclear distribution charge for P-atom**

The radial expectation value $\langle r^{-1}\rangle$ using different Basis set in HF and DHF for phosphors atom

Spinor	$\langle r^{-1}\rangle$ (a.u) by Charlott [46]	$\langle r^{-1}\rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\langle r^{-1}\rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\langle r^{-1}\rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\langle r^{-1}\rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	14.57355	14.573599	14.573577	14.659129	14.659103
$2s_{1/2}$	2.83171	2.8319558	2.8319536	2.850073	2.8500704
$2p_{1/2}$				2.7216195	2.7216198
$2p_{3/2}$	2.70627	2.7058874	2.7058876	2.7060096	2.7060099
$3s_{1/2}$	0.69473	0.69672375	0.69672336	0.69949768	0.69949724
$3p_{1/2}$				0.56474717	0.56474727
$3p_{3/2}$	0.57015	0.56305764	0.56305773	0.56255485	0.56255496

Table (4.31) and Table (4.32) shows comparison between of the radial expectation values $\langle r^{-1}\rangle$ between HF level and DHF level for arsenic and antimony atoms respectively. The results from our obtained comparing with Charlotte, results [46].

Table 4.31: **Comparison between HF and DHF results for $\left\langle r^{-1}\right\rangle$ using different nuclear distribution charge for As-atom**

The radial expectation value $\left\langle r^{-1}\right\rangle$ using different basis set in HF and DHF for arsenic atom

Spinor	$\left\langle r^{-1}\right\rangle$ (a.u) by Charlotte [46]	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	32.50504	32.505052	32.50463	33.474142	33.473378
$2s_{1/2}$	7.19237	7.1923916	7.1923431	7.4460108	7.4459195
$2p_{1/2}$				7.3752342	7.3752363
$2p_{3/2}$	7.13463	7.1346293	7.1346314	7.164172	7.1641751
$3s_{1/2}$	2.33228	2.3323115	2.3322998	2.3950766	2.3950559
$3p_{1/2}$				2.264621	2.2646218
$3p_{3/2}$	2.20711	2.2067441	2.2067448	2.2164539	2.216455
$4s_{1/2}$	0.63755	0.63909921	0.63909611	0.65243815	0.65243311
$3d_{3/2}$				1.921065	1.9210667
$3d_{5/2}$	1.91776	1.9179967	1.9179978	1.9074214	1.907423
$4p_{1/2}$				0.51249971	0.51250042
$4p_{3/2}$	0.50999	0.50356505	0.50356555	0.50268002	0.50268079

Table 4.32: **Comparison between HF and DHF results for $\left\langle r^{-1}\right\rangle$using different nuclear distribution charge for Sb-atom**

The radial expectation value $\left\langle r^{-1}\right\rangle$ using different basis set in HF and DHF for antimony atom

Spinor	$\left\langle r^{-1}\right\rangle$ (a.u) by Charlotte [46]	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	50.47339	50.473394	50.471325	54.331316	54.323984
$2s_{1/2}$	11.57531	11.57532	11.575075	12.648484	12.647496
$2p_{1/2}$				12.59093	12.590915
$2p_{3/2}$	11.55263	11.552633	11.552639	11.695378	11.695395
$3s_{1/2}$	4.20963	4.2096374	4.2095752	4.5000984	4.4998665
$3p_{1/2}$				4.3986384	4.398637
$3p_{3/2}$	4.12293	4.1229239	4.1229265	4.1823082	4.182315
$4s_{1/2}$	1.66186	1.6618819	1.6618619	1.7480219	1.7479559
$3d_{3/2}$				4.0183532	4.0183612
$3d_{5/2}$	3.97362	3.9736304	3.9736334	3.9620995	3.9621073
$4p_{1/2}$				1.6324101	1.6324109
$4p_{3/2}$	1.55376	1.5533881	1.5533892	1.5673909	1.5673939
$5s_{1/2}$	0.53214	0.53325162	0.53324375	0.56035518	0.5603323
$4d_{3/2}$				1.3004467	1.3004519
$4d_{5/2}$	1.29566	1.2958777	1.2958797	1.2816701	1.2816752
$5p_{1/2}$				0.44817472	0.44817674
$5p_{3/2}$	0.43378	0.42886936	0.42887038	0.42797671	0.42797951

Table (4.33) shows comparison between of the radial expectation values $\left\langle r^{-1}\right\rangle$ between HF level and DHF level for bismuth atom. The results from our obtained comparing with Charlotte, results [46].

Table 4.33: **Comparison between HF and DHF results for $\left\langle r^{-1}\right\rangle$using different nuclear distribution charge for Bi-atom**

The radial expectation value $\left\langle r^{-1}\right\rangle$ using different basis set in HF and DHF for bismuth atom					
Spinor	$\left\langle r^{-1}\right\rangle$ (a.u) by Charlott [48]	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-HF-point model using Dunning basis set	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-HF-Gaussain model using Dunning basis set	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\left\langle r^{-1}\right\rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	82.44526	82.445261	82.433058	103.40544	103.16879
$2s_{1/2}$	19.47367	19.473674	19.472197	25.621494	25.579814
$2p_{1/2}$				25.492566	25.488533
$2p_{3/2}$	19.48264	19.482642	19.482666	20.232288	20.232575
$3s_{1/2}$	7.60157	7.601575	7.6011722	9.3992803	9.388873
$3p_{1/2}$				9.2868081	9.2857119
$3p_{3/2}$	7.54562	7.5456171	7.5456269	7.9154819	7.9155985
$4s_{1/2}$	3.36363	3.3636386	3.3634939	3.9773022	3.9741684
$3d_{3/2}$				7.7961567	7.7962877
$3d_{5/2}$	7.46834	7.4683434	7.4683542	7.4931312	7.4932489
$4p_{1/2}$				3.8627395	3.8624335
$4p_{3/2}$	3.27571	3.2757056	3.27571	3.4089562	3.4090077
$5s_{1/2}$	1.42219	1.4222049	0.4942788	1.63582	1.6348326
$4d_{3/2}$				3.2095222	3.2095897
$4d_{5/2}$	3.10039	3.100396	3.1004018	3.1040405	3.1041044
$5p_{1/2}$				1.5166225	1.5165458
$5p_{3/2}$	1.32017	1.3198223	1.3198247	1.3541795	1.3542096
$6s_{1/2}$	0.49337	0.49430486	0.4942788	0.57481131	0.57443856
$4f_{5/2}$				2.7683685	2.7684434
$4f_{7/2}$	2.79235	2.7923602	2.7923671	2.7282743	2.7283475
$5d_{3/2}$				1.090407	1.0904661
$5d_{5/2}$	1.07680	1.0770163	1.0770214	1.0483735	1.0484338
$6p_{1/2}$				0.45898247	0.45897853
$6p_{3/2}$	0.40289	0.39850629	0.39850921	0.39637609	0.3964181

Table (4.34) shows comparison between of the radial expectation values $\langle r^{-1} \rangle$ between HF level and DHF level for uninpentum atom. The results from our obtained comparing with Charlotte, results [46].

Table 4.34: **Comparison between HF and DHF results for $\langle r^{-1} \rangle$ using different nuclear distribution charge for Uup-atom**

The radial expectation value $\langle r^{-1} \rangle$ using different basis set in HF and DHF for Uunipentum atom				
Spinor	$\langle r^{-1} \rangle$ (a.u)-Ourwork-HF-point model using Dyall basis set	$\langle r^{-1} \rangle$ (a.u)-Ourwork-HF-Gaussain model using Dyall basis set	$\langle r^{-1} \rangle$ (a.u)-Ourwork-DHF-point model using Dyall basis set	$\langle r^{-1} \rangle$ (a.u)-Ourwork-DHF-Gaussain mode using Dyall basis set
$1s_{1/2}$	114.42865	114.38964	209.31907	199.58879
$2s_{1/2}$	27.407021	27.402256	56.482765	54.011862
$2p_{1/2}$			55.779538	55.077457
$2p_{3/2}$	27.43988	27.439936	29.666562	29.674043
$3s_{1/2}$	11.019803	11.01847	19.352219	18.724111
$3p_{1/2}$			19.070599	18.871243
$3p_{3/2}$	10.983002	10.983025	12.149627	12.152927
$4s_{1/2}$	5.2306864	5.2301905	8.0931133	7.8996009
$3d_{3/2}$			12.023768	12.027196
$3d_{5/2}$	10.945638	10.945663	11.085826	11.088579
$4p_{1/2}$			7.9140604	7.8529661
$4p_{3/2}$	5.1568963	5.1569077	5.6187717	5.6204182
$5s_{1/2}$	2.5932047	2.5929964	3.681542	3.6159538
$4d_{3/2}$			5.4424725	5.4442275
$4d_{5/2}$	5.0270567	5.0270704	5.1053595	5.1068906
$5p_{1/2}$			3.5402234	3.5206097
$5p_{3/2}$	2.5105796	2.5105854	2.676657	2.6776364
$6s_{1/2}$	1.1930215	1.1929202	1.6597404	1.6356449
$4f_{5/2}$			4.8858591	4.8874344
$4f_{7/2}$	4.848579	4.8485933	4.7614332	4.7629168
$5d_{3/2}$			2.47473	2.4758258
$5d_{5/2}$	2.3362415	2.3362502	2.3377796	2.3388013
$6p_{1/2}$			1.5364796	1.5299405
$6p_{3/2}$	1.1059354	1.1059388	1.1539922	1.1548279
$7s_{1/2}$	0.44347959	0.44342716	0.63916057	0.63025309
$5f_{5/2}$			1.9873625	1.9885229
$5f_{7/2}$	2.019385	2.0193957	1.9363584	1.9374819
$6d_{3/2}$			0.92232123	0.92348826
$6d_{5/2}$	0.89960851	0.89961747	0.85532781	0.85643528
$7p_{1/2}$			0.52153114	0.51958695
$7p_{3/2}$	0.35889404	0.35889939	0.34899698	0.35015506

4.7 The Radial Functions and Electron Density Distribution for $1s_{1/2}$

All the orbitals in atom have zero amplitude at the nucleus except for $s-orbital$ which has a cusp of the form $exp(-\zeta r)$. In relativistic calculations $s_{1/2}$ spinor instead has a weak singularity at the nucleus. In atomic calculations one expands the wave function in to a large set of Gaussian basis functions to solve the weak singularity. In our project we adopted two models to describe the nuclear charge distribution; point model and Gaussian distribution model. The figures below provide ground state radial functions of the elements in group15. Fig (4.2) displays the radial function $P_{1s_{1/2}}(r)$ component and $Q_{1s_{1/2}}(r)$ component for $1s_{1/2}$ of nitrogen (Z=7). The Gaussian basis-set type $dyall.2zp$, has $10s$-set contractive functions to describe large component for $1s_{1/2}$spinor and has $6s$-set contractive functions to describe small radial component for $1s_{1/2}$spinor . We see that the small component for nitrogen (Z=7) has small value. This is due to nuclear charge for nitrogen (Z=7) being light .

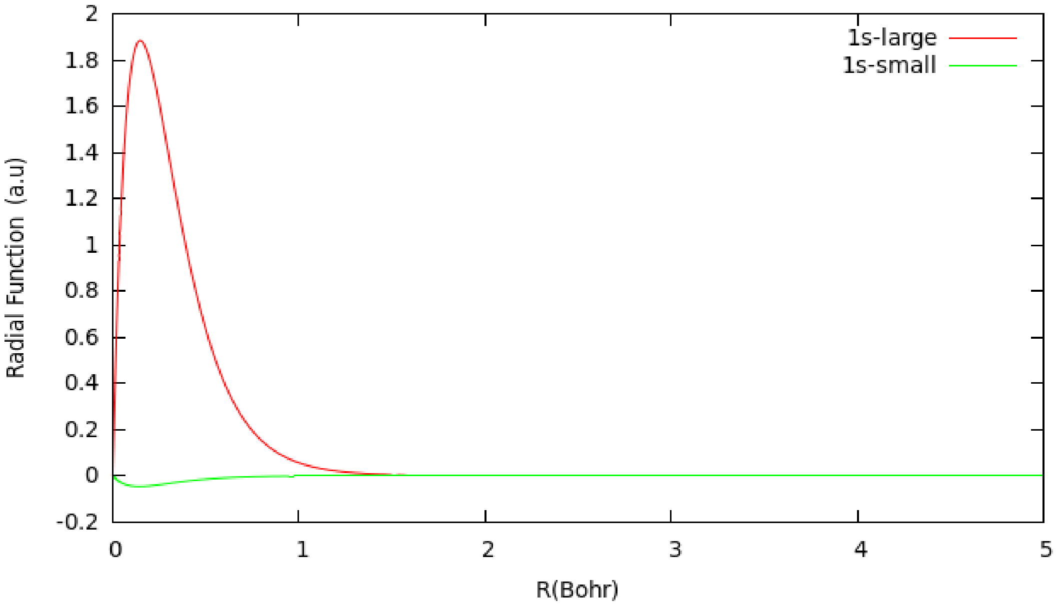


Figure 4.2: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of N-atom using Gaussian dyall-2zp basis sets with Gaussian model**

We see that the radial functions $P_{1s_{1/2}}(r)$ and $Q_{1s_{1/2}}(r)$ take zero values at the origin and the weak singularity at the origin is not visible when adopting the point model, because Z is small in Fig (4.3). The electron density is obtained as the square of the orbital in each of the four-component as $\rho_i(r) = P_i^2(r) + Q_i^2(r)$. The electron density does not possess any nodes, because large component and small component have nodes at different position. Fig (4.4) displays the radial density for $1s_{1/2}$ of the nitrogen atom. The radial density $\rho_{1s_{1/2}}(r)$ approaches values which are very close to zero if $P_{1s_{1/2}}(r)$ is zero, because the radial functions $P_{1s_{1/2}}(r)$ and $Q_{1s_{1/2}}(r)$ take zero values at the origin.

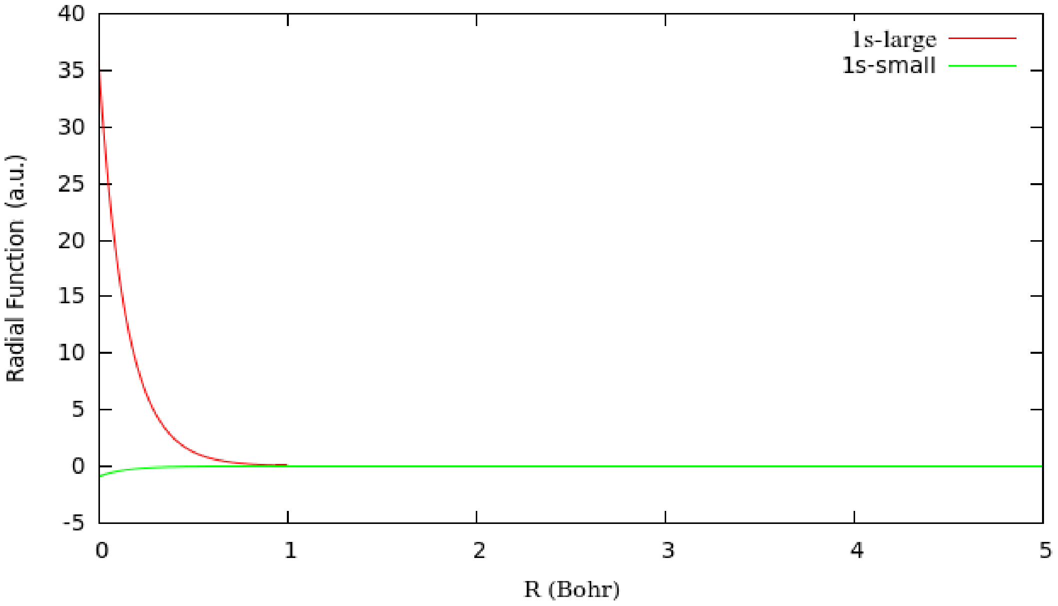


Figure 4.3: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of N-atom using Slater type basis sets with point model**

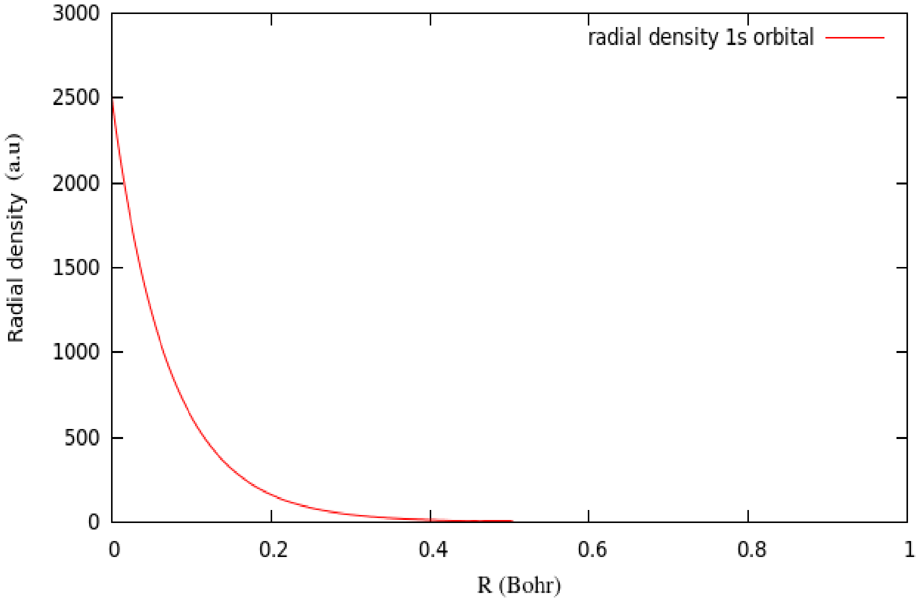


Figure 4.4: **The radial density distribution versus R(Bohr) for $1s_{1/2}$orbital of N-atom using Gaussian model**

Fig (4.5) displays the radial functions $P_{1s_{1/2}}(r)$ and $Q_{1s_{1/2}}(r)$ for $1s_{1/2}$ of the phosphorous atom. The Gaussian basis-set type *dyall.2zp*, has 12s-set contractive functions to describe large component for $1s_{1/2}$spinor, and 8s-set contractive function to describe small component for $1s_{1/2}$spinor. Comparing between Fig (4.2) to Fig (4.5), we see that, there is a little increase in the small radial component of phosphorus when nuclear charge of phosphorus increases relative to nitrogen. Fig (4.6) shows the weak singularity at the origin that becomes visible when we adopt the point model. The radial functions $P_{1s_{1/2}}(r)$ and $Q_{1s_{1/2}}(r)$ do not have zero values at the origin, because of the increase of the nuclear charge for phosphorus relative to nitrogen. Fig (4.7) displays the radial density for $1s_{1/2}$ of the phosphorus atom. The radial density $p_i(r)$ has higher value for phosphorus compared to nitrogen.

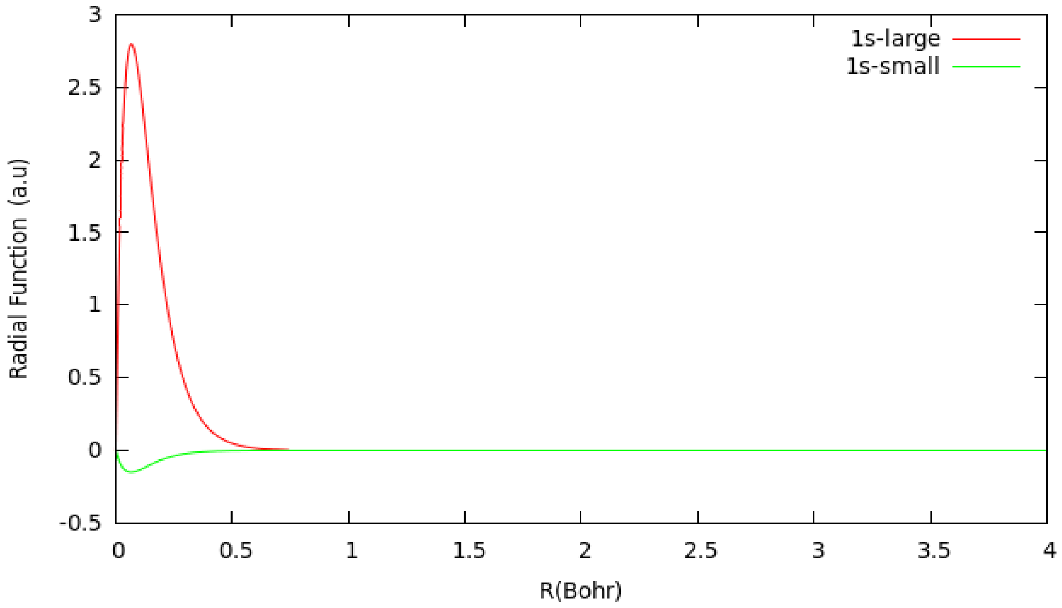


Figure 4.5: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of P-atom using Gaussian dyall-2zp basis sets with Gaussian model**

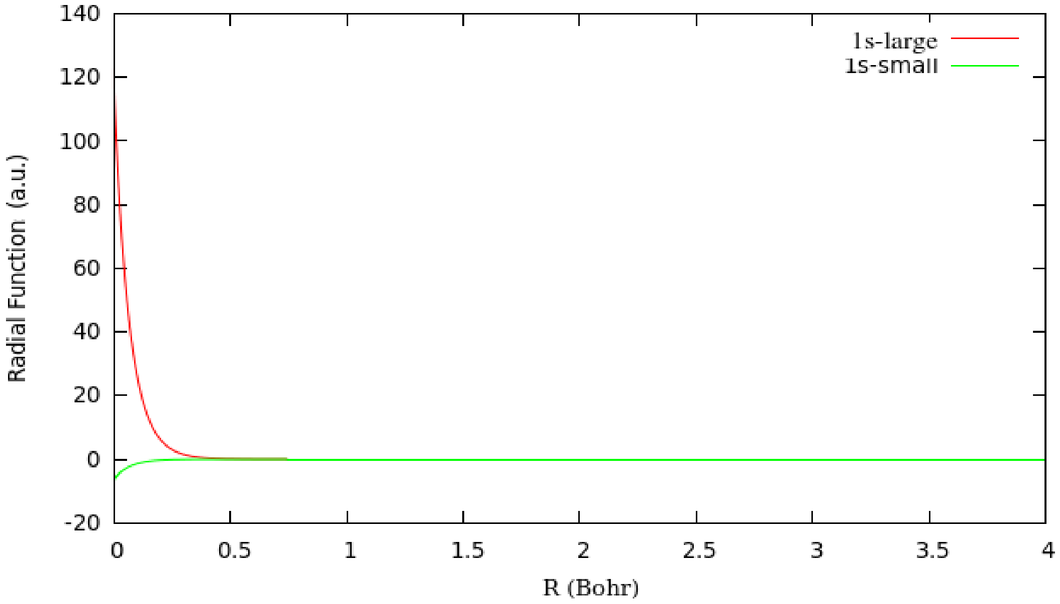


Figure 4.6: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of P-atom using Slater type basis sets with point model**

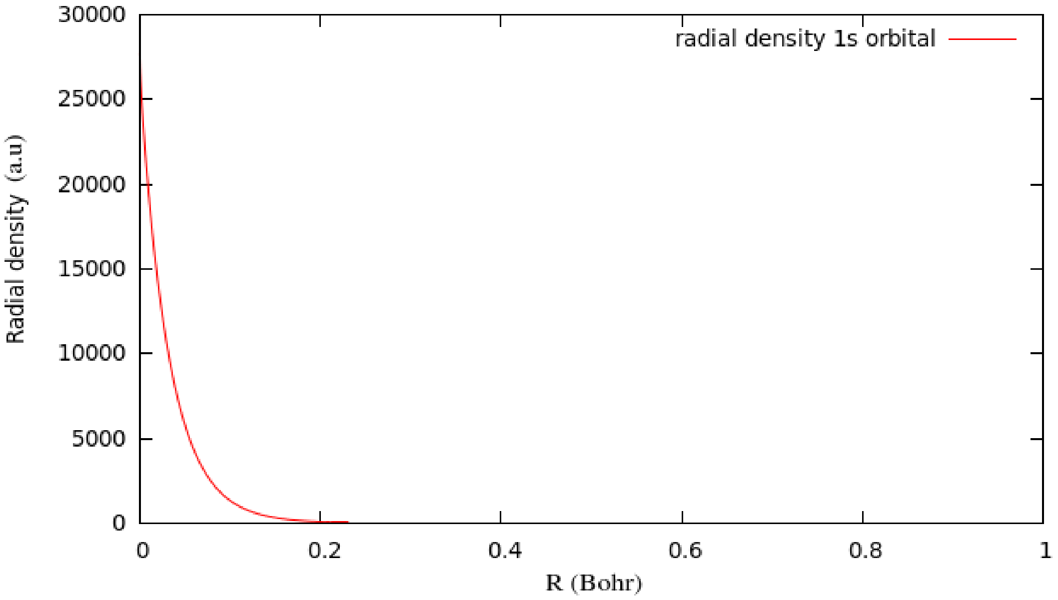


Figure 4.7: **The radial density distribution versus R(Bohr) for $1s_{1/2}$orbital of P-atom using Gaussian model**

Fig (4.8) shows large radial component $P_{1s_{1/2}}(r)$ and small radial component $Q_{1s_{1/2}}(r)$ for $1s_{1/2}$ of arsenic atom. The Gaussian basis-set type *dyall.2zp*, has 15s-set contractive functions to describe large component for $1s_{1/2}$spinor and 11s-set contractive functions to describe small component for $1s_{1/2}$spinor. Comparing between Fig (4.3), Fig (4.5) and Fig (4.8), we notice that there is increase in small component of arsenic atom because of increased in the nuclear charge of arsenic atom relative to nuclear charge of nitrogen and phosphorus atoms, respectively. The singularity behavior at the origin for $1s_{1/2}$ of radial functions $P_{1s_{1/2}}(r)$ and $Q_{1s_{1/2}}(r)$ increases when nuclear charge increases. Fig (4.9) shows the radial functions $P_{1s_{1/2}}(r)$ and $Q_{1s_{1/2}}(r)$ when we adopt the point model for arsenic atom. Fig (4.10) displays the radial density for $1s_{1/2}$ of arsenic atom.

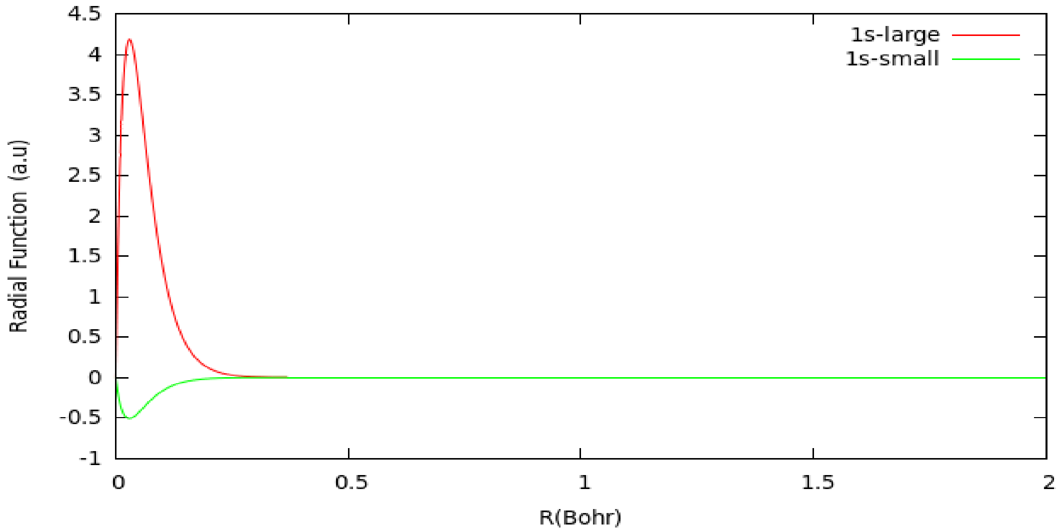


Figure 4.8: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of As-atom using Gaussian dyall-2zp basis sets with Gaussian model**

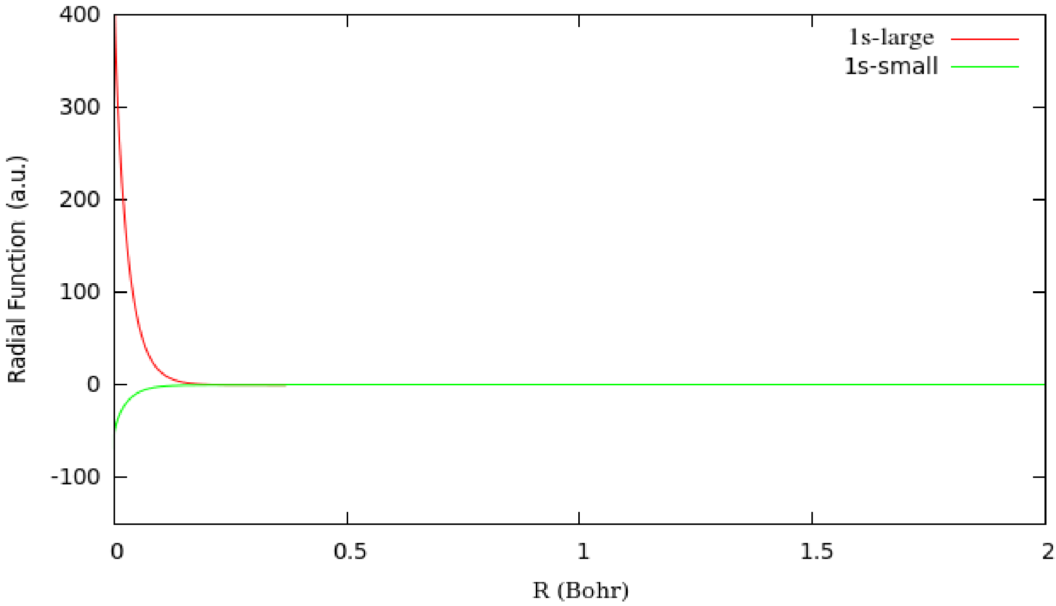


Figure 4.9: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of As-atom using Slater type basis sets with point model**

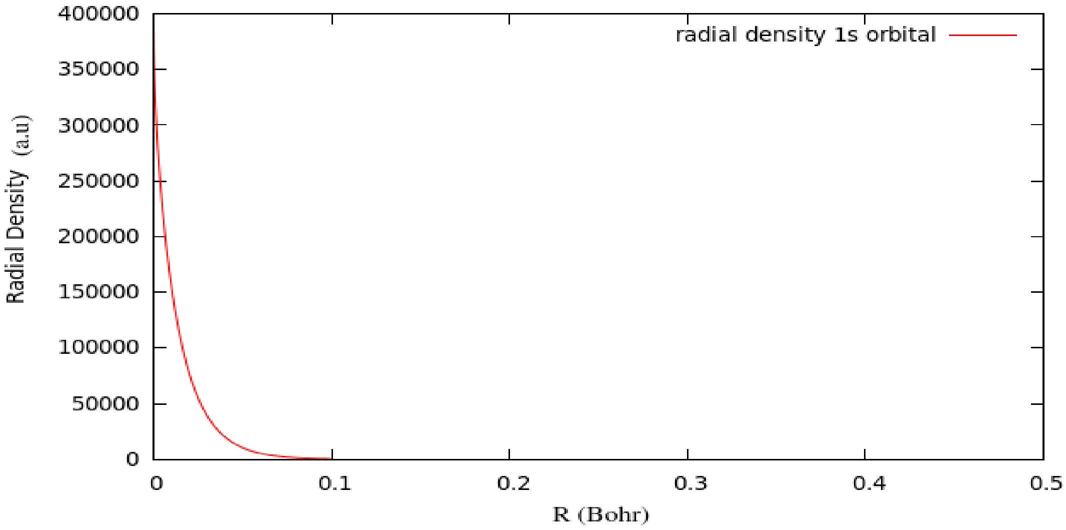


Figure 4.10: **The radial density distribution versus R(Bohr) for $1s_{1/2}$orbital of As-atom using Gaussian model**

Fig (4.11) shows large radial component $P_{1s_{1/2}}(r)$ and small radial component $Q_{1s_{1/2}}(r)$ for $1s_{1/2}$ of antimony atom. The Gaussian basis-set type *dyall.2zp*, has 21s-set contractive functions to describe large component for $1s_{1/2}$spinor and 15s-set contractive function to describe small component for $1s_{1/2}$spinor. In Fig (4.11) the small component is clear increasing due to increased nuclear charge of antimony atom with respect to previous elements. Fig (4.9) shows the singularity behavior at the origin for $1s_{1/2}$ of radial functions $P_{1s_{1/2}}(r)$ and $Q_{1s_{1/2}}(r)$ increases when the nuclear charge increase when we adopt the point model for antimony atom. Fig (4.13) displays the radial density for $1s_{1/2}$ of antimony atom.

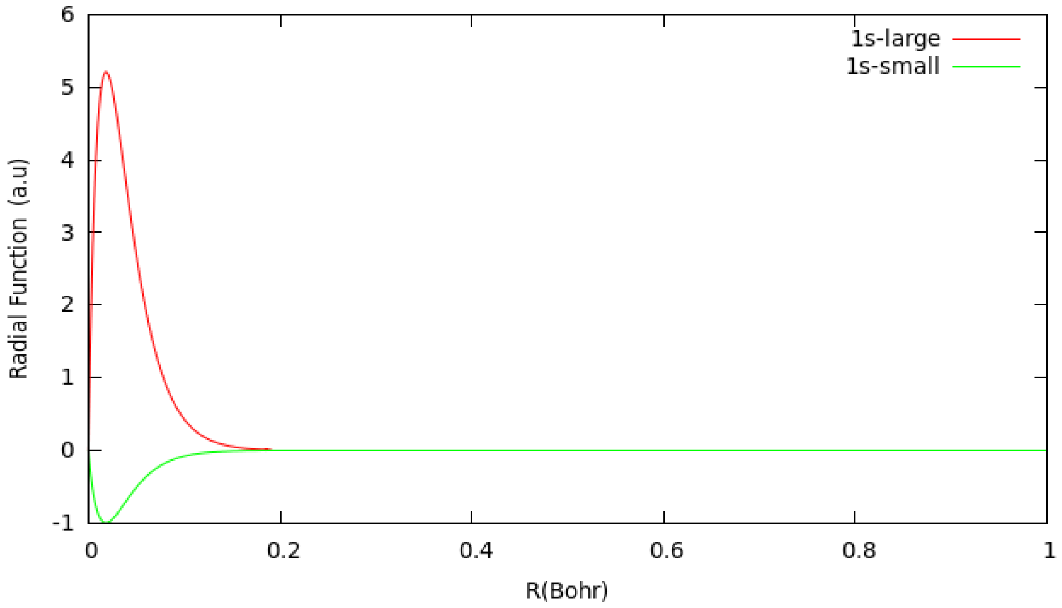


Figure 4.11: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of Sb-atom using Gaussian dyall-2zp basis sets with Gaussian model**

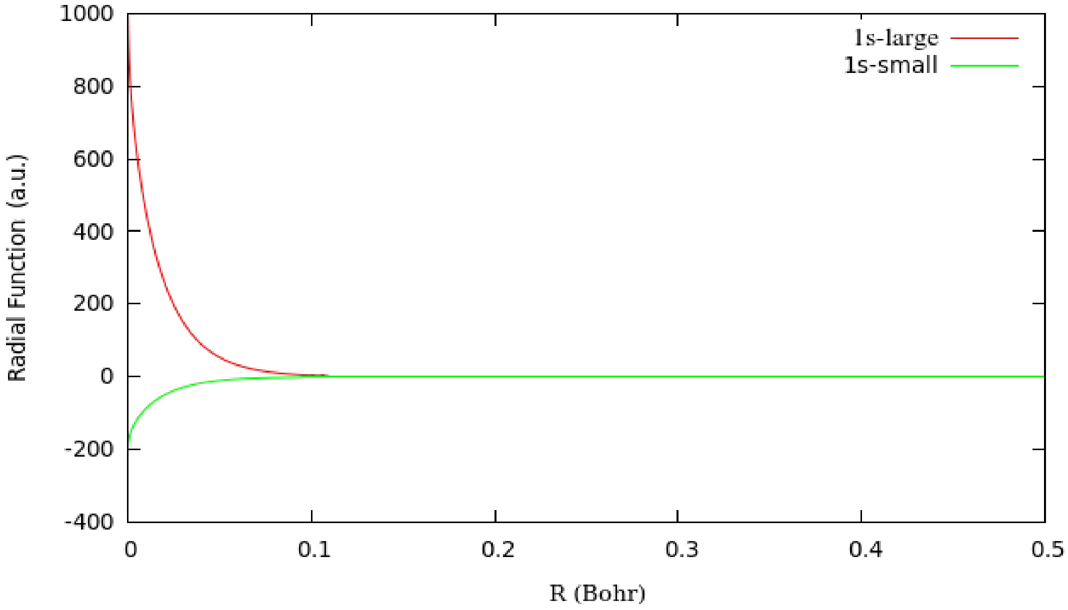


Figure 4.12: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of Sb-atom using Slater type basis sets with point model**

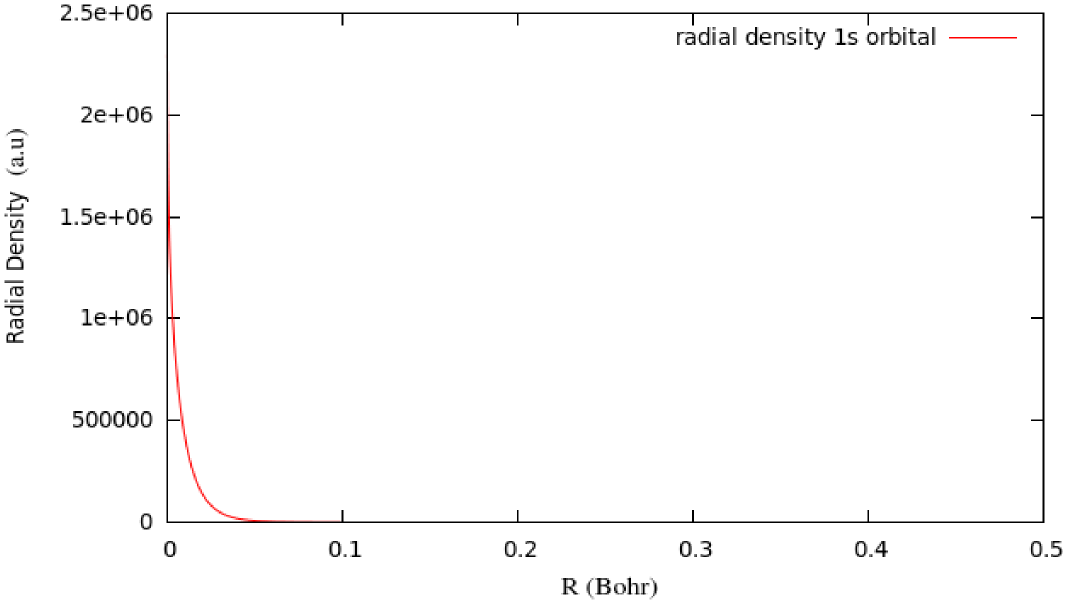


Figure 4.13: **The radial density distribution versus R(Bohr) for $1s_{1/2}$orbital of Sb-atom using Gaussian model**

Fig (4.14) shows large radial component $P_{1s_{1/2}}(r)$ and small radial component $Q_{1s_{1/2}}(r)$ for $1s_{1/2}$ of bismuth. The Gaussian basis-set type *dyall.2zp*, has 24s-set contractive functions to describe large component for $1s_{1/2}$spinor, and 20s-set contractive functions to describe small component for $1s_{1/2}$spinor. In fig (4.14) small component is more increased due to increasing of nuclear charge of bismuth atom with respect to previous elements. Fig (4.15) shows the singularity behavior at the origin for $1s_{1/2}$ of radial functions $P_{1s_{1/2}}(r)$ and $Q_{1s_{1/2}}(r)$, respectively when we adopt the point model. Fig (4.16) displays the radial density for $1s_{1/2}$ of bismuth atom.

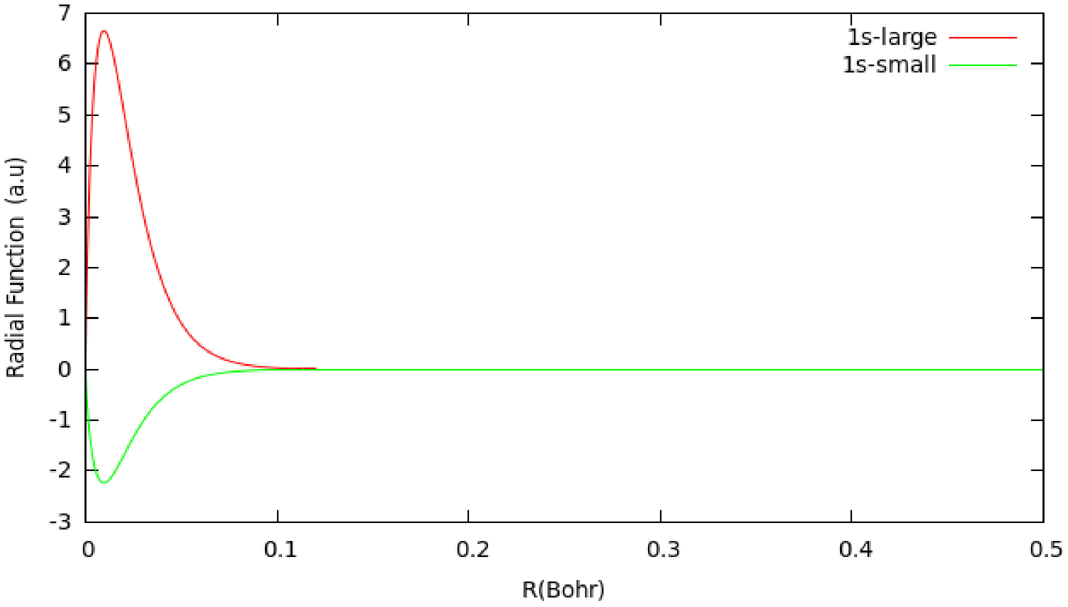


Figure 4.14: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of Bi-atom using Gaussian dyall-2zp basis sets with Gaussian model**

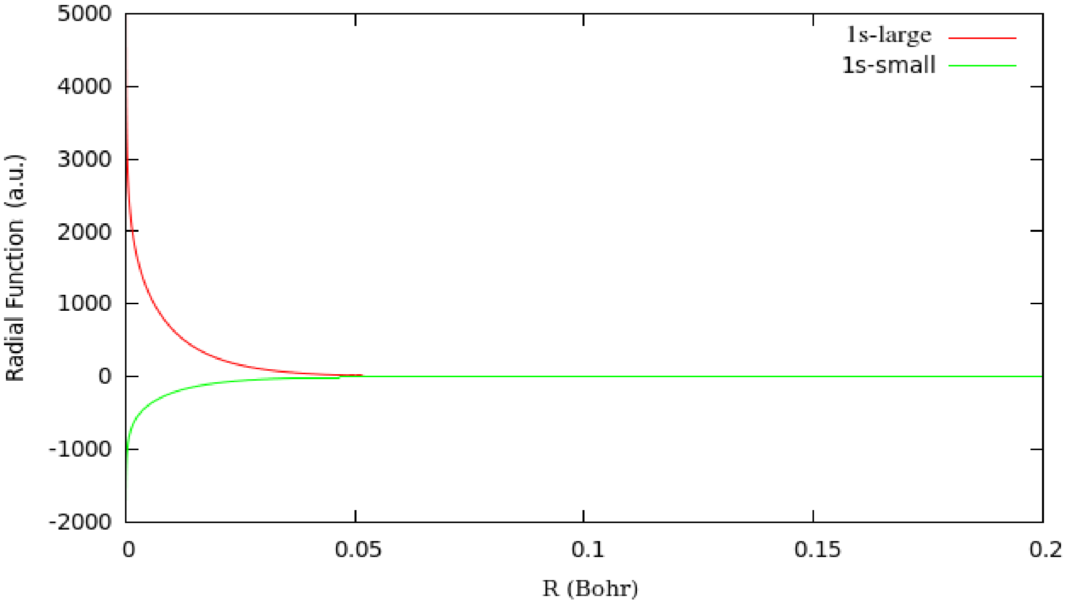


Figure 4.15: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of Bi-atom using Slater type basis sets with point model**

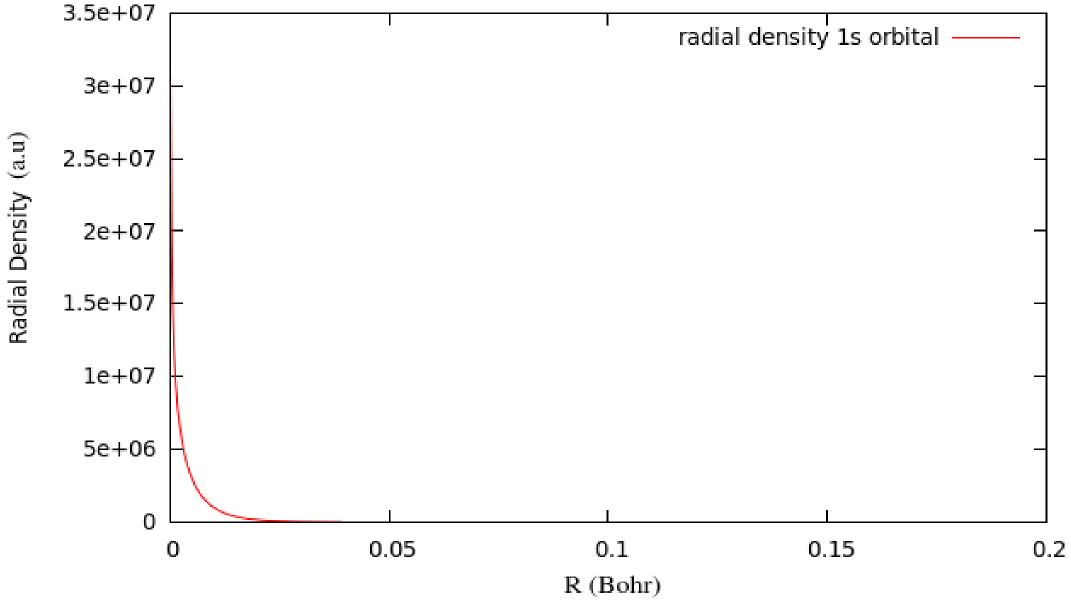


Figure 4.16: **The radial density distribution versus R(Bohr) for $1s_{1/2}$orbital of Bi-atom using Gaussian model**

Fig (4.17) shows large radial component $P_{1s_{1/2}}(r)$ and small radial component $Q_{1s_{1/2}}(r)$ for $1s_{1/2}$ of Uninpentum. The Gaussian basis-set type *dyall.2zp*, has 26s-set contractive functions to describe large component for $1s_{1/2}$spinor and 23s-set contractive functions to describe small component for $1s_{1/2}$spinor. In Fig (4.17) the small component is much like the large component for super heavy atom (uninpentum), because the increased of the nuclear charge(Z=115) relative to previous elements. This means that for super heavy atoms , $Z > 100$, the small component is no longer small. The magnitude of the small component is similar the large component but different sign when $Z = 115$. We also note from Fig (4.17) that only small component gives a significant contribution to the density close to the nucleus. The highly localized small component density in Uup contributes more than the large component for the total density, and majority of this comes from the core-spinors. Fig (4.18) shows the singularity behavior at the origin for $1s_{1/2}$ of radial functions $P_{1s_{1/2}}(r)$ and $Q_{1s_{1/2}}(r)$, respectively when we adopt point model. Fig (4.19) displays the radial density for $1s_{1/2}$ of uninpentum atom.

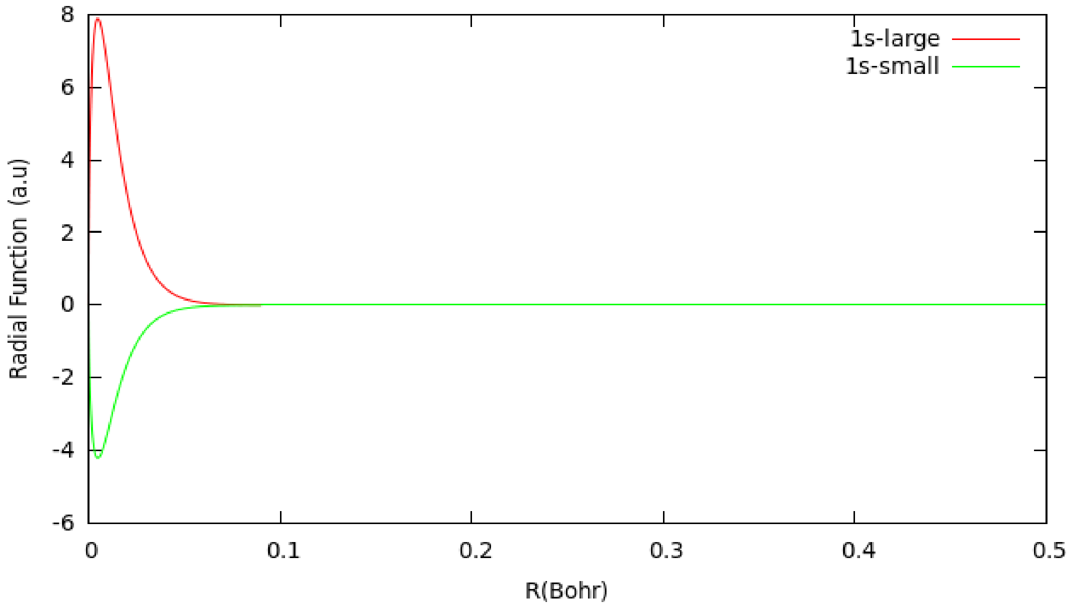


Figure 4.17: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of Uup-atom using Gaussian dyall-2zp basis sets with Gaussian model**

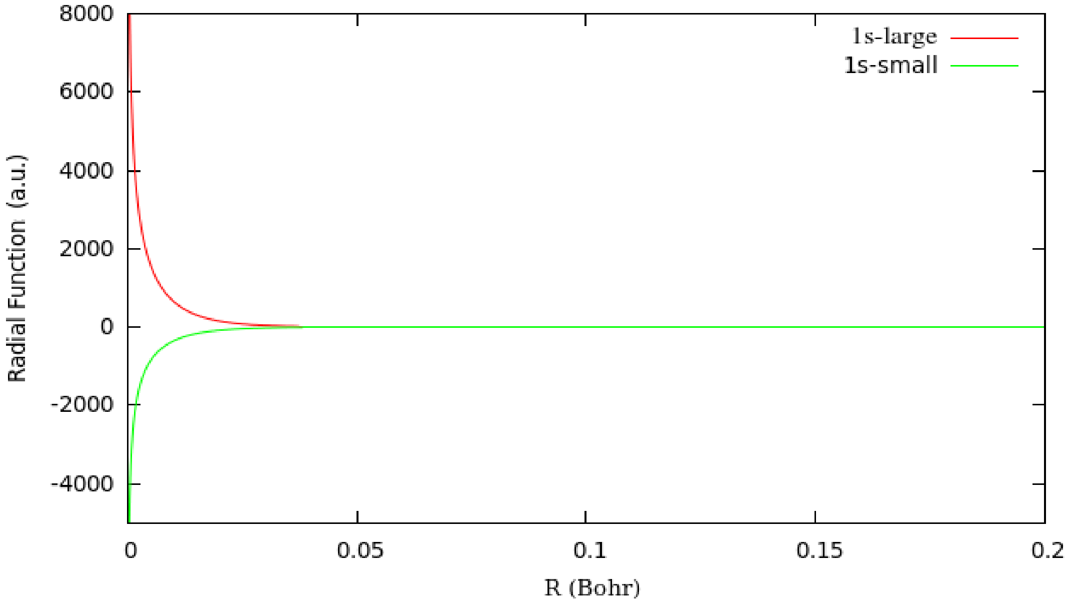


Figure 4.18: **The radial large $P_{1s_{1/2}}(r)$ and small $Q_{1s_{1/2}}(r)$ components in atomic units versus R(Bohr) for $1s_{1/2}$orbital of Uup-atom using Slater type basis sets with point model**

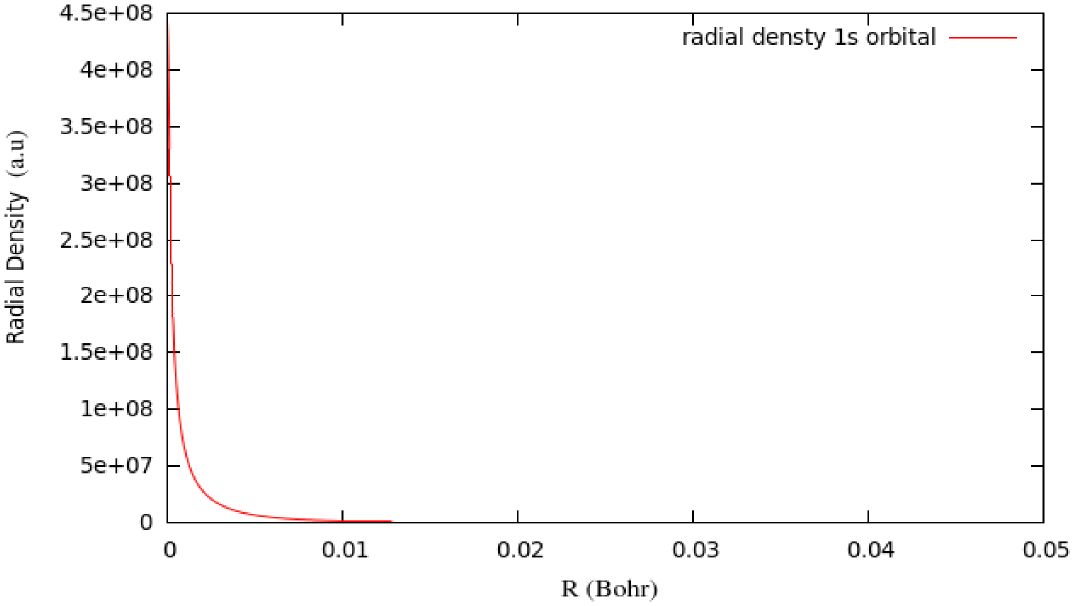


Figure 4.19: **The radial density distribution versus R(Bohr) for $1s_{1/2}$orbital of Uup-atom using Gaussian model**

4.8 Relativistic Radial Functions for All Orbitals of Group15

The group of figures below represent two sets of radial functions, $P_{n\kappa}(r)\, and\, Q_{n\kappa}(r)$, respectively. The electronic wave function of the group15 is obtained by approximating the four component spinor into relativistic Gaussian basis set. The Dirac–Hartree-Fock radial functions of the shells occupied in the ground state are determined for the neutral atoms (group15). The large components of the occupied shells and the small components are depicted in the graphs for each atom. Notic that the number of nodes of the radial functions depend on the quantum numbers. The number of nodes in these functions and also the small components $Q_i(r)$ of a shell i are short-ranged. Moreover, the spin–orbit- coupling induced splitting of the radial shells is visible for the p-shell of group 15. An important aspect of the radial functions of the 4-spinor are the number of (radial) nodes, i.e., the number of positions where these functions are zero. Hence, the number of nodes solely depends on the quantum numbers that are used to classify the spinor. $P_{n\kappa}(r)$ always has$(n{-}l{-}1)$ radial nodes like its non-relativistic analog. However, $Q_{n\kappa}(r)$ has as many nodes as $P_{n\kappa}(r)$ for negative values of κ and one additional node for positive values ofκ_i. From the figures it is also clear that the small-component radial functions $Q_{n_i\kappa_i}(r)$ are more compact and short-ranged than the large-component functions. This, depends on the atomic number Z as can be seen for the heavy and super heavy atoms, where the radial extension of the small-component radial functions is less compared to the set of large-component radial functions. Fig (4.20) represents large radial components $P_{n_i\kappa_i}(r)$ for all orbitals of nitrogen atom. The radial large components are described by relativistic Gaussian basis-set type $dyall-2zp$ has set [10s6p1d] contractive functions. The large radial components appear as three components in Fig (4.20), but in reality they are four components, because the relativistic effect is small on $p_{1/2} and\ p_{3/2}$ large components. Therefore, the large radial components $p_{1/2} and\ p_{3/2}$ appear as one component.

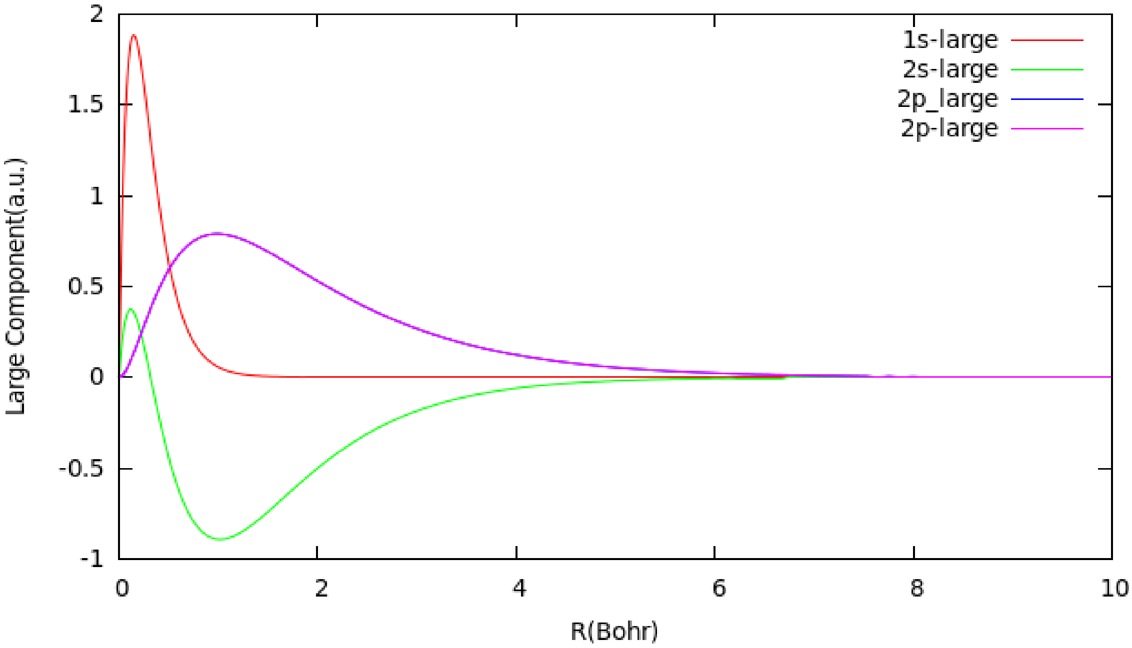


Figure 4.20: **Large radial functions $P_{n\kappa}(r)$ in atomic units against R(Bohr) for all N-atom orbitals**

Fig (4.21) shows the small radial components $Q_{n_i\kappa_i}(r)$ for all orbitals of nitrogen atom. The small components described by relativistic Gaussian basis-set type $dyall-2zp$ has set [6s11p6d1f] contractive functions for nitrogen atom. The small radial components are compact than the large component functions and short ranged.

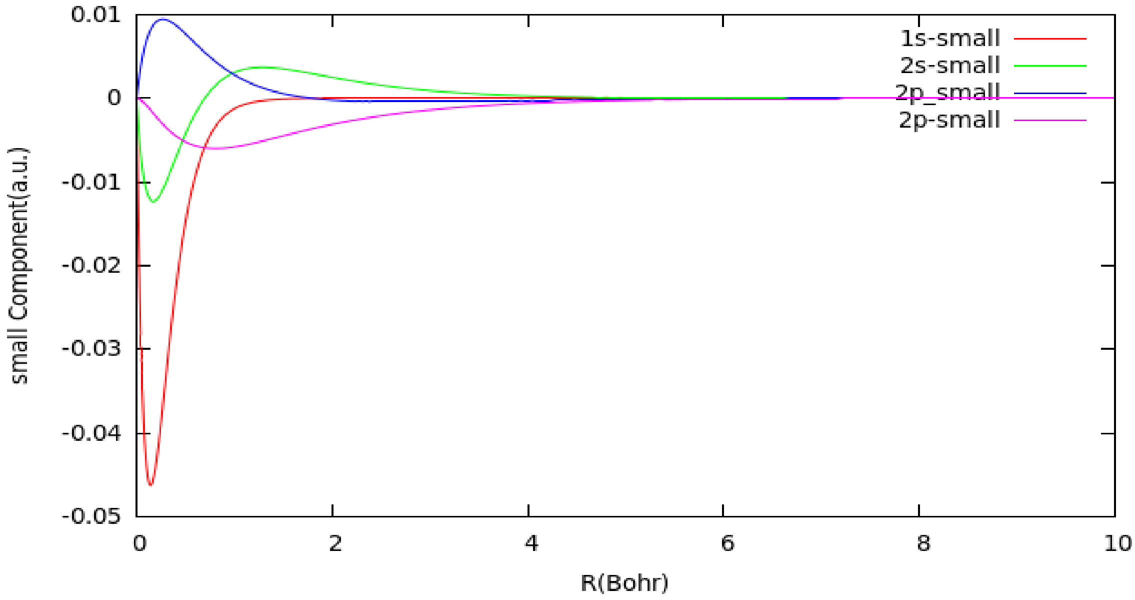


Figure 4.21: **Small radial functions $Q_{n\kappa}(r)$ in atomic units against R(Bohr) orbitals for all N-atom orbitals**

Fig (4.22) represents the large radial components $P_{n_i\kappa_i}(r)$ for all orbitals of phosphorus atom. The large components are described by relativistic Gaussian basis-set type *dyall.2zp* has set [12s16p2d] contractive functions. The large radial components are extended and long range than the small component functions when Z increased .

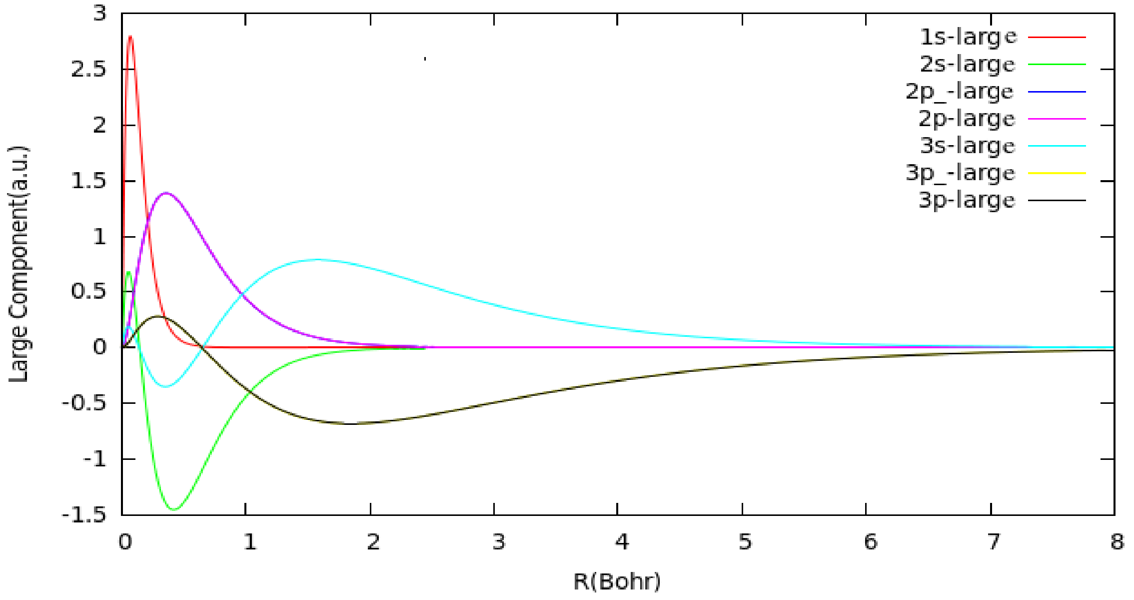


Figure 4.22: **Large radial functions $P_{n\kappa}(r)$ in atomic units against R(Bohr) for all P-atom orbitals**

Fig (4.23) shows the radial small components $Q_{n_i\kappa_i}(r)$ for all orbitals of phosphorus atom. The small components described by relativistic Gaussian basis-set type $dyall-2zp$ has set [8s16p8d1f] contractive functions. The small radial components are more compact than the large component functions and short ranged.

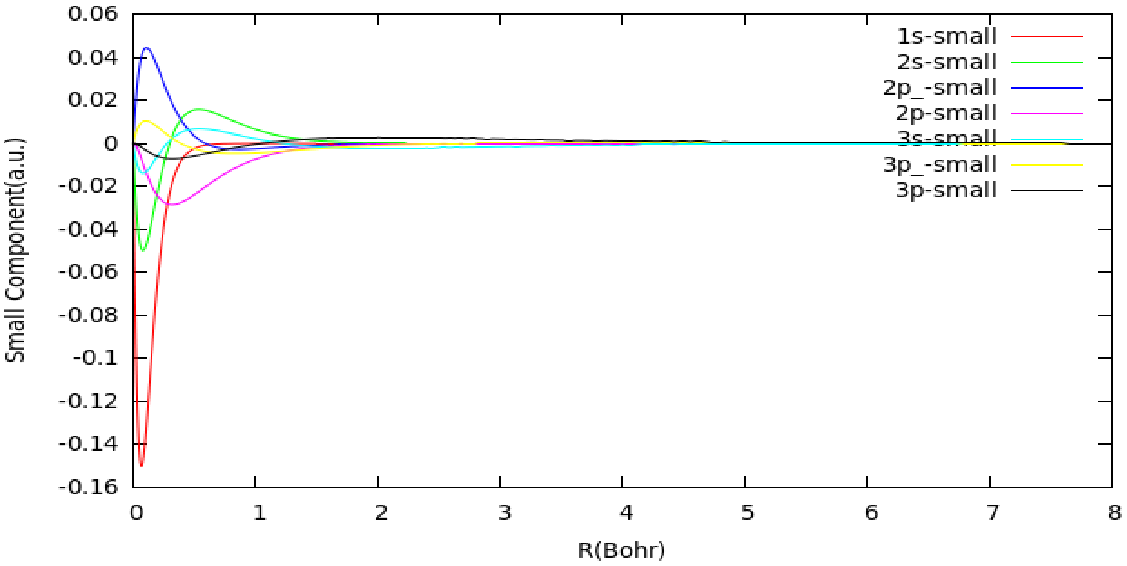


Figure 4.23: **Small radial functions $Q_{n\kappa}(r)$ in atomic units against R(Bohr) for all orbitals for all P-atom orbitals**

Fig (4.24) represents the large radial components $P_{n_i\kappa_i}(r)$ for all orbitals of arsenic atom. The large radial components are described by relativistic Gaussian basis-set type $dyall.2zp$ has set [15s11p7d1f] contractive functions. The large radial components are extended and long range than the small component functions when increased Z.

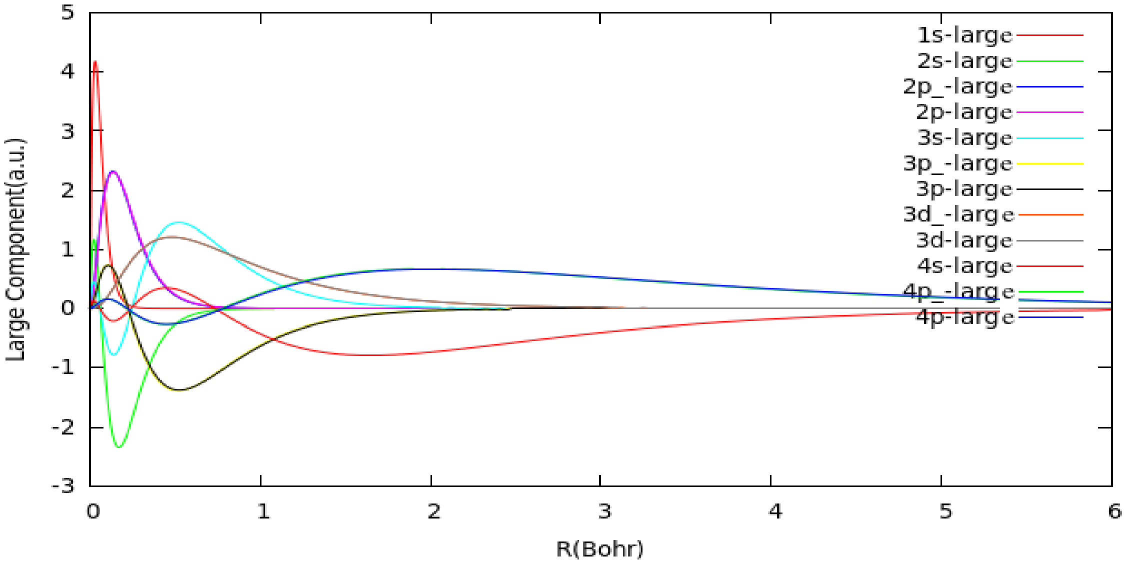


Figure 4.24: **Large radial functions $P_{n\kappa}(r)$ in atomic units against R(Bohr) for all As-atom orbitals**

Fig (4.25) shows the radial small component $Q_{n_i\kappa_i}(r)$ for all orbitals of arsenic. The small components are described by relativistic Gaussian basis-set type $dyall - v2z$ has set [11s22p12d7f1g] contractive functions. The small radial components are more compact than the large component functions and short range when increased Z.

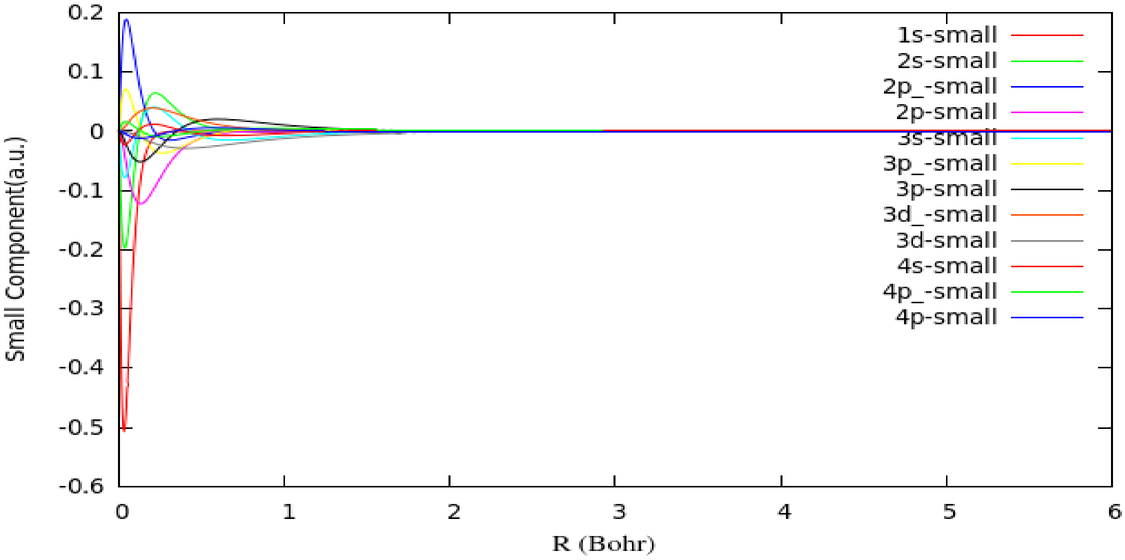


Figure 4.25: **Small radial functions $Q_{n\kappa}(r)$ in atomic units against R(Bohr) for all orbitals for all orbitals**

Fig (4.26) represents the large radial components $P_{n_i\kappa_i}(r)$ for all orbitals of antimony. The large radial components are described by relativistic Gaussian basis-set type *dyall.2zp* has set [21s15p11d1f] contractive functions.

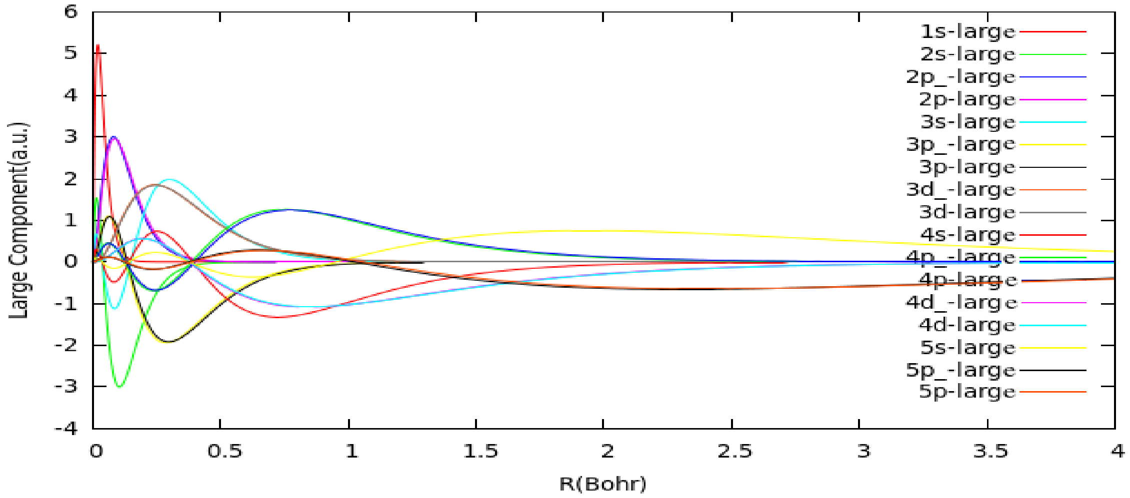


Figure 4.26: **Large radial functions $P_{n\kappa}(r)$ in atomic units against R(Bohr) for all Sb-atom orbitals**

Fig (4.27) shows the radial small components $Q_{n_i\kappa_i}(r)$ for all orbitals of antimony atom. The small components describe by relativistic Gaussian basis-set type $dyall - v2z$ have set [15s32p16d11f1g] contractive functions.

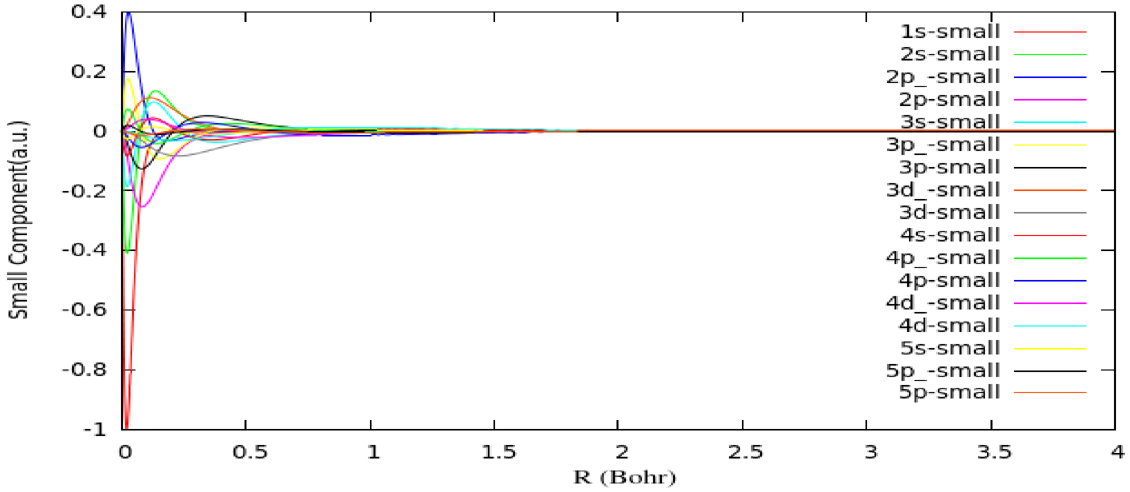


Figure 4.27: **Small radial functions $Q_{n\kappa}(r)$ in atomic units against R(Bohr) for all orbitals for all Sb-atom orbitals**

Fig (4.28) represents the large radial components $P_{n_i\kappa_i}(r)$ for all orbitals of bismuth atom. The large radial components are described by relativistic Gaussian basis-set type $dyall-2zp$ has set [24s20p14d9f] contractive functions. The large radial components are more extended and long range than the small component functions when Z increased .

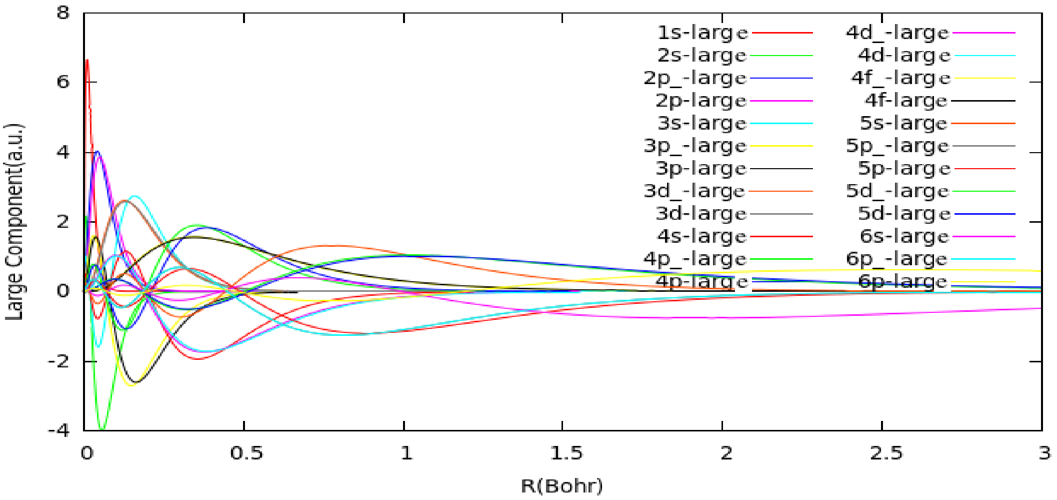


Figure 4.28: **Large radial functions $P_{n\kappa}(r)$ in atomic units against R(Bohr) for all Bi-atom orbitals**

Fig (4.29) shows the radial small components $Q_{n_i\kappa_i}(r)$ for all orbitals of bismuth atom. The small components describe by relativistic Gaussian basis-set type $dyall-2zp$ has set [20s38p29d14f9g] contractive functions. The small radial components are more compact than the large component functions and short range when increased Z.

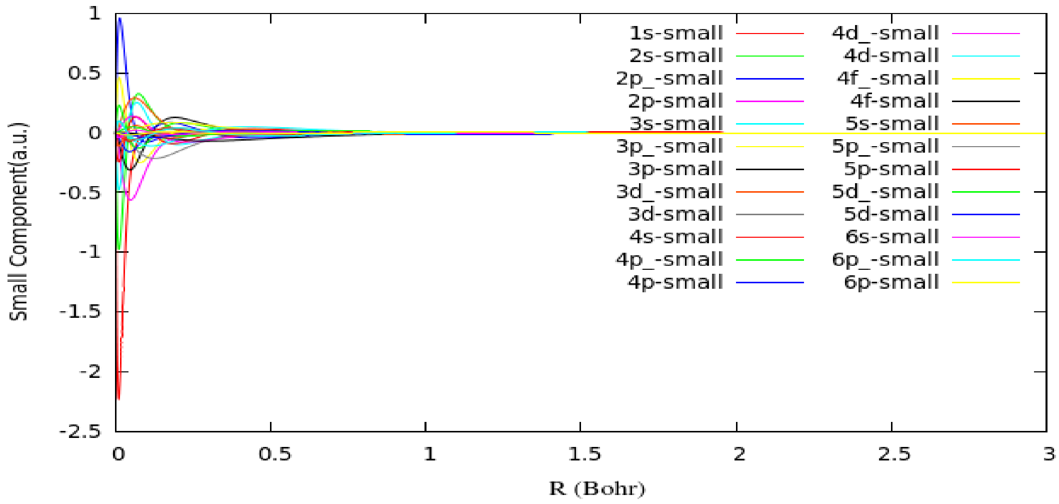


Figure 4.29: **Small radial functions $Q_{n\kappa}(r)$ in atomic units against R(Bohr) for all orbitals for all Bi-atom orbitals**

Fig (4.30) represents the large radial components $P_{n_i\kappa_i}(r)$ in atomic unit for all orbitals of uninpentum atom. The large radial components describe by relativistic Gaussian basis-set type *dyall*.2*zp* has set [26s23p16d12f] contractive functions.

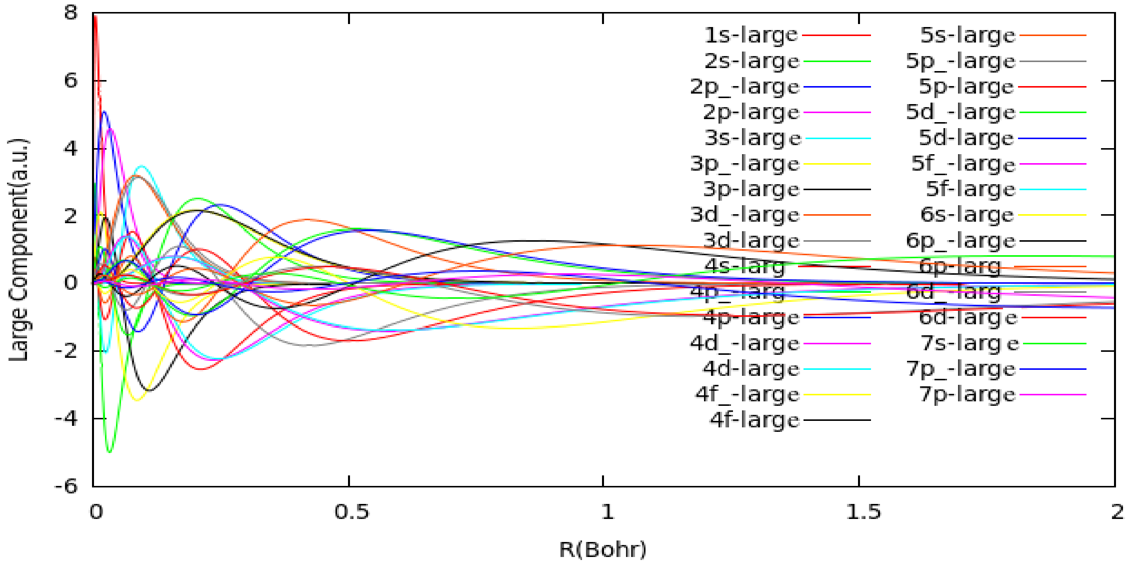


Figure 4.30: **Large radial functions $P_{n\kappa}(r)$ in atomic units against R(Bohr) for all Uup-atom orbitals**

Fig (4.31) shows the radial small component $Q_{n_i\kappa_i}(r)$ for all orbitals of ununpentum. The small radial components describe by relativistic Gaussian basis-set type $dyall - v2z$ has set [23s42p35d16f12g] contractive functions.

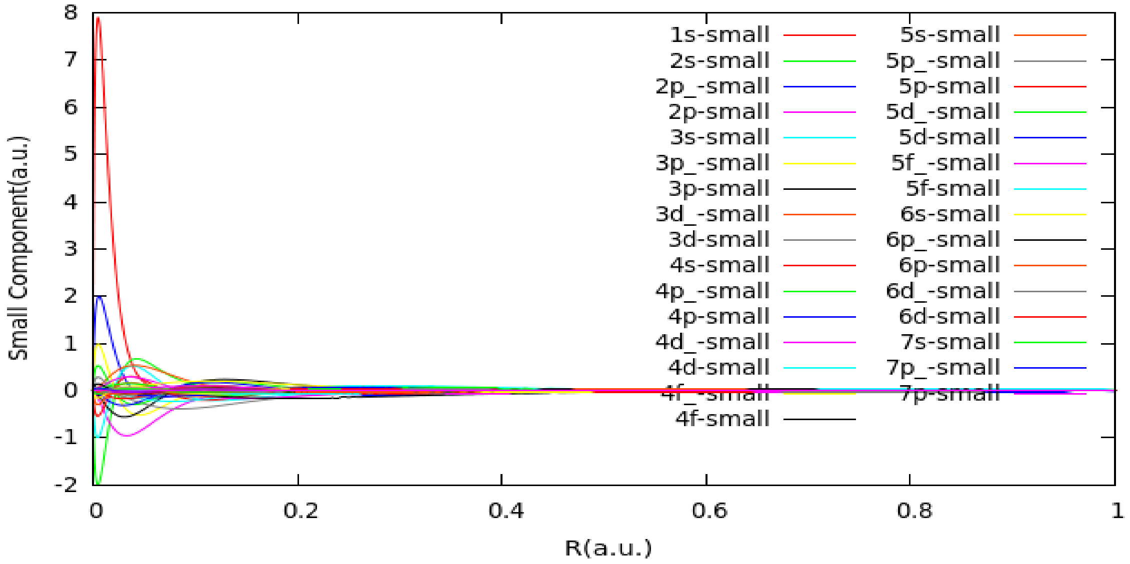


Figure 4.31: **Small radial functions $Q_{n\kappa}(r)$ in atomic units against R(Bohr) for all orbitals for all Uup-atom orbitals**

4.9 The Radial Overlap Density for $2p_{1/2}$ and $2p_{3/2}$ of Group15

The radial overlap density functions between two different radial spinors are described by relativistic Gaussian basis sets type $dyall - 2zp$. The behavior of the overlap of the radial density functions due to spin-orbit effect, specially for $2p_{1/2}$ and $2p_{3/2}$ shell functions for group15 has been study. The difference within each pair of radial density functions is more pronounced when the nuclear charge Z is increas, because the repulsion force between electrons can be canceled if the nuclear force is high. The overlapping of adjacent orbitals leads to orbital degeneracy and reorganization of orbitals. Fig (4.32) shows the overlapping radial density functions between $2p_{1/2}$ and $2p_{3/2}$ for nitrogen. The radial density functions for $2p_{1/2}$ and $2p_{3/2}$ are totally overlapped between for these two state, because the fine structure is small. This means the overlapping electrons don't collide, as in such a condition the wave function becomes undefined as two electrons are occupying the same state momentarily, but thankfully the Pauli exclusion principle prevents exactly this.

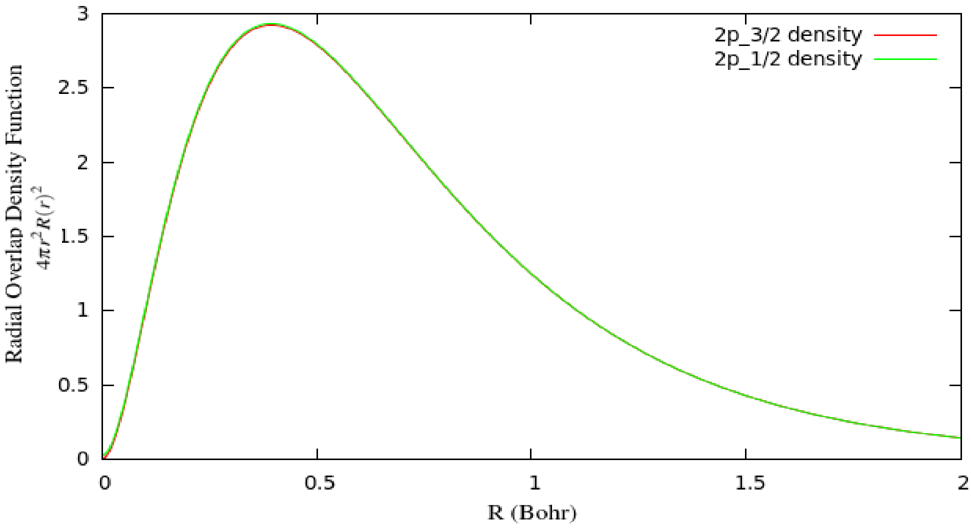


Figure 4.32: **The radial overlap between $2p_{1/2}$ and $2p_{3/2}$ against R(Bohr) for N-atom**

Fig (4.33) shows overlapping radial density functions between $2p_{1/2}$ and $2p_{3/2}$ for phosphorus atom. The overlap of the radial density functions between $2p_{1/2}$ and $2p_{3/2}$ is decreases , because the fine structure starts to increase .

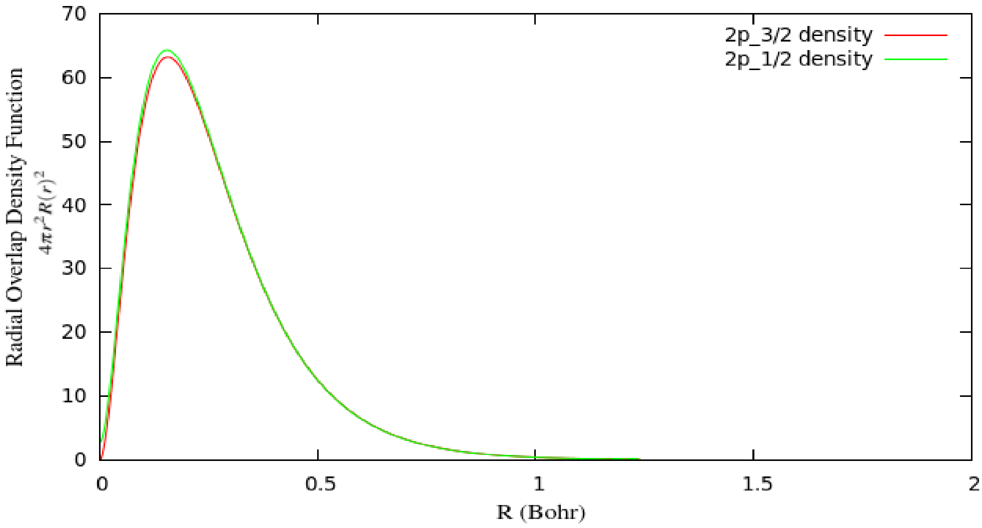


Figure 4.33: **The radial overlap between $2p_{1/2}$ and $2p_{3/2}$ against R(Bohr) for P-atom**

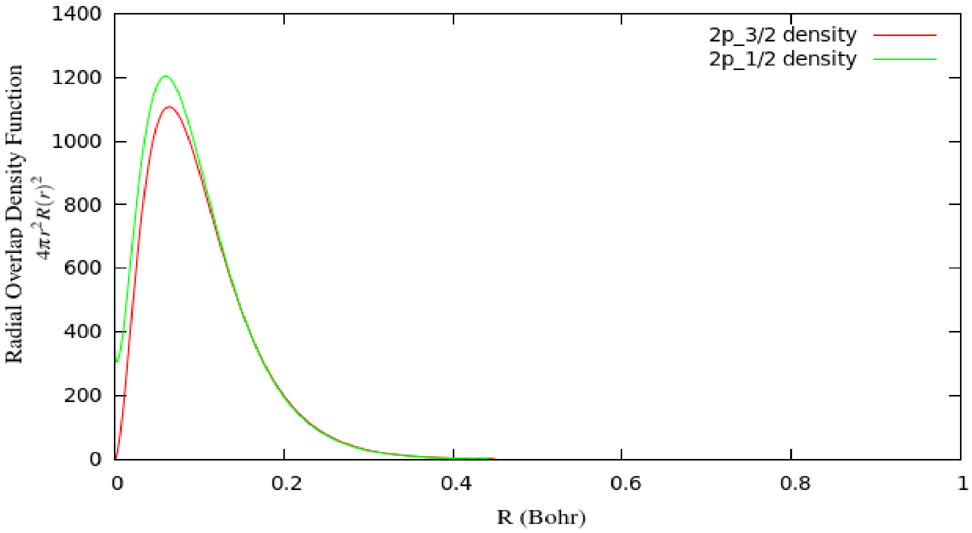


Figure 4.34: **The radial overlap between $2p_{1/2}$ and $2p_{3/2}$ against R(Bohr) for As-atom**

Fig (4.34) shows the overlapping radial density functions between $2p_{1/2}$ and $2p_{3/2}$ for arsenic atom. The overlap of the radial density functions for $2p_{1/2}$ and $2p_{3/2}$ is more decreased, because the spin-orbit has more effect on the behavior radial density. We also note that only $2p_{1/2}$radial density gives a significant contribution to the overlapping behavior . Fig (4.35) shows the overlapping radial density functions between $2p_{1/2}$ and $2p_{3/2}$ for antimony atom. The overlap of the radial density functions for $2p_{1/2}$ and $2p_{3/2}$ is clear decreasing because the spin-orbit has more effect on the behavior radial density.

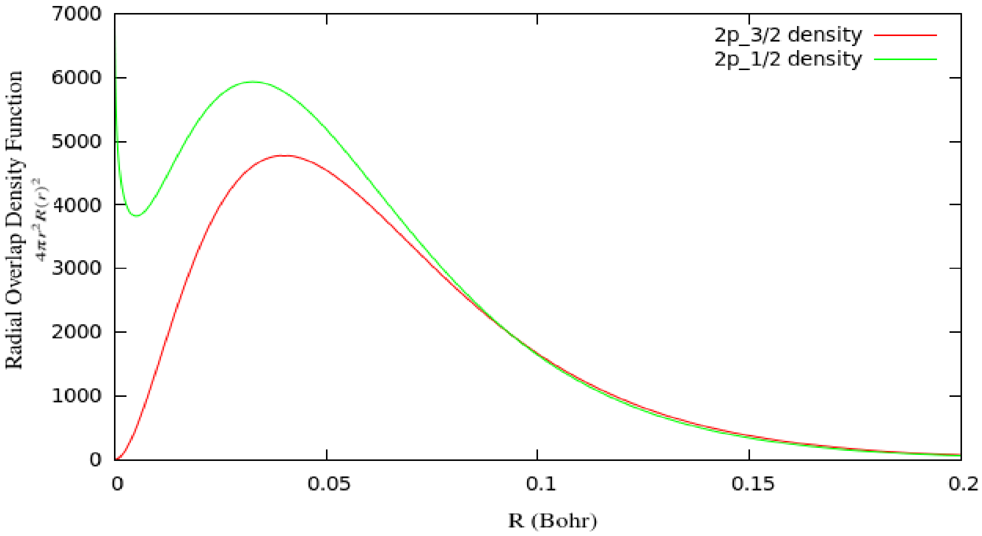


Figure 4.35: **The radial overlap between $2p_{1/2}$ and $2p_{3/2}$ against R(Bohr) for Sb-atom**

Fig (4.36) shows the overlapping radial density functions between $2p_{1/2}$ and $2p_{3/2}$ for bismuth. The overlap of the radial density functions for $2p_{1/2}$ and $2p_{3/2}$ is become decreses because the spin-orbit effect has strong on the behavior for these two states.

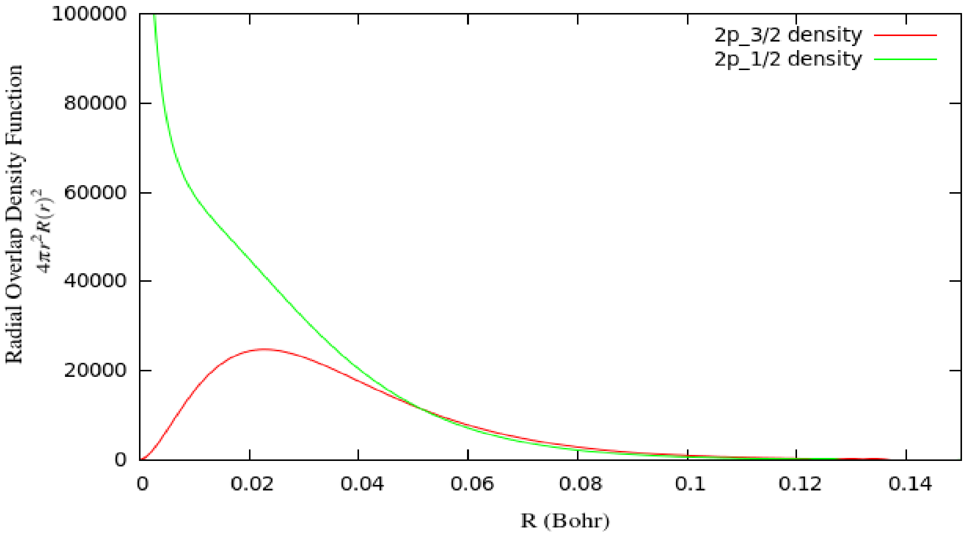


Figure 4.36: **The radial overlap between $2p_{1/2}$ and $2p_{3/2}$ against R(Bohr) for Bi-atom**

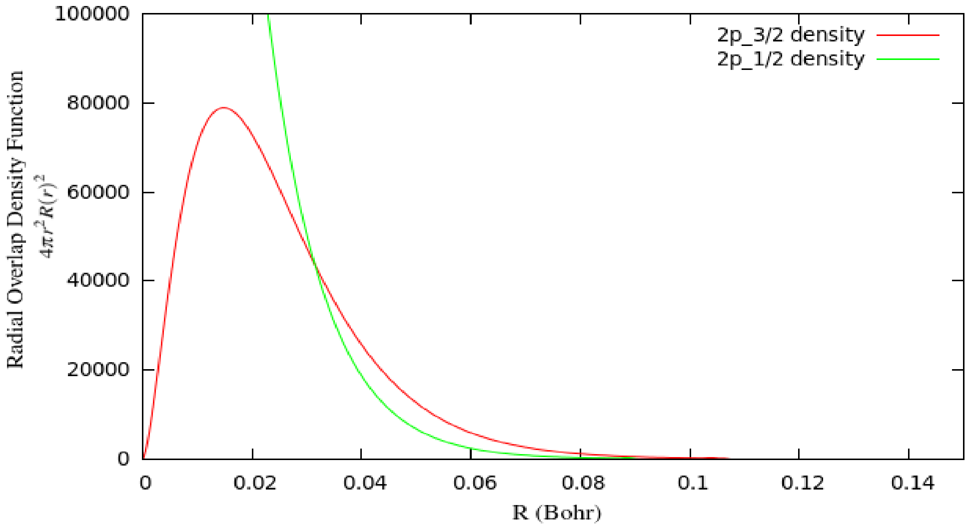


Figure 4.37: **The radial overlap between $2p_{1/2}$ and $2p_{3/2}$ against R(Bohr) for Uup-atom**

Fig (4.37) shows the overlapping radial density functions between $2p_{1/2}$ and $2p_{3/2}$ for *uninpentum*. The overlap radial density functions for $2p_{1/2}$ and $2p_{3/2}$ is missing between two states, because the spin-orbit effect is very strong on the behavior of the radial density for these two states.

4.10 Comparison Between Radial Wave Functions for Point Model And Gaussian Model

Fig (4.38) explains the radial wave functions for large component and small components for the $1s_{1/2}$of the super heavy atom $Uup, Z = 115$. Both radial amplitudes $u(r)/r$ and $v(r)/r$ for the Dirac-Hartree-Fock $1s_{1/2}$ orbital have been plotted. In calculation on $1s_{1/2}$ state, the large radial component $u(r)/r$ is expanded to $u(r) = \sum_{i=1}^{N} rexp\left(-\zeta_i r^2\right)\xi_i$, where N is the number of $1S$ $GTFs$ and the small radial component expanded to $v(r) = \sum_{i=1}^{N} r^2 exp\left(-\zeta_i r^2\right)\eta_i$ by Gaussian type functions (GTFs) when using Gaussian distribution model. The large and small components are expanded to $rexp(-\zeta r)$ by Slater type functions (STFs) when using the point model (for more details see [150] p(106-117)). As the fig illustrates, the wave functions for the point and Gaussian nuclear charge distribution models are identical, except in the nuclear region. At the center of the nucleus the point nuclear solution diverges, whereas the more physically correct Gaussian nucleus gives a smooth and continuous wave function at the origin.

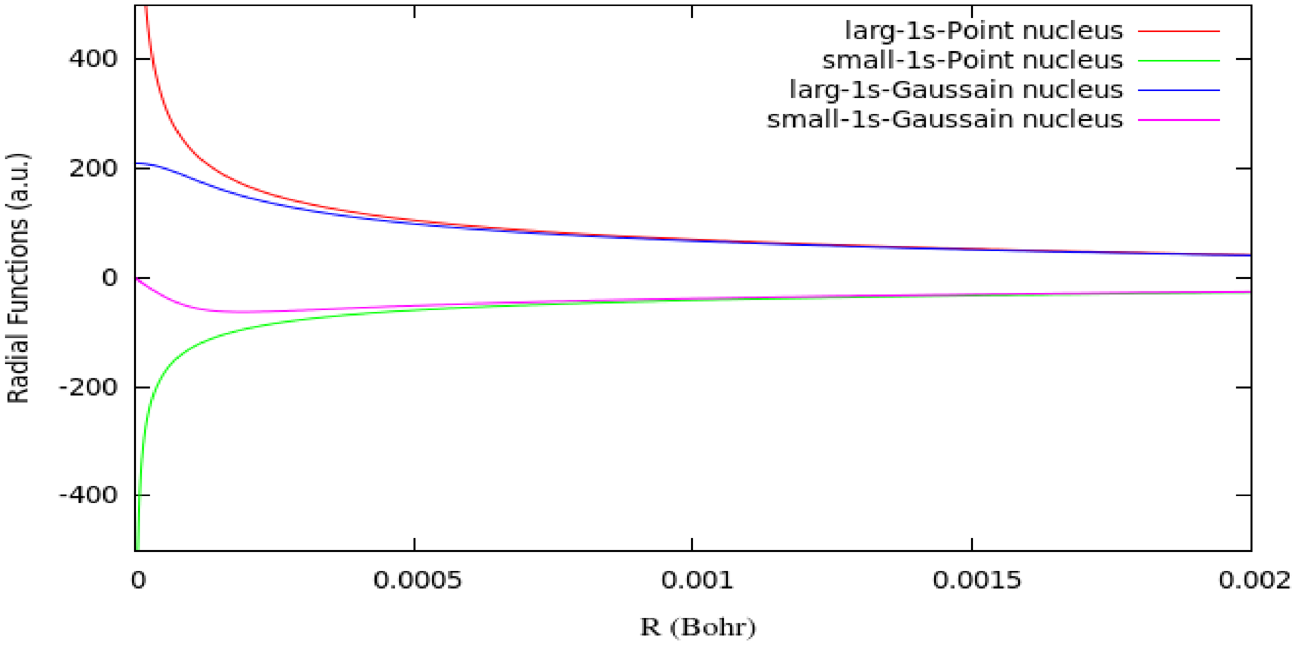


Figure 4.38: **Comparison of radial wave functions in (a.u) against R(Bohr) for point model and Gaussian model of super heavy element Z=115**

4.11 The Hartree Fock Energy for Diatomic Molecules

The Hartree-Fock approach with Born-Oppenheimer approximation was applied on diatomic molecules, such as Li_2, N_2, F_2, Se_2 . To computation of the total electronic energy for molecules and energy for each molecular orbital of ground state can be achieved by using DIRAC14.2 program in case of non-relativistic treatment. The wave function of molecular orbitals is described by Dunning Gaussian basis set type cc-pVDZ and used two different potential in present work. Table (4.35) shows the non-relativistic orbital energies for Li_2 diatomic molecule in atomic units. The configuration of the ground state, ${}^1\sum_g^+$, for Li_2 diatomic molecule is $\sigma\left(1s\right)_{grad}\sigma\left(1s\right)_{ungrad}\sigma\left(2s\right)_{grad}$, where $\sigma\left(1s\right)_{grad}$ is the molecular orbital composed from two atomic 1s orbitals. The radial wave function in non-relativistic case is described by Gaussian basis-set type Dunning $(cc-pVDZ)$. In our calculations we used two model nuclear charge distributions. The first model is point charge and the second is Gaussian charge distribution model. The basis-set *cc-pVDZ* has [3s2p1d]+[3s2p1d] contractive functions for Li_2 diatomic molecule, and has (9s4p1d)+ (9s4p1d) primitive functions for Li_2 diatomic molecule. Table (4.36) explained the total electronic energy for Li_2 diatomic molecule of two model nuclear charge distributions.

Table 4.35: **The orbital energies for Li_2 molecule**

The non-relativistic orbital energy for Li_2using Dunning basis-set $(cc-pVDZ)$			
Molecular orbital	Ourwork-Orbital energy (a.u.)- point model	Ourwork-Orbital energy (a.u.)- Gaussian model	Orbital energy (a.u.)[141]
$\sigma_{(1s)grad}$	-2.447944729833274	-2.447944662189034	-2.4506
$\sigma_{(1s)ungrad}$	-2.447605537669246	-2.447605469886924	-2.4504
$\sigma_{(2s)grad}$	-0.180369113516792	-0.180369111444094	-0.1778

Table 4.36: **Total Hartree Fock electronic energy for Li_2**

The non-relativistic total energy for Li_2using Dunning basis-set $(cc-pVDZ)$			
Electronic energy (a.u.) -point model	Nuclear repulsion energy (a.u.)-point model	SS Coulomb correction (a.u.)-point model	Total energy (a.u.) -point model
-16.651306129734770	1.781808101575068	-	-14.869498028159700
Electronic energy (a.u.) -Gaussian model	Nuclear repulsion energy (a.u.) -Gaussian model	SS Coulomb correction (a.u.)-Gaussian model	Total energy (a.u.) -Gaussian model
-16.651305849789882	1.781808101575068	-	-14.869497748214812

Table (4.37) shows the non-relativistic orbital energies for N_2 diatomic molecule using basis-set *Dunning* type $cc-pVDZ$ with different nuclear charge distribution models . To obtain a good description of N_2 diatomic molecule we used basis-set type *cc-pVDZ* that has [3s2p1d]+[3s2p1d] contractive functions and (9s4p1d)+ (9s4p1d) primitive functions .

Table 4.37: **The orbital energies for N_2 molecule**

The non-relativistic orbital energy for N_2using Dunning basis-set $(cc-pVDZ)$

Molecular orbital	Our work-Orbital energy (a.u.)- point model	Our work-Orbital energy (a.u.)- Gaussian model	Orbital energy (a.u.)[141]
$\sigma_{(1s)grad}$	-15.68643304886525	-15.68642983753813	-15.6800
$\sigma_{(1s)ungrad}$	-15.68303016407930	-15.68302695027274	-15.6761
$\sigma_{(2s)grad}$	-1.47120850873232	-1.47120837685820	-1.4863
$\sigma_{(2s)ungrad}$	-0.77409693725683	-0.77409681772065	-0.7674
$\sigma_{(2p_z)grad}$	-0.62622747931744	-0.62622749440319	-0.6279
$\pi_{(2p_x)ungrad}$	-0.60815941494309	-0.60815944682894	-0.6170
$\pi_{(2p_y)ungrad}$	-0.60815941494310	-0.60815944682894	-0.6170

Table 4.38: **Total Hartree Fock electronic energy for N_2**

The non-relativistic total energy for N_2using Dunning basis-set $(cc-pVDZ)$

Electronic energy (a.u.) -point model	Nuclear repulsion energy (a.u.)-point model	SS Coulombic correction (a.u.)-point model	Total energy (a.u.)-point model
-132.57639152777543	23.62226077426937	-	-108.95413075350606

Electronic energy (a.u.)-Gaussian model	Nuclear repulsion energy (a.u.)-Gaussian model	SS Coulombic correction (a.u.)-Gaussian model	Total energy (a.u.)-Gaussian model
-132.57637774891205	23.62226077426937	-	-108.95411697464269

Table (4.39) shows the non-relativistic orbital energies for F_2 diatomic molecule using basis-set *Dunning* type $cc-pVDZ$ with different nuclear charge distribution models . The basis-set *cc-pVDZ* has [3s2p1d]+[3s2p1d] contractive functions for F_2 diatomic molecule, and (9s4p1d)+ (9s4p1d) primitive functions for F_2 diatomic molecule.

Table 4.39: **The orbital energies for F_2 molecule**

The non-relativistic orbital energy for F_2using Dunning basis-set $(cc-pVDZ)$

Molecular orbital	Ourwork-Orbital energy (a.u.)- point model	Ourwork-Orbital energy (a.u.)- Gaussian model	Orbital energy (a.u.)[141]
$\sigma_{(1s)grad}$	-26.43290235546674	-26.43289180512685	-26.4256
$\sigma^*_{(1s)ungrad}$	-26.43265909296129	-26.43264854178556	-26.4253
$\sigma_{(2s)grad}$	-1.76790239636716	-1.76790191113075	-1.8044
$\sigma^*_{(2s)ungrad}$	-1.49949399389019	-1.49949340736751	-1.4816
$\pi_{(2p_x)ungrad}$	-0.80663177618714	-0.80663185450282	-0.8217
$\pi_{(2p_y)ungrad}$	-0.80663177618714	-0.80663185450281	-0.8217
$\sigma_{(2p_z)grad}$	-0.74418213377055	-0.74418219635494	-0.7694
$\pi^*_{(2p_x)grad}$	-0.66254748812802	-0.66254756686554	-0.6495
$\pi^*_{(2p_y)grad}$	-0.66254748812802	-0.66254756686554	-0.6495

Table 4.40: **Total Hartree Fock electronic energy for F_2**

The non-relativistic total energy for F_2using Dunning basis-set $(cc-pVDZ)$

Electronic energy (a.u.) -point model	Nuclear repulsion energy (a.u.)-point model	SS Coulombic correction (a.u.)-point model	Total energy (a.u.)-point model
-229.04365827711368	30.35798791179450	-	-198.68567036531917
Electronic energy (a.u.)-Gaussian model	Nuclear repulsion energy (a.u.)-Gaussian model	SS Coulombic correction (a.u.)-Gaussian model	Total energy (a.u.)-Gaussian model
-229.04361291664441	30.35798791179450	-	-198.68562500484992

Table (4.41) shows the non-relativistic orbital energies for Se_2 diatomic molecule using basis-set *Dunning* type $cc-pVDZ$ with different nuclear charge distribution models . The basis-set *cc-pVDZ* has [14s11p6d]+[14s11p6d] contractive functions for Se_2 diatomic molecule, and (14s11p6d)+ (14s11p6d) primitive functions for Se_2 diatomic molecule.

Table 4.41: **The orbital energies for Se_2 molecule**

The non-relativistic orbital energy for Se_2using Dunning basis-set $(cc-pVDZ)$

Molecular orbital	Ourwork-Orbital energy (a.u.)-point model	Ourwork-Orbital energy (a.u.)-Gaussain model	Orbital energy (a.u.)[141]
$\sigma_{(1s)grad}$	-460.896804738	-460.891732154	-460.9296
$\sigma^*_{(1s)ungrad}$	-460.896805279	-460.891732696	-460.9255
$\sigma_{(2s)grad}$	-60.697079669	-60.696588287	-60.7260
$\sigma^*_{(2s)ungrad}$	-60.697083954	-60.696592572	-60.7235
$\pi_{(2p_x)ungrad}$	-54.297982449	-54.298022922	-54.3269
$\pi^*_{(2p_x)grad}$	-54.297982990	-54.298023463	-54.3297
$\pi_{(2p_y)ungrad}$	-54.297982449	-54.298022922	-54.3297
$\pi^*_{(2p_y)grad}$	-54.297982990	-54.298023463	-54.3297
$\sigma_{(2p_z)grad}$	-54.298471368	-54.298511833	-54.3273
$\sigma^*_{(2p_z)ungrad}$	-54.298471986	-54.298512451	-54.3273
$\sigma_{(3s)grad}$	-8.956667158	-8.956590622	-8.9677
$\sigma^*_{(3s)ungrad}$	-8.956570480	-8.956493937	-8.9592
$\pi_{(3p_x)ungrad}$	-6.685508951	-6.685517389	-6.6997
$\pi^*_{(3p_x)grad}$	-6.685439080	-6.685447517	-6.6997
$\pi_{(3p_y)ungrad}$	-6.685508951	-6.685517389	-6.6997
$\pi^*_{(3p_y)grad}$	-6.685439080	-6.685447517	-6.6997
$\sigma_{(3p_z)grad}$	-6.689770227	-6.689778639	-6.6975
$\sigma^*_{(3p_z)ungrad}$	-6.689221816	-6.689230230	-6.6969
$\sigma 3d\left(d_{z^2}-d_{z^2}\right)_g$	-2.676627068	-2.676633627	-2.6840
$\sigma^* 3d\left(d_{z^2}-d_{z^2}\right)_u$	-2.669952464	-2.669959058	-2.6792
$\pi\left(3d_{xz}\right)_u$	-2.672205511	-2.672212087	-2.6792
$\pi^*\left(3d_{xz}\right)_g$	-2.669836892	-2.669843482	-2.6768
$\pi\left(3d_{yz}\right)_u$	-2.672205511	-2.672212087	-2.6768
$\pi^*\left(3d_{yz}\right)_g$	-2.669836892	-2.669843482	-2.6768
$\delta\left(3d_{xy}\right)_g$	-2.667025728	-2.667032331	-2.6757
$\delta^*\left(3d_{xy}\right)_u$	-2.666657932	-2.666664536	-2.6757
$\delta\left(3d_{x^2-y^2}\right)_g$	-2.667025728	-2.667032331	-2.6755
$\delta^*\left(3d_{x^2-y^2}\right)_u$	-2.666657932	-2.666664536	-2.6755
$\sigma_{(4s)grad}$	-1.000239302	-1.000234212	-1.0340
$\sigma^*_{(4s)ungrad}$	-0.777954222	-0.777947487	-0.8330
$\pi_{(4p_x)ungrad}$	-0.424551560	-0.424553123	-0.4834
$\pi_{(4p_y)ungrad}$	-0.424551560	-0.424553123	-0.4834
$\sigma_{(4p_z-4p_z)grad}$	-0.471333124	-0.471334387	-0.4825
$\pi^*_{(4p_x)grad}$	-0.185288060	-0.185289438	-0.3545
$\pi^*_{(4p_y)grad}$	-0.185288060	-0.185289438	-0.3545

Table 4.42: **Total Hartree Fock electronic energy for** Se_2

The non-relativistic total energy for Se_2using Dunning basis-set $(cc-pVDZ)$			
Electronic energy(a.u.) -point model	Nuclear repulsion energy(a.u.)-point model	SS Coulombic correction(a.u.)-point model	Total energy(a.u.)-point model
-5081.8951770555941	282.4232930723915	-	-4799.4718839832030
Electronic energy(a.u.)-Gaussian model	Nuclear repulsion energy(a.u.)-Gaussian model	SS Coulombic correction(a.u.)-Gaussian model	Total energy(a.u.)-Gaussian model
-5081.8718194138437	282.4232930723915	-	-4799.4485263414517

4.12 The Dirac-Hartree-Fock Energy for Diatomic Molecules

The Dirac-Coulomb energy of a four-component spinor is expanded into separate one-particle basis sets for the large (L) and small (S) components. Dirac-Hartree-Fock approach has been developed which allows relativistic Dirac-Hartree-Fock calculations for molecules by computing integrlas formed by expanding basis atomic spinors in Gaussian functions. The results obtained by using DIRAC14.2 program in relativistic treatment for Li_2, N_2, F_2, Se_2 show the orbital energies and total enrgies for each diatomic molecule. Table (4.43) shows the relativistic orbital energies for Li_2 diatomic molecule has configuration ground state $\sigma\left(1s_{1/2}\right)_{grad}\sigma\left(1s_{1/2}\right)_{ungrad}\sigma\left(2s_{1/2}\right)_{grad}$, in atomic units. The large and small componet radial wave functions in the relativistic case are described by two type of Gaussian basis set; first one type used $Dunning\ (cc-pVDZ)$ basis set and second one used dyall-2zp basis set. In our calculations we used two model nuclear charge distributions. The first model is point charge and the second is Gaussian charge distribution model. The large components basis-set $cc-pVDZ$ [3s2p1d]+[3s2p1d] contractive functions and (9s4p1d)+(9s4p1d) primitive functions for Li_2 diatomic molecule . The small components basis-set $cc-pVDZ$ has [4s10p4d1f]+[4s10p4d1f] contractive functions and has (4s10p4d1f)+(4s10p4d1f) primitive functions for Li_2 diatomic molecule.

Table 4.43: **The relativistic orbital energies for Li_2 molecule**

The relativistic orbital energy forLi_2using Dunning basis-set $(cc-pVDZ)$			
Molecular orbital	Ourwork-Orbital energy(a.u.)-point model	Ourwork-Orbital energy(a.u.)-Gaussain model	Orbital energy (a.u.)[141]
$\sigma_{1/2(1s)grad}$	-2.448321973613917	-2.448321905974459	-2.4506
$\sigma_{1/2(1s)ungrad}$	-2.447983756309737	-2.447983688534220	-2.4504
$\sigma_{1/2(2s)grad}$	-0.180390459486164	-0.180390457414968	-0.1778

Table (4.44) gives the contribution energies of the total energy for Li_2 molecule using basis set type $Dunning\ cc-pVDZ$ with different nuclear charge distribution models in case of relativistic treatment.

Table 4.44: **Total Dirac-Hartree-Fock electronic energies for Li_2**

The relativistic total energy for Li_2using Dunning basis-set $(cc-pVDZ)$			
Electronic energy (a.u.) -point model	Nuclear repulsion energy (a.u.)-point model	SS Coulombic correction (a.u.)-point model	Total energy (a.u.)-point model
-16.652923250501118	1.781808101575068	0.000000007919147	-14.871115141006904
Electronic energy (a.u.)-Gaussian model	Nuclear repulsion energy (a.u.)-Gaussian model	SS Coulombic correction (a.u.)-Gaussian model	Total energy (a.u.)-Gaussian model
-16.652922970577741	1.781808101575068	0.000000007919147	-14.871114861083527

Table (4.45) shows the relativistic orbital energies for N_2 diatomic molecule in atomic units. In our calculations we used two model nuclear charge distributions. The first model is point charge and the second is Gaussian charge distribution model. The large components basis-set $cc-pVDZ$ [3s2p1d]+[3s2p1d] contractive functions and has (9s4p1d)+(9s4p1d) primitive functions for N_2 diatomic molecule. Small components basis-set $cc-pVDZ$ [4s10p4d1f]+[4s10p4d1f] contractive functions and has (4s10p4d1f)+(4s10p4d1f) primitive functions for N_2 diatomic molecule.

Table 4.45: **The relativistic orbital energies for N_2 molecule**

The relativistic orbital energy for N_2using Dunning basis-set $(cc-pVDZ)$			
Molecular orbital	Ourwork-Orbital energy(a.u.)- point model	Ourwork-Orbital energy(a.u.)- Gaussain model	Orbital energy (a.u.)[141]
$\sigma_{1/2(1s)grad}$	-15.69885511146428	-15.69885190123023	-15.6800
$\sigma_{1/2(1s)ungrad}$	-15.69546445993603	-15.69546124720449	-15.6761
$\sigma_{1/2(2s)grad}$	-1.47210403707627	-1.47210390553577	-1.4863
$\sigma_{1/2(2s)ungrad}$	-0.77502071020440	-0.77502059090265	-0.7674
$\sigma_{1/2(2p_z)grad}$	-0.62617584005632	-0.62617585513071	-0.6279
$\pi_{1/2(2p_x)ungrad}$	-0.60811528071560	-0.60811531245615	-0.6170
$\pi_{3/2(2p_y)ungrad}$	-0.60772033020855	-0.60772036194977	-0.6170

Table (4.46) gives the contribution energies to the total energy for N_2 molecule using basis set type *Dunning* $cc-pVDZ$ with differenet nuclear charge distribution models in case of relativistic treatment.

Table 4.46: **Total Dirac-Hartree-Fock electronic energies for N_2**

The relativistic total energy for N_2using Dunning basis-set $(cc-pVDZ)$			
Electronic energy(a.u.) -point model	Nuclear repulsion energy(a.u.)-point model	SS Coulombic correction(a.u.)-point model	Total energy(a.u.)-point model
-132.63869671411101	23.62226077426937	0.00000094489043	-109.01643499495120
Electronic energy(a.u.)-Gaussian model	Nuclear repulsion energy(a.u.)-Gaussian model	SS Coulombic correction(a.u.)-Gaussian model	Total energy(a.u.)-Gaussian model
-132.63868294277756	23.62226077426937	0.00000094489043	-109.01642122361777

Table (4.47) shows the relativistic orbital energies for F_2 diatomic molecule in atomic units. In our calculation we used two model nuclear charge distributions. The first model is point charge and the second is Gaussian charge distribution model. The large components basis-set $cc-pVDZ$ [3s2p1d]+[3s2p1d] contractive functions and has (9s4p1d)+(9s4p1d) primitive functions for F_2 diatomic molecule. Small components basis-set $cc-pVDZ$ [4s10p4d1f]+[4s10p4d1f] contractive functions and has (4s10p4d1f)+(4s10p4d1f) primitive functions for F_2 diatomic molecule.

Table 4.47: **The relativistic orbital energies for F_2 molecule**

The relativistic orbital energy for F_2using Dunning basis-set $(cc-pVDZ)$			
Molecular orbital	Ourwork-Orbital energy(a.u.)- point model	Ourwork-Orbital energy(a.u.)- Gaussain model	Orbital energy (a.u.)[141]
$\sigma_{1/2(1s)grad}$	-26.46704231214135	-26.46703176785501	-26.4256
$\sigma_{1/2(1s)ungrad}$	-26.46680213504469	-26.46679158993980	-26.4253
$\sigma_{1/2(2s)grad}$	-1.77065868226464	-1.77065819887817	-1.8044
$\sigma_{1/2(2s)ungrad}$	-1.50304506722407	-1.50304448335979	-1.4816
$\pi_{1/2(2p_x)ungrad}$	-0.80695796949387	-0.80695804711272	-0.8217
$\pi_{3/2(2p_y)ungrad}$	-0.80536804066645	-0.80536811830971	-0.8217
$\sigma_{1/2(2p_z)grad}$	-0.74367743971153	-0.74367750180086	-0.7694
$\pi_{1/2(2p_x)grad}$	-0.66311122746396	-0.66311130550478	-0.6495
$\pi_{3/2(2p_y)grad}$	-0.66126636412975	-0.66126644220854	-0.6495

Table (4.48) gives the contribution energies to the total energy for F_2 molecule using basis set type *Dunning* $cc-pVDZ$ with differenet nuclear charge distribution models in case of relativistic treatment.

Table 4.48: **Total Dirac-Hartree-Fock electronic energies for F_2**

The relativistic total energy for F_2using Dunning basis-set $(cc-pVDZ)$			
Electronic energy(a.u.) -point model	Nuclear repulsion energy(a.u.)-point model	SS Coulombic correction(a.u.)-point model	Total energy(a.u.)-point model
-229.22614528674632	30.35798791179450	0.00000253358023	-198.86815484137156
Electronic energy(a.u.)-Gaussian model	Nuclear repulsion energy(a.u.)-Gaussian model	SS Coulombic correction(a.u.)-Gaussian model	Total energy(a.u.)-Gaussian model
-229.22609996816070	30.35798791179450	0.00000253358023	-198.86810952278597

Table (4.49) shows the relativistic orbital energies for Li_2 diatomic molecule in atomic units . The large and small radial functions are described by Gaussian basis-set *Dyall* type $dyall-2zp$. In our calculations we used two model nuclear charge distributions. The first model is point charge and the second is Gaussian charge distribution model. The large components basis-set $dyall-2zp$ has [10s6p]+[10s6p] contractive functions and (10s6p)+(10s6p) primitive functions for Li_2 diatomic molecule. Small components basis-set $dyall-2zp$ [6s10p6d]+[6s10p6d] contractive functions and has (6s10p6d)+(6s10p6d) primitive functions for Li_2 diatomic molecule.

Table 4.49: **The relativistic orbital energies for Li_2 molecule**

The relativistic orbital energy for Li_2using Dyall basis-set $(dyall-2zp)$			
Molecular orbital	Ourwork-Orbital energy(a.u.)-point model	Ourwork-Orbital energy(a.u.)-Gaussain model	Orbital energy (a.u.)[141]
$\sigma_{1/2(1s)grad}$	-2.453330864916	-2.453330813364	-2.4506
$\sigma_{1/2(1s)ungrad}$	-2.453007142856	-2.453007091260	-2.4504
$\sigma_{1/2(2s)grad}$	-0.181796291210	-0.181796290046	-0.1778

Table (4.50) gives the contribution energies to the total energy for Li_2 molecule using basis set type $dyall-2zp$ with differen t nuclear charge distribution models in case of relativistic treatment.

Table 4.50: Total Dirac-Hartree-Fock electronic energies for Li_2

The relativistic total energy for Li_2using Dyall basis-set $(dyall-2zp)$			
Electronic energy (a.u.)-point model	Nuclear repulsion energy(a.u.)-point model	SS Coulombic correction(a.u.)-point model	Total energy(a.u.)-point model
-16.654632674234374	1.781808101575069	0.000000007919147	-14.872824564740158
Electronic energy(a.u.)-Gaussian model	Nuclear repulsion energy(a.u.)-Gaussian model	SS Coulombic correction(a.u.)-Gaussian model	Total energy(a.u.)-Gaussian model
-16.654632390349875	1.781808101575069	0.000000007919147	-14.872824280855658

Table (4.51) gives the relativistic orbital energies for N_2 diatomic molecule in atomic units. The large and small radial components are described by relativistic Gaussian basis-set type $dyall-2zp$. The large components basis-set $dyall-2zp$ has [10s6p1d]+[10s6p1d] contractive functions and (10s6p1d)+ (10s6p1d) primitive functions for N_2 diatomic molecule. Small components basis-set $dyall-2zp$ [6s11p6d1f]+[6s11p6d1f] contractive functions and (6s11p6d1f)+ (6s11p6d1f) primitive functions for N_2 diatomic molecule.

Table 4.51: **The relativistic orbital energies for N_2 molecule**

The relativistic orbital energy for N_2using Dyall basis-set $(dyall-2zp)$			
Molecular orbital	Ourwork-Orbital energy(a.u.)-point model	Ourwork-Orbital energy(a.u.)-Gaussian model	Orbital energy (a.u.)[141]
$\sigma_{1/2(1s)grad}$	-15.69463506145	-15.69463214399	-15.6800
$\sigma_{1/2(1s)ungrad}$	-15.69112149888	-15.69111857878	-15.6761
$\sigma_{1/2(2s)grad}$	-1.47609780971	-1.47609768698	-1.4863
$\sigma_{1/2(2s)ungrad}$	-0.77834125171	-0.77834113430	-0.7674
$\sigma_{1/2(2p_z)grad}$	-0.63305787177	-0.63305790701	-0.6279
$\pi_{1/2(2p_x)ungrad}$	-0.61338496630	-0.61338501493	-0.6170
$\pi_{3/2(2p_y)ungrad}$	-0.61296620200	-0.61296625061	-0.6170

Table (4.52) gives the contribution energies of the total energy for N_2 molecule using basis set type $dyall-2zp$ with different nuclear charge distribution models in case of relativistic treatment.

Table 4.52: **Total Dirac-Hartree-Fock electronic energies for N_2**

The relativistic total energy for N_2using Dyall basis-set $(dyall-2zp)$			
Electronic energy(a.u.) -point model	Nuclear repulsion energy(a.u.)-point model	SS Coulombic correction(a.u.)-point model	Total energy(a.u.)-point model
-132.66194824136170	23.62226077426937	0.00000094489043	-109.03968652220188
Electronic energy(a.u.)-Gaussian model	Nuclear repulsion energy(a.u.)-Gaussian model	SS Coulombic correction(a.u.)-Gaussian model	Total energy(a.u.)-Gaussian model
-132.66193426009073	23.62226077426937	0.00000094489043	-109.03967254093092

Table (4.53) shows the relativistic orbital energies for F_2 diatomic molecule in atomic units. The large components basis-set $dyall-2zp$ has [10s6p1d]+[10s6p1d] contractive functions and (10s6p1d)+(10s6p1d) primitive functions for F_2 diatomic molecule. Small components basis-set $dyall-2zp$ [6s11p6d1f]+[6s11p6d1f] contractive functions and (6s11p6d1f)+(6s11p6d1f) primitive functions for F_2 diatomic molecule.

Table 4.53: **The relativistic orbital energies for F_2 molecule**

The relativistic orbital energy for F_2using Dyall basis-set $(dyall-2zp)$			
Molecular orbital	Ourwork-Orbital energy(a.u.)-point model	Ourwork-Orbital energy(a.u.)-Gaussian model	Orbital energy (a.u.)[141]
$\sigma_{1/2(1s)grad}$	-26.45727863889	-26.45726868836	-26.4256
$\sigma_{1/2(1s)ungrad}$	-26.45704237212	-26.45703242134	-26.4253
$\sigma_{1/2(2s)grad}$	-1.77167300127	-1.77167249884	-1.8044
$\sigma_{1/2(2s)ungrad}$	-1.50327988021	-1.50327926771	-1.4816
$\pi_{1/2(2p_x)ungrad}$	-0.81185046644	-0.81185058332	-0.8217
$\pi_{3/2(2p_y)ungrad}$	-0.81011688501	-0.81011700169	-0.8217
$\sigma_{1/2(2p_z)grad}$	-0.75173152076	-0.75173160928	-0.7694
$\pi_{1/2(2p_x)grad}$	-0.66936224315	-0.66936236895	-0.6495
$\pi_{3/2(2p_y)grad}$	-0.66735974267	-0.66735986830	-0.6495

The table (4.54) explain the contribution energies of the total energy for F_2 molecule using basis set type $dyall-2zp$ with differenet nuclear charge distribution model in case of relativistic treatment.

Table 4.54: **Total Dirac-Hartree-Fock electronic eneries for F_2**

The relativistic total energy for F_2using Dyall basis-set $(dyall-2zp)$			
Electronic energy(a.u.) -point model	Nuclear repulsion energy(a.u.)-point model	SS Coulombic correction(a.u.)-point model	Total energy(a.u.)-point model
-229.29766920007242	30.35798791179450	0.00000253358023	-198.93967875469770
Electronic energy(a.u.)-Gaussian model	Nuclear repulsion energy(a.u.)-Gaussian model	SS Coulombic correction(a.u.)-Gaussian model	Total energy(a.u.)-Gaussian model
-229.29762278972032	30.35798791179450	0.00000253358023	-198.93963234434560

Table (4.55) shows the relativistic orbital energies for Se_2 diatomic molecule in atomic units. The large components basis-set described by using $dyall-2zp$ has [15s11p7d]+[15s11p7d] contractive functions and (15s11p7d) +(15s11p7d) primitive functions for Se_2 diatomic molecule. Small components basis-set $dyall-2zp$ has [11s22p11d7f]+[11s22p11d7f] contractive functions and (11s22p11d7f)+ (11s22p11d7f) primitive functions for Se_2 diatomic molecule.

Table 4.55: **The relativistic orbital energies for Se_2 molecule**

The relativistic orbital energy forSe_2using Dyall basis-set $(dyall-2zp)$

Molecular orbital	Ourwork-Orbital energy(a.u.)-point model	Ourwork-Orbital energy(a.u.)-Gaussian model	Orbital energy (a.u.)[141]
$\sigma_{1/2}(1s)grad$	-468.3968445957	-468.3898757870	-460.9296
$\sigma^*_{1/2}(1s)ungrad$	-468.3968449599	-468.3898761514	-460.9255
$\sigma_{1/2}(2s)grad$	-62.3869769670	-62.3862650685	-60.7260
$\sigma^*_{1/2}(2s)ungrad$	-62.3869809138	-62.3862690155	-60.7235
$\sigma_{1/2}(2p_z)grad$	-55.7283263056	-55.7283813211	-54.3269
$\sigma^*_{1/2}(2p_z)ungrad$	-55.7283261883	-55.7283812038	-54.3297
$\pi_{1/2}(2p_x)ungrad$	-54.1793876982	-54.1794456065	-54.3297
$\pi^*_{1/2}(2p_x)grad$	-54.1793876521	-54.1792991264	-54.3297
$\pi^*_{3/2}(2p_y)grad$	-54.1792416864	-54.1792996456	-54.3273
$\pi_{3/2}(2p_y)ungrad$	-54.1792411671	-54.1794456525	-54.3273
$\sigma_{1/2}(3s)grad$	-9.2382830387	-9.2381713969	-8.9677
$\sigma^*_{1/2}(3s)ungrad$	-9.2382133994	-9.2381017502	-8.9592
$\pi^*_{1/2}(3p_x)grad$	-6.8985124388	-6.8985240257	-6.6997
$\pi_{1/2}(3p_x)ungrad$	-6.8983954229	-6.8984070108	-6.6997
$\sigma_{1/2}(3p_z)grad$	-6.6706977829	-6.6707098825	-6.6975
$\sigma^*_{1/2}(3p_z)ungrad$	-6.6703643973	-6.6703764987	-6.6969
$\pi_{3/2}(3p_y)ungrad$	-6.6682012074	-6.6682133252	-6.6997
$\pi^*_{3/2}(3p_y)grad$	-6.6681375089	-6.6681496264	-6.6997
$\sigma_{1/2}3d\left(d_{z^2}-d_{z^2}\right)_{grad}$	-2.6397868600	-2.6397962399	-2.6840
$\sigma^*_{1/2}3d\left(d_{z^2}-d_{z^2}\right)_{ungrad}$	-2.6382894900	-2.6382988829	-2.6792
$\pi_{3/2}\left(3d_{yz}\right)_{ungrad}$	-2.6346812060	-2.6047775192	-2.6768
$\pi^*_{3/2}\left(3d_{yz}\right)_{grad}$	-2.6343635954	-2.6021205015	-2.6768
$\pi_{1/2}\left(3d_{xz}\right)_{ungrad}$	-2.6019107439	-2.6346906161	-2.6792
$\pi^*_{1/2}\left(3d_{xz}\right)_{grad}$	-2.6047682232	-2.6343730095	-2.6768
$\delta_{3/2}\left(3d_{xy}\right)_{grad}$	-2.6002496794	-2.6019200594	-2.6757
$\delta^*_{3/2}\left(3d_{xy}\right)_{ungrad}$	-2.6021111934	-2.6002590006	-2.6757
$\delta_{5/2}\left(3d_{x^2-y^2}\right)_{grad}$	-2.5980416860	-2.5980510183	-2.6755
$\delta^*_{5/2}\left(3d_{x^2-y^2}\right)_{ungrad}$	-2.5976294950	-2.5976388302	-2.6755
$\sigma_{1/2}(4s)grad$	-1.0170801826	-1.0170726172	-1.0340
$\sigma_{1/2}(4s)ungrad$	-0.8010991267	-0.8010891539	-0.8330
$\pi_{1/2}(4p_x)ungrad$	-0.4703729912	-0.4703748139	-0.4834
$\pi_{3/2}(4p_y)ungrad$	-0.4268913522	-0.4268935581	-0.4834
$\sigma_{1/2}(4p_z-4p_z)grad$	-0.4172412470	-0.4172434719	-0.4825
$\pi^*_{1/2}(4p_x)grad$	-0.1883613363	-0.1883633090	-0.3545
$\pi^*_{3/2}(4p_y)grad$	-0.1786884386	-0.1786884386	-0.3545

The table (4.56) gives the contribution energies of the total energy for Se_2 molecule using basis set type $dyall-2zp$ with differenet nuclear charge distribution models in relativistic treatment.

Table 4.56: **Total Dirac-Hartree-Fock electronic energies for** Se_2

The relativistic total energy for Se_2 using Dyall basis-set $(dyall-2zp)$			
Electronic energy(a.u.) -point model	Nuclear repulsion energy(a.u.)-point model	SS Coulombic correction(a.u.)-point model	Total energy(a.u.)-point model
-5139.5160225689351	282.4232930723915	0.0010227070267	-4857.0917067895170
Electronic energy(a.u.)-Gaussian model	Nuclear repulsion energy(a.u.)-Gaussian model	SS Coulombic correction(a.u.)-Gaussian model	Total energy(a.u.)-Gaussian model
-5139.4836560419189	282.4232930723915	0.0010227070267	-4857.0593402625009

Chapter 5

Conclusions and Future Work

5.1 Conclusions

From the results shown in chapter four we conclude that

- For heavy and super heavy atoms, the high nuclear charge creates a more pronounced singularity in the relativistic case. Therfore, a number of Gaussian type functions of high exponent must be included in a basis-set in order to mimic the region of the wave function near the origin.

- For $Z = 115$ the $P_{1s}(r)$ and $Q_{1s}(r)$ have similar absolute magnitude value but with -ve sign at any distance r.
- The $Uup(Z = 115)$ atom, has most contractive $1s_{1/2}$ and diffuse $7p_{3/2}$ spinors. The expectation value for these spinors are $\langle r \rangle = 0.0093155189\,a.u.$ and $\langle r \rangle = 3.6095804\,a.u.$ respectively, suggesting that for the calculations of the properties of atoms and molecules only the outer parts of the valence spinors are important. The choice of nuclear charge distribution model will have no significant effect on the valance properties, but the properties of the spinors at or closer to the nuclei are important in the choice of the nuclear charge distribution model.
- For relativistic calculations, the point charge model is not recommendable, especially, at or closer to the nuclei. This is because of the singularity appearance. Therefore, we adopted the Gaussian-charge model combined with Gaussian type basis functions which are computationally favourable and physically more accurate than the point nucleus model.
- The total Dirac-Hartree-Fock energies for atoms (group15) depend quite a lot on the model nuclear charge distribution, and this dependecy is more obvious in the lower part of the group15 for atoms.
- For molecules, to obtain a better approximation of the exact relation between the large and small component, we must take into account the atomic balance procedure which consists of two steps:

1. An atomic calculation is performed using primitive basis functions where the small component is generated from the large component using the kinetic balance relation.
2. A new set of large and small component contracted basis function is constructed from the primitive basis combined with the expansion coefficients from this atomic calculation.

- For the superheavy element (Z=115) one set of exponents to describe the $s_{1/2}$ state, another set to describe $p_{1/2}$ and $p_{3/2}$ states, and another set to describe the $d_{3/2}$ and $d_{5/2}$, etc. This approach is favorable for superheavy elements where the $p_{1/2}$ and the $p_{3/2}$ functions have considerably different radial behaviours.

5.2 Future Work

We suggest some studies as follows:

1. Study the effects of Gaunt Interaction and Breit retardation for the heavy molecules using configuration interaction method.
2. The development of relativistic versions using the coupled cluster method to study the Nuclear Magnetic Resonance (NMR) Spectroscopy of heavy atoms and diatomic molecules.

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Publications

List of Publications:

1-Bilal K. Jasim, Ayad A. Al-Ani, and Saad N. Abood, “ Correction Four-Component Dirac-Coulomb Using Gaussian Basis-Set and Gaussian Model Distribution for Super Heavy Element (Z=115)” ,Iraqi Journal of Applied Physics , vol. (12), no. (1),pp. 17-21 January-March (2016).

2- Bilal K. Jasim, Ayad A. Al-Ani, and Saad N. Abood,” Using Gaussian Basis- Sets with Gaussian Nuclear Charge Distribution to Solve Dirac Hartree-Fock Equation for $_{83}Bi$-Atom” , Journal of Al-Nahrain University Science,vol.(19),no.(3),Sep. (2016).

الملخص

تعتبر الذرات والجزيئات من المكونات الاساسية للمادة، وتعد المفتاح الرئيسي لفهم ديناميكية وتركيب المواد. أن الحسابات الفيزيائية للذرات والجزيئات تهدف الى ايجاد الحلول العددية للمعادلات التقريبية، ومن خلال هذه الحلول يمكن الحصول على الخصائص المراد حسابها للذرات والجزيئات.

في هذا البحث تم تقديم معالجة دقيقة تشمل كلاً من الميكانيك الكمي النسبي والميكانيك الكمي غير النسبي، تم تطبيق هذه المعالجة على ذرات الزمرة 15 والتي تضم $_{7}N$، $_{15}P$، $_{33}As$، $_{51}Sb$، $_{83}Bi$، $_{115}Uup$ من الجدول الدوري والجزيئات الثنائية الذرة مثل Li_2، N_2، F_2، Se_2 . هذه المعالجات تعتمد على ثلاث تقنيات أساسية وهي مجموعة الاساسات لدوال الموجة ودالة مؤثر الطاقة (دالة هاملتن) ونوع طريقة المعالجة. النتائج المستحصلة باستخدام برنامج GRASP1.0.0 المعدل وبرنامج DIRAC14.2 تم مقارنتها مع النتائج التجريبية ونتائج حسابية لكل من C.F.Fischer (المعالجة غير النسبية) ونتائج Visscher (المعلجة النسبية).

تعتمد التقنية الأولى على تقريب مركبات البرم (spinors) النسبية الأربعة وتوسيع البرم (spinors) الى مجموعة أساسات محددة. أن كل مركبة من مركبات البرم النسبية الأربعة هي عبارة عن تراكيب خطية لدوال الأساسات العددية. أن مجموعة الأساسات العددية تتكون من دوال أساسات جاوس الكارتيزية الأولية والتي تنقسم الى مركبات كبيرة وصغيرة والتي تستخدم لوصف المركبات الكبيرة والمركبات الصغيرة لمركبات البرم النسبية على التتالي. تم تبني دوال أساسات جاوس من مجموعة أساس Dunning نوع cc-pVDZ في المعالجة غير النسبية، بينما تم استخدام مجموعة أساس Dyall من نوع dyall-2zp للمعالجة النسبية. أشتقت مجموعة أساسات دوال جاوس الصغرى في الحالة النسبية من مجموعة أساسات جاوس الكبيرة باستخدام علاقة التوازن الحركية. التقنية الثانية وتعتمد على دالة مؤثر الطاقة (دالة هاملتن) وبشكل خاص على الجهد. لهذه التقنية تم أستخدام نموذجين لوصف توزيع شحنة النواة، الأول هو نموذج توزيع الشحنة النقطية والثاني يدعى نموذج توزيع جاوس والذي يمكن تركيبة مع مجموعة أساسات جاوس ولكلا المعالجتين النسبية وغير نسبية. الحسابات الدقيقة لكل من الذرات والجزيئات تتطلب طرائق لها مرونة في معالجة الحسابات غير النسبية والنسبية. التقنية الثالثة تعتمد على طريقتين، الأولى طريقة Hartree-Fock مع مجموعة أساس Dunning في الحالة غير النسبية ، والثانية طريقة Dirac-Hartree-Fock مع مجموعة أساس Dyall في الحالة النسبية لمعالجة الأنظمة التي تحتوي على عدد من الألكترونات في الذرات والجزيئات .

أظهرت النتائج في حالة الذرات الثقيلة $_{51}$Sb، $_{83}$Bi والذرة الثقيلة جداً $_{115}$Uup أن مركبات البرم الداخلية أو القريبة من النواة من نوع $s_{1/2}$، $p_{1/2}$ تكون متعاقدة بقوة، بالأضافة الى أن لها تصرف شاذ عند النواة. من أجل وصف توزيع شحنة النواة ومعالجة السلوك الشاذ بالقرب من النواة للمدارات $s_{1/2}$، $p_{1/2}$ تم تسخير نموذج مركب من توزيع جاوس مع مجموعه دوال أساسات جاوس. النتائج المستحصلة للذرات والتي تشمل الطاقة الكلية للذرة في الحالة الأرضية ، طاقة كل مدار ذري، القيمة المتوقعة لنصف قطر كل مدار ذري، سلوك المركبات الكبيرة والمركبات الصغيرة للأوربيتالات القريبة من النواة ، تصرف التراكب القطري للأوربيتالات $P_{1/2}$، $P_{3/2}$ لكل ذرة في الزمرة 15، الطاقة الالكترونية للجزيئة وطاقة كل مدار جزيئي، كانت أفضل عند مقارنتها مع نتائج **C.F.Fischer** في حالة المعالجة غير نسبيه ونتائج **Visscher** في حالة المعالجة النسبية. أن النتائج الجيدة التي حصلنا عليها تعزى الى دقة التقنيات المنبثقة من مجموعة أساسات جاوس المتضمنة مجموعة أساس دوال **Dunning-Gauss** للحالة غير النسبية ومجموعة أساس دوال **Dyall-Gauss** للحالة النسبية لوصف الاستقطاب والارتباط للدوال الموجية في المدارات الخارجية للذرات والجزيئات وكذلك نتيجة استخدام نموذج جاوس لوصف توزيع شحنة النواة لمعالجة السلوك الشاذ للمدارات الداخلية.

وزارة التعليم العالي والبحث العلمي
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حسابات هارتري- فوك النسبية لمجموعة 15 الذرية و بعض الجزيئات ثنائية الذرة

أطروحة

مقدمة الى مجلس كلية العلوم ، جامعة النهرين، كجزء من متطلبات نيل
درجة دكتوراة فلسفة في الفيزياء

من قبل

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