

dissertation file

by Laksh Arora

Submission date: 02-May-2022 12:20PM (UTC+0530)

Submission ID: 1826014963

File name: Laksh_MSc_Dissertation.pdf (2.94M)

Word count: 5662

Character count: 27335

To Solve The Dirac Equation For Many Electron Atoms Using Dirac Hartree Fock Self Consistent Field Method



16

*A Thesis**Submitted by***LAKSH ARORA**

20615013

*For the award of the degree**Of***MASTER OF SCIENCE**

May 2022



DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE

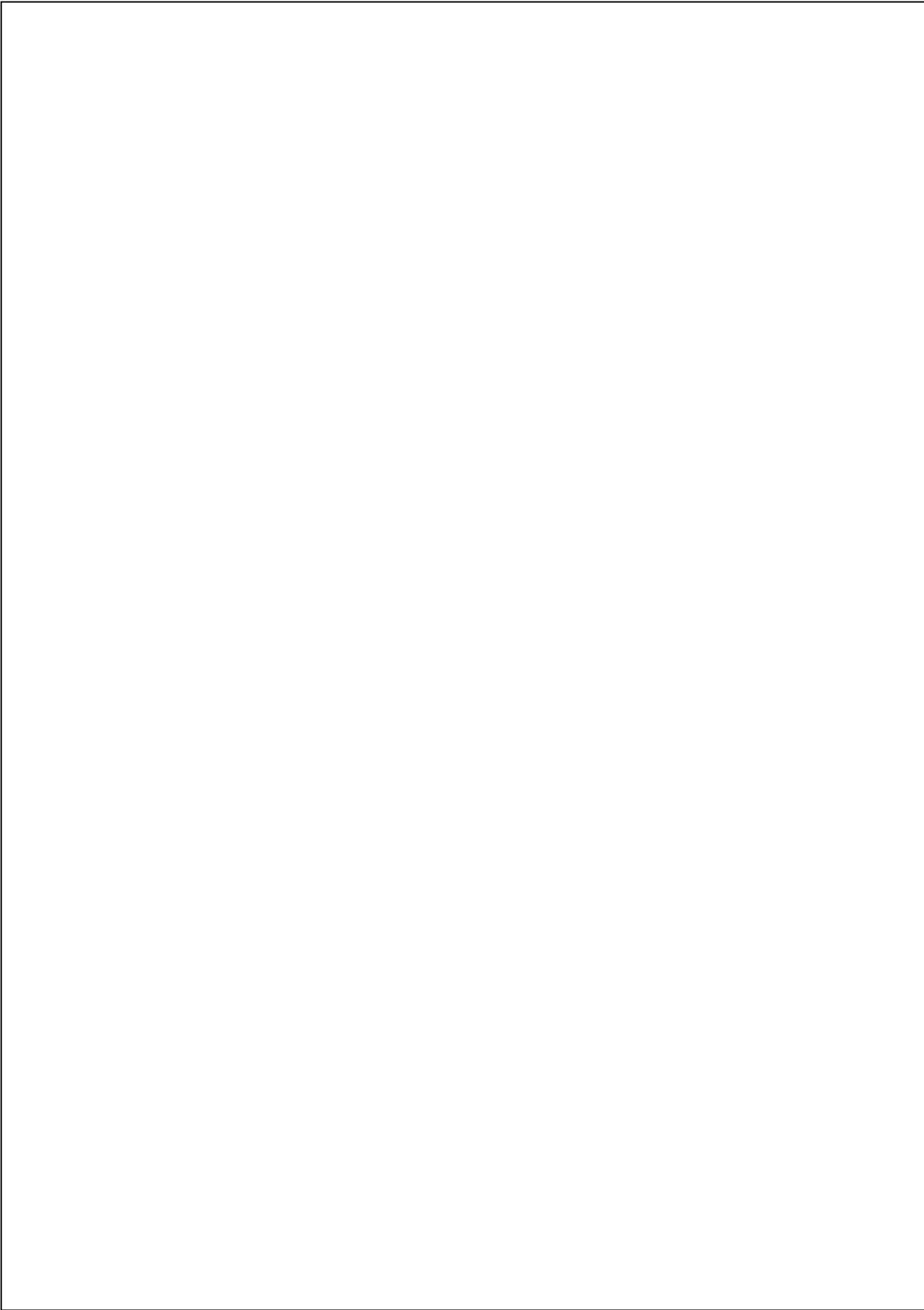
ROORKEE – 247667

To Solve The Dirac Equation For Many Electron Atoms Using Dirac Hartree Fock Self Consistent Field Method



¹
A Thesis
Submitted by
LAKSH ARORA
20615013

For the award of the degree
Of
MASTER OF SCIENCE
May 2022



THESIS CERTIFICATE

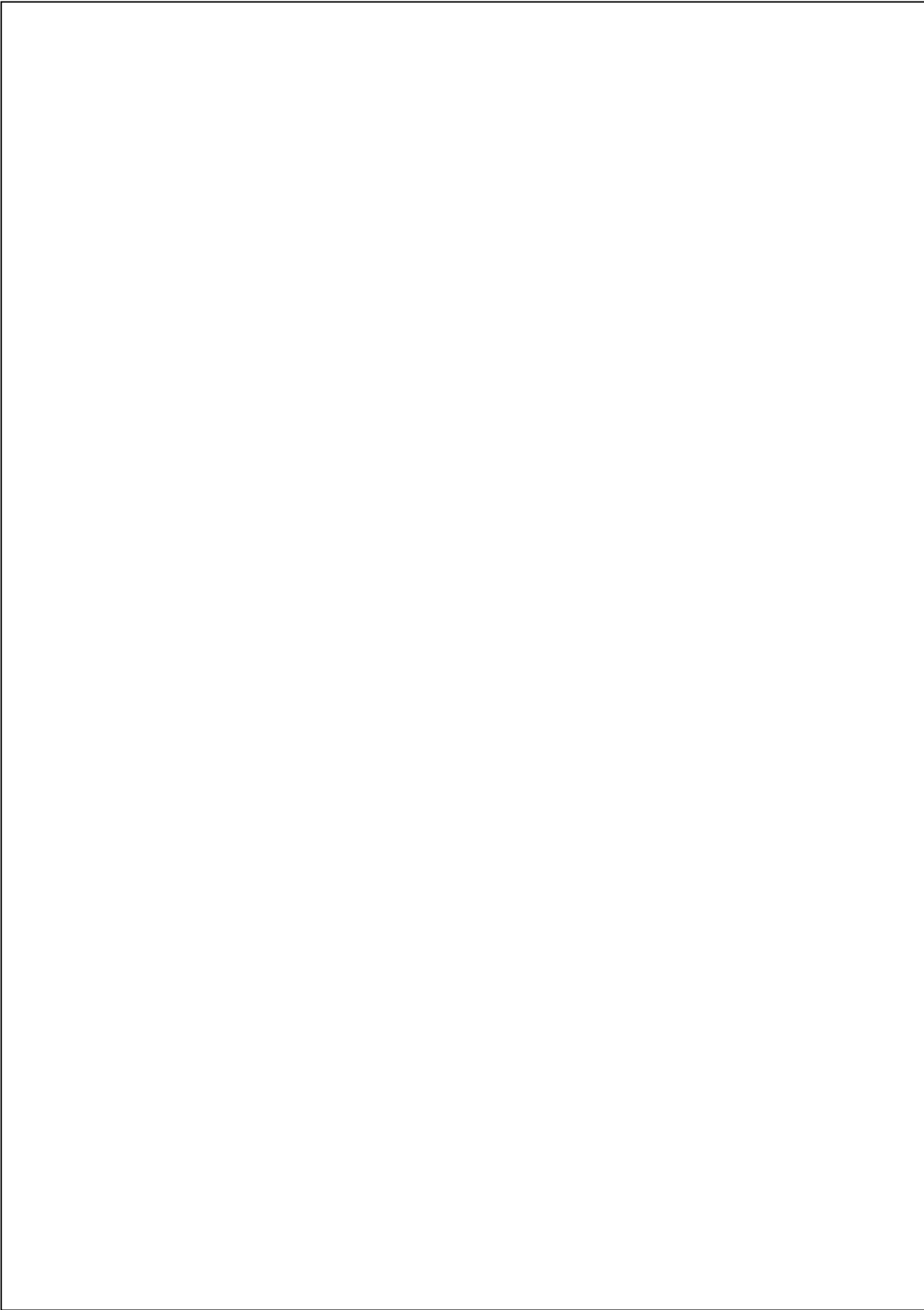
This is to undertake that the Thesis titled **TO SOLVE THE DIRAC EQUATION FOR MANY ELECTRON ATOMS USING DIRAC HARTREE FOCK SELF CONSISTENT FIELD METHOD**,¹ submitted by me to the Indian Institute of Technology Roorkee, for the award of **Master of Science**, is a bona fide record of the research work done by me under the supervision of **Dr. H. S. Nataraj**. The contents of this Thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Roorkee 247667
Date: 02 May 2022



Laksh Arora
20615013

Dr. H. S. Nataraj
Project Supervisor
Assistant Professor
Department of Physics
IIT Roorkee



CONTENTS

	Page
CHAPTER 1 DIRAC HARTREE FOCK THEORY	1
1.1 Dirac Hamiltonian	1
1.2 Hartree Fock Equations	2
1.3 Interpretation of solutions of the Hartree-Fock equations	4
1.4 Restricted closed shell Hartree Fock	5
1.5 Introduction of Basis: Roothan Equations	6
1.6 Charge Density	7
1.7 Orthogonalisation of Basis: Solving the Roothan Equations	8
1.8 The Self Consistent Field Procedure	10
1.9 Total Energy	12
CHAPTER 2 GAUSSIAN BASIS SET EXPRESSIONS	13
2.1 Basis	13
2.2 Relativistic Roothan Equations	15
CHAPTER 3 CODE CONSIDERATIONS	19
3.1 Input Parameters	19
3.2 Grid	19
3.3 Integration	19
3.4 Wigner-3j	20
3.5 SCF Procedure	20
CHAPTER 4 FAILURE AND SUGGESTIONS	21
APPENDIX A CODE	23
A.1 Main	23
A.2 Read Input	24
A.3 Set Grid	26
A.4 Factorial	27
A.5 Set Basis	28
A.6 Integral	29
A.7 One electron operator	30
A.8 Inner Integral	31
A.9 Two electron operator	31
A.10 SCF Procedure	34
A.11 Sample Input	37

CHAPTER 1

DIRAC HARTREE FOCK THEORY

This chapter is a summary of Szabo and Ostlund (1996) and Nataraj (2021b).

1.1 DIRAC HAMILTONIAN

The total Dirac-Breit Hamiltonian for a many electron system has two terms, a ²one electron part consisting of kinetic energy, mass energy and nuclear attraction given by

$$h(i) = c\boldsymbol{\alpha} \cdot \mathbf{p}_i + c^2(\beta - 1) + V_{nuc}(r_i)$$

where ²we have subtracted the rest mass energy. For a point nucleus,

$$V_{nuc}(r_i) = -\frac{Z}{r_i} \quad (1.1)$$

The second term is a two electron term consisting of a Coulomb repulsion term and the Breit interaction,

$$H_{12} = \sum_{ij, i < j} \frac{1}{r_{ij}} + \sum_{ij, i < j} B_{ij}$$

In the low frequency limit,

$$B_{12} = -\frac{1}{2r_{12}} \left\{ \boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right\}$$

²where Dirac operators $\boldsymbol{\alpha}$ and β are expressed by matrices,

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{bmatrix} \text{ and } \beta = \begin{bmatrix} I & 0 \\ 0 & I \end{bmatrix}$$

where $\boldsymbol{\sigma}$ are ²the three Pauli matrices and I is the 2×2 unit matrix.

Atomic units ($e = \hbar = m = 1$) will be used throughout this dissertation unless explicitly mentioned otherwise. We will not be considering Breit Interaction throughout this discussion.

1.2 HARTREE FOCK EQUATIONS

We are interested in finding a set of spin orbitals $\{\chi_a\}$ such that the Slater determinant formed from these spin orbitals,

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_n\rangle$$

is the best approximation to the ground state of the system.

The total energy is given by

$$E_0 = \langle\Psi_0|H|\Psi_0\rangle = \sum_a \langle a|h|a\rangle + \frac{1}{2} \sum_{ab} \langle ab||ab\rangle \quad (1.2)$$

where,

$$\langle i|h|j\rangle = \langle\chi_i|h|\chi_j\rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

$$\langle ij|kl\rangle = \langle\chi_i\chi_j|\chi_k\chi_l\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)$$

$$\langle ij||kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle$$

We can now vary the spin orbitals $\{\chi_a\}$, such that they remain orthonormal,

$$\langle\chi_a|\chi_b\rangle = \delta_{ab}$$

until the energy E_0 is minimum. The corresponding spin orbitals are the best approximation to the ground state of the system according to the variational principle.

The resulting equation is called the Hartree-Fock integro-differential equation,

$$h(1)\chi_a(1) + \sum_{b \neq a} \left[\int d\mathbf{x}_2 |\chi_b(2)|^2 r_{12}^{-1} \right] \chi_a(1) - \sum_{b \neq a} \left[\int d\mathbf{x}_2 \chi_b^*(2) \chi_a(2) r_{12}^{-1} \right] \chi_b(1) = \epsilon_a \chi_a(1) \quad (1.3)$$

where h is the one electron operator.

The two summation terms in equation 1.3 represent electron electron interaction.

The first is the Direct Coulomb term which can be interpreted as the average potential acting on the electron in χ_a from the $(N - 1)$ other electrons.

$$J_b(1) = \int d\mathbf{x}_2 |\chi_b(2)|^2 r_{12}^{-1}$$

is defined as the coulomb operator.

The second term is called the Exchange term which arises from the antisymmetric nature of the Slater determinant. It is due to a quantum phenomenon and therefore does not have a simple classical interpretation.

None the less, we can write the Hartree-Fock integro-differential equation as an eigenvalue equation,

$$\left[h(1) + \sum_{b \neq a} J_b(1) - \sum_{b \neq a} K_b(1) \right] \chi_a(1) = \epsilon_a \chi_a(1) \quad (1.4)$$

provided that

$$K_b(1) \chi_a(1) = \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_a(2) \right] \chi_b(1)$$

which involves an "exchange" of electron 1 and 2 compared to

$$J_b(1) \chi_a(1) = \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \right] \chi_a(1)$$

Since $[J_a(1) - K_a(1)] \chi_a(1) = 0$, we can add this to equation 1.4 to obtain the usual form of the Hartree-Fock equation,

$$f |\chi_a\rangle = \epsilon_a |\chi_a\rangle$$

where

$$f(1) = h(1) + \sum_b [J_b(1) - K_b(1)]$$

1.3 INTERPRETATION OF SOLUTIONS OF THE HARTREE-FOCK EQUATIONS

The orbital energies can be expressed as

$$\begin{aligned}\epsilon_i &= \langle \chi_i | f | \chi_i \rangle \\ &= \langle \chi_i | h + \sum_b (J_b - K_b) | \chi_i \rangle \\ &= \langle i | h | i \rangle + \sum_b \langle ib | ib \rangle\end{aligned}$$

If we add up all the orbital energies, we get,

$$\sum_a \epsilon_a = \sum_a \langle a | h | a \rangle + \sum_a \sum_b \langle ab | ab \rangle$$

Comparing this to equation 1.2, we can see that

$$E_0 \neq \sum_a \epsilon_a$$

Now, given a single determinant $|\Psi_0\rangle$, the ionization potential to produce an (N-1) electron single determinant $|\Psi_a\rangle$ by removing an electron from χ_a is given by,

$$\begin{aligned}IP &= {}^{N-1}E_a - {}^N E_0 \\ &= \sum_{c \neq a} \langle c | h | c \rangle + \frac{1}{2} \sum_{c \neq a} \sum_{b \neq a} \langle cb | cb \rangle - \sum_c \langle c | h | c \rangle - \frac{1}{2} \sum_c \sum_b \langle cb | cb \rangle \\ &= -\langle a | h | a \rangle - \frac{1}{2} \sum_c \langle ca | ca \rangle - \frac{1}{2} \sum_b \langle ab | ab \rangle \\ &= -\langle a | h | a \rangle - \sum_b \langle ab | ab \rangle \\ &= -\epsilon_a\end{aligned}$$

Therefore, the orbital energies are the negative of ionisation potentials to remove the corresponding electrons (Koopman's Theorem).

This difference is because we have not solved the exact electronic Schrodinger equation,

$$H |\Phi_0\rangle = E_0 |\Phi_0\rangle$$

but rather we have used the variational principle to find an approximate solution which instead are exact solutions of a Hamiltonian given by,

$$H_0 = \sum_{i=1}^N f(i)$$

1.4 RESTRICTED CLOSED SHELL HARTREE FOCK

For the rest of this thesis, we are only concerned with restricted closed shell spin orbitals, that is, we are only allowed to have an even number of electrons with all electrons paired such that all spatial orbitals are doubly occupied.

The restricted set of spin orbitals have the form,

$$\chi_i(\mathbf{x}) = \begin{cases} \psi_j(r)\alpha(\omega) \\ \psi_j(r)\beta(\omega) \end{cases}$$

Using the above, we can integrate out the spin functions to give the following closed shell equations:

$$f(1)\psi_j(1) = \epsilon_j\psi_j(1) \quad (1.5)$$

$$f(1) = h(1) + \sum_a^{N/2} 2J_a(1) - K_a(1) \quad (1.6)$$

$$J_a(1) = \int dr_2 \psi_a^*(2) r_{12}^{-1} \psi_a(2)$$

$$K_a(1)\psi_i(1) = \left[\int dr_2 \psi_a^*(2) r_{12}^{-1} \psi_i(2) \right] \psi_a(1)$$

$$E_0 = 2 \sum_a h_{aa} + \sum_a \sum_b 2J_{ab} - K_{ab}$$

1.5 INTRODUCTION OF BASIS: ROOTHAN EQUATIONS

Introduce K basis functions $\{\phi_\mu(r), \mu = 1, 2, \dots, K\}$

such that,

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_\mu \quad (1.7)$$

Substituting this into equation 1.5 gives

$$f(1) \sum_v C_{vi} \phi_v(1) = \epsilon_i \sum_v C_{vi} \phi_v(1)$$

Multiplying $\phi_\mu^*(1)$ on the left and integrating, we get,

$$\sum_v C_{vi} \int dr_1 \phi_\mu^*(1) f(1) \phi_v(1) = \epsilon_i \sum_v C_{vi} \int dr_1 \phi_\mu^*(1) \phi_v(1) \quad (1.8)$$

We define,

1.

$$S_{\mu\nu} = \int dr_1 \phi_\mu^*(1) \phi_\nu(1)$$

called the overlap matrix. It is a $K \times K$ Hermitian matrix with diagonal elements unity and $0 \leq |S_{\mu\nu}| \leq 1$, since the basis functions are generally normalised and linearly independent but not orthogonal.

2.

$$F_{\mu\nu} = \int dr_1 \phi_\mu^*(1) f(1) \phi_\nu(1)$$

called the Fock matrix.

With these, equation 1.8 can be written as

$$\sum_v F_{\mu\nu} C_{vi} = \epsilon_i \sum_v S_{\mu\nu} C_{vi},$$

$$i = 1, 2, \dots, K.$$

or more compactly,

$$FC = SC\epsilon \quad (1.9)$$

These are called the Roothan equations.

Where C is a $K \times K$ matrix of expansion coefficients $C_{\mu i}$.

$$C = \begin{bmatrix} C_{11} & C_{12} & \cdots & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & \cdots & C_{2K} \\ \vdots & \vdots & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ C_{K1} & C_{K2} & \cdots & \cdots & C_{KK} \end{bmatrix}$$

and ϵ is a diagonal matrix of orbital energies ϵ_i ,

$$\epsilon = \begin{bmatrix} \epsilon_1 & 0 & 0 & \cdots & 0 \\ 0 & \epsilon_2 & 0 & \cdots & 0 \\ \vdots & 0 & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & 0 \\ 0 & 0 & \cdots & 0 & \epsilon_K \end{bmatrix}$$

6 CHARGE DENSITY

The probability of finding an electron in a volume element dr at point r is $|\psi_a(r)|^2 dr$.

Therefore, the total charge density,

$$\rho(r) = 2 \sum_{a=1}^{N/2} |\psi_a(r)|^2$$

and

$$\begin{aligned} \int \rho(r) dr &= 2 \sum_a^{N/2} \int dr |\psi_a(r)|^2 \\ &= 2 \sum_a^{N/2} 1 \\ &= N \end{aligned}$$

Inserting the basis functions 1.7 into the above gives,

$$\rho(r) = \sum_{\mu\nu} P_{\mu\nu} \phi_{\mu}(r) \phi_{\nu}^*(r)$$

where,

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a}^* C_{\nu a}$$

is called the density matrix.

Since P is directly related to the expansion coefficients C, the spatial orbitals can be characterised by either C or P.

1.7 ORTHOGONALISATION OF BASIS: SOLVING THE Roothan EQUATIONS

If the basis were orthogonal, S would be an identity matrix and the Roothan equations 1.9 would become,

$$FC = C\epsilon$$

which is just a usual matrix eigenvalue problem.

Because of the non-orthogonality, we need a way to solve the pseudo-eigenvalue problem,

$$FC = SC\epsilon$$

This is done by orthogonalising the basis functions.

We need to find a transformation matrix X , such that,

$$\phi'_{\mu} = \sum_{\nu} X_{\nu\mu} \phi_{\nu},$$

$$\mu = 1, 2, \dots, K.$$

forms an orthonormal set.

i.e.,

$$\int dr \phi_{\mu}^{\prime*}(r) \phi_{\nu}'(r) = \delta_{\mu\nu}$$

Now,

$$\begin{aligned} \int dr \phi_{\mu}^{\prime*}(r) \phi_{\nu}'(r) &= \int dr \left[\sum_{\lambda} X_{\lambda\mu}^* \phi_{\lambda}^*(r) \right] \left[\sum_{\sigma} X_{\sigma\nu} \phi_{\sigma}(r) \right] \\ &= \sum_{\lambda} \sum_{\sigma} X_{\lambda\mu}^* \int dr \phi_{\lambda}^*(r) \phi_{\sigma}(r) X_{\sigma\nu} \\ &= \sum_{\lambda} \sum_{\sigma} X_{\lambda\mu}^* S_{\lambda\sigma} X_{\sigma\nu} \\ &= \delta_{\mu\nu} \end{aligned}$$

or,

$$X^{\dagger} S X = \mathbb{1} \quad (1.10)$$

Since S is Hermitian, it can be diagonalised by a unitary matrix U ,

$$U^{\dagger} S U = s$$

where, s is the diagonal matrix of eigenvalues of S .

There are two common ways of orthogonalising the basis set:

1. Symmetric orthogonalisation

$$X \equiv S^{-1/2} = U s^{-1/2} U^{\dagger}$$

This leads to a problem for basis sets with linear dependence and hence, is not used.

2. Canonical orthogonalisation

$$X \equiv U s^{-1/2}$$

that is, the columns of U are divided by the square root of the corresponding eigenvalues.

Now, we can eliminate columns corresponding to eigenvalues equal to zero and circumvent the problem discussed in symmetric orthogonalisation.

Now, considering

$$\begin{aligned}C' &= X^{-1}C \\C &= XC'\end{aligned}\tag{1.11}$$

$$FC = SC\epsilon$$

becomes

$$FXC' = SC'\epsilon$$

Multiplying by X^\dagger on the left, we get

$$(X^\dagger \overset{4}{FX})C' = (X^\dagger SX)C'\epsilon$$

Defining $F' = X^\dagger FX$ and using equation 1.10, we get,

$$F'C' = C'\epsilon$$

These are the transformed Roothan equations.

These can be solved by simply diagonalising F' . Once C' is obtained, C can be calculated using equation 1.11.

1.8 THE SELF CONSISTENT FIELD PROCEDURE

Since the Fock operator itself depends on the expansion coefficients, the Roothan equations are non-linear and have to be solved iteratively till there is self-consistency.

The SCF procedure can be depicted by the following flowchart:

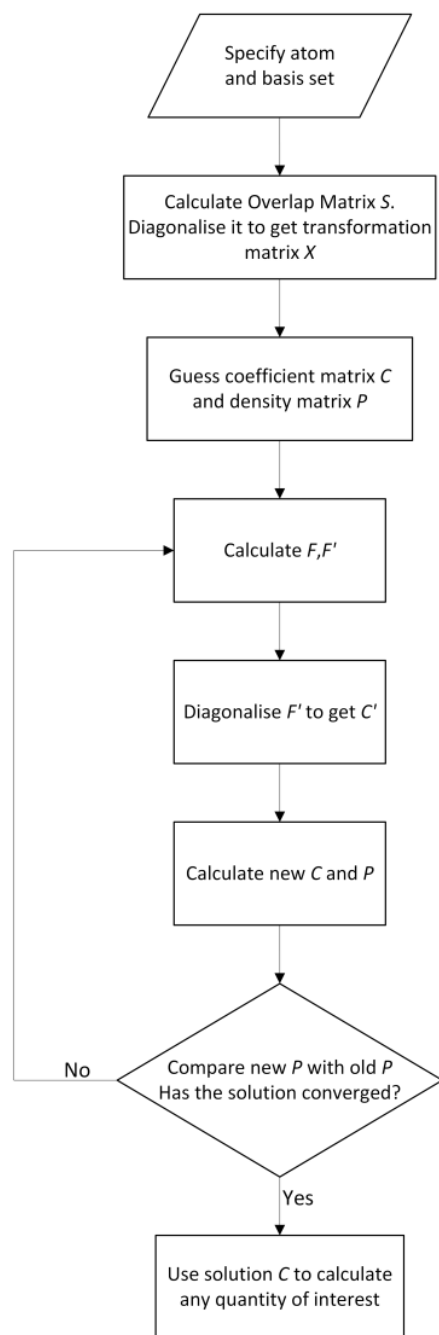


Figure 1.1: The SCF Procedure

The density matrices can be compared by calculating the standard deviation of successive density matrix elements.

1.9 TOTAL ENERGY

$$E_0 = 2 \sum_a h_{aa} + \sum_a \sum_b 2J_{ab} - K_{ab}$$

Using equation 1.6, we get,

$$E_0 = \sum_a^{N/2} (h_{aa} + f_{aa})$$

Substituting the basis function expansion from equation 1.7, we get,

$$E_0 = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\nu\mu} (h_{\mu\nu} + F_{\mu\nu}) \quad (1.12)$$

CHAPTER 2

GAUSSIAN BASIS SET EXPRESSIONS

2.1 BASIS

In the central field approximation, the solution to the Dirac equation is given by four component spinors

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

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components of the radial wave function. They satisfy the orthonormality condition,

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

The spinor $\chi_{\kappa m}(\theta, \phi)$ is given by,

$$\chi_{\kappa m} = \sum_{\sigma} Y_{l, m-\sigma}(\theta, \phi) \phi^{\sigma} c(l, 1/2, j; m - \sigma, \sigma)$$

The angular state is characterised by the quantum number κ given by

$$\kappa = -2(j - l)(j + 1/2)$$

where l is the orbital quantum number and $j = l \pm 1/2$ is the total angular momentum number, c are the Clebsch-Gordon coefficients and ϕ^{σ} are the two component spinors,

$$\phi^{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \phi^{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The radial functions are expanded in terms of the N basis functions as

$$P_{n\kappa}(r) = \sum_p^N C_{\kappa p}^L g_{\kappa p}^L(r)$$

and

$$Q_{n\kappa}(r) = \sum_p^N C_{\kappa p}^S g_{\kappa p}^S(r)$$

For the large component, we have taken Gaussian Type Orbitals (GTOs) of the form:

$$g_{\kappa i}^L(r) = C_{N_{\kappa i}}^L r^{n_{\kappa}} e^{-\alpha_i r^2}$$

where

Table 2.1: Values of n_{κ} and κ for different symmetries

Symmetry	32				
	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$
n_{κ}	1	2	2	3	3
κ	-1	+1	-2	+2	-3

The normalisation constants are

$$C_{N_{\kappa i}}^L = \left[\frac{\sqrt{\pi}}{2^{2n_{\kappa}+3/2}} \frac{(2n_{\kappa}-1)!!}{\alpha_i^{\frac{2n_{\kappa}+1}{2}}} \right]^{-1/2}$$

Using the constraint on the small component using the kinetic balance condition to prevent variational collapse, we get,

$$g_{\kappa i}^S(r) = C_{N_{\kappa i}}^S \left(\frac{d}{dr} + \frac{\kappa}{r} \right) g_{\kappa i}^L(r)$$

where,

$$C_{N_{\kappa i}}^S = \left\{ \frac{\alpha_i}{2n_{\kappa}-1} \left[(4\kappa^2-1) + 4(n_{\kappa}+\kappa) \right] \right\}^{-1/2}$$

The exponents α'_i s are generated according to

$$\alpha_i = \alpha_0 \beta^{i-1},$$

$$i = 1, 2, \dots, N.$$

where α_0 and β are input parameters.

2.2 RELATIVISTIC Roothaan Equations

The Fock matrix is of $2N_\kappa \times 2N_\kappa$ dimension. The matrices are block diagonalised according to the symmetry type κ .

$$F_\kappa C_\kappa = \epsilon_\kappa S_\kappa C_\kappa$$

where

$$C_\kappa = \begin{bmatrix} C_\kappa^L \\ C_\kappa^S \end{bmatrix}$$

$$S_\kappa = \begin{bmatrix} S_\kappa^{LL} & 0 \\ 0 & S_\kappa^{SS} \end{bmatrix}$$

Let the fock operator be $F_\kappa = h_\kappa + g_\kappa$, where

$$h_\kappa = \begin{bmatrix} V_\kappa^{LL} & c\Pi_\kappa^{LS} \\ c\Pi_\kappa^{SL} & V_\kappa^{SS} - 2c^2 S_\kappa^{SS} \end{bmatrix}$$

is the one electron operator, c is the speed of light and

$$g_\kappa = \begin{bmatrix} J_\kappa^{LL} - K_\kappa^{LL} & -K_\kappa^{LS} \\ -K_\kappa^{SL} & J_\kappa^{SS} - K_\kappa^{SS} \end{bmatrix}$$

is the two electron operator.

The various terms in the above matrices are given by the following integrals. I make no attempts to derive these in this dissertation. Refer to Clementi (1991) for derivations and further reading.

The one electron matrix has the elements,

$$S_{kij}^{TT} = \int_0^\infty g_{ki}^T(r) g_{kj}^T(r) dr$$

$$V_{kij}^{TT} = \int_0^\infty g_{ki}^T(r) V_{nuc}(r) g_{kj}^T(r) dr$$

where $V_{nuc}(r)$ is given by equation 1.1 and TT indicates LL or SS .

$$\Pi_{kij}^{SL} = \int_0^\infty g_{ki}^S(r) \left[\frac{d}{dr} + \frac{\kappa}{r} \right] g_{kj}^L(r) dr$$

and

$$\Pi_{kij}^{LS} = \Pi_{kij}^{SL\dagger}$$

The two electron matrix has the elements,

$$J_{kpq}^{TT} = \sum_{\kappa'rs} \left[D_{\kappa'rs}^{TT} J_{kpq,\kappa'rs}^{TTTT} + D_{\kappa'rs}^{\tilde{T}\tilde{T}} J_{kpq,\kappa'rs}^{0TT\tilde{T}\tilde{T}} \right]$$

and

$$K_{kpq}^{TT'} = \sum_{\nu} \sum_{\kappa'rs} [\bar{b}_{\nu}^c(jj')] D_{\kappa'rs}^{TT'} K_{kpq,\kappa'rs}^{\nu TT'TT'}$$

4 where $T\tilde{T}$ indicates LS or SL and T, T' are either L or S .

The density matrices are defined as,

$$D_{kpq}^{TT'} = N_{\kappa} C_{kp}^T C_{kq'}^T$$

where $N_{\kappa} = 2j + 1$ for closed shells.

ν is in the range

$$|j_p - j_q| \leq \nu \leq j_p + j_q$$

and the coefficient $\bar{b}_{\nu}^c(jj')$ is given by,

$$\bar{b}_{\nu}^c(jj') = \begin{bmatrix} j_p & \nu & j_q \\ 1/2 & 0 & -1/2 \end{bmatrix}^2$$

where

$$\begin{bmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{bmatrix}$$

is the Wigner-3j symbol.

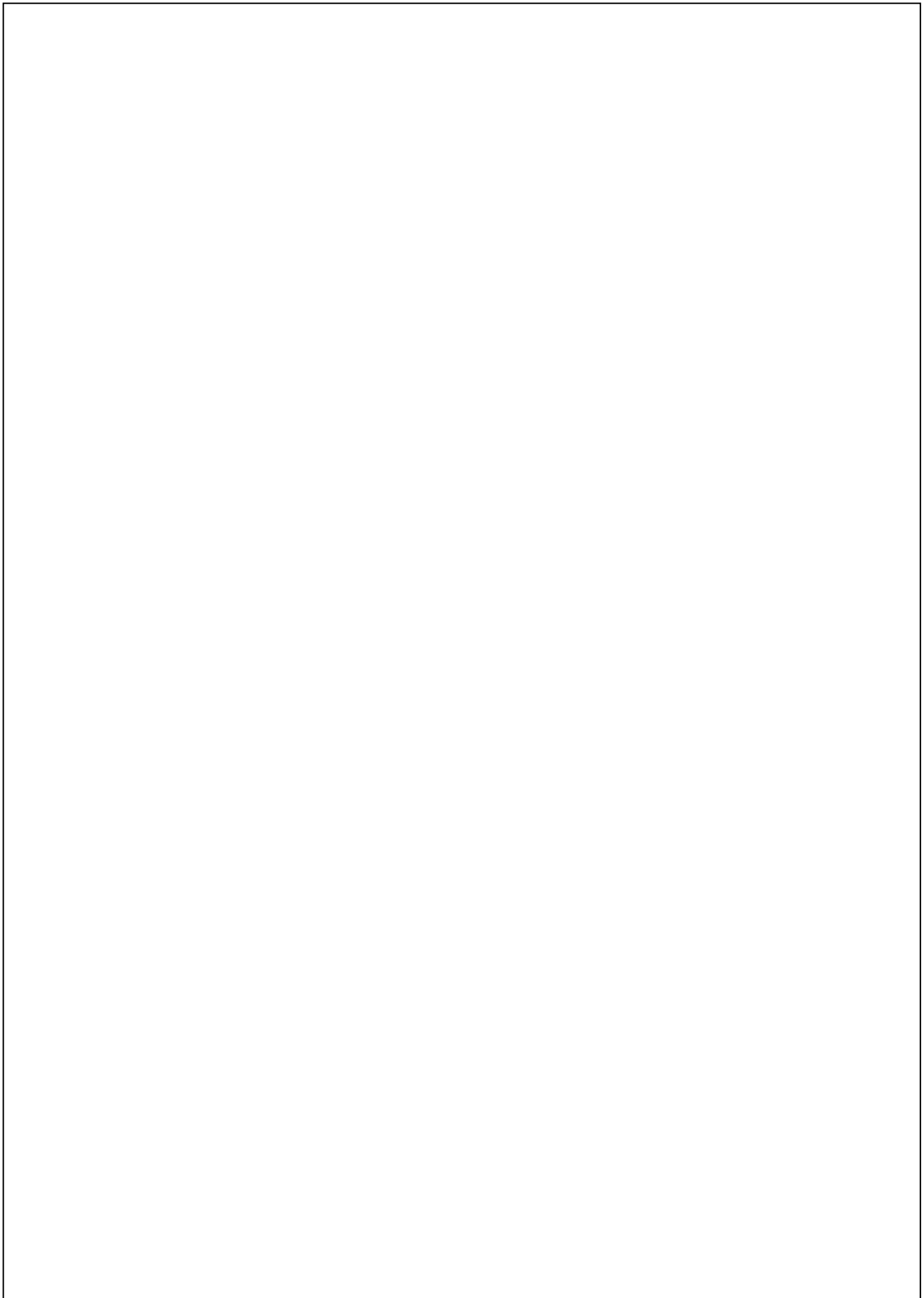
The Coulomb integrals are given by,

$$J_{kpq,\kappa'rs}^{\nu TT,T'T'} = \int_0^{\infty} \int_0^{\infty} g_{kp}^T(r_1) g_{kq}^T(r_1) U_{\nu}(r_1, r_2) g_{\kappa'r}^{T'}(r_2) g_{\kappa's}^{T'}(r_2) dr_1 dr_2$$

$$K_{kpq,\kappa'rs}^{\nu TT',TT'} = \int_0^{\infty} \int_0^{\infty} g_{kp}^T(r_1) g_{\kappa'r}^T(r_1) U_{\nu}(r_1, r_2) g_{kq}^{T'}(r_2) g_{\kappa's}^{T'}(r_2) dr_1 dr_2$$

where,

$$U_Y(r_1, r_2) = \begin{cases} \frac{r_1^Y}{r_2^{Y+1}}, & \text{if } r_1 < r_2 \\ \frac{r_2^Y}{r_1^{Y+1}}, & \text{if } r_1 > r_2 \end{cases}$$



CHAPTER 3

CODE CONSIDERATIONS

3.1 INPUT PARAMETERS

1. Atomic number, Atomic mass.
2. Number of symmetries, number of basis and occupied orbitals for each symmetry.
3. Parameters α_0 and β for the Gaussian Type Orbitals.
4. Maximum number of iterations, critical value to establish convergence.

3.2 GRID

We choose a grid which is ²⁸ nearly linear near the origin and exponentially increasing at large r ,

$$r(i) = a(e^{h(i-1)} - 1),$$
$$i = 1, 2, \dots, 740.$$

where $h = 0.03$ and $a = \frac{e^{-65/16}}{z}$.

This is done because such a grid ¹¹ gives the optimum placement of mesh points in the sense of minimizing the error in energy for a given number of degrees of freedom. For more details and derivation, refer to Levine and Wilkins (1991).

For use in calculating various integrals, we also store the following:

$$\Delta r = ae^{h(i-1)}$$

and

$$\frac{\Delta r}{r} = \frac{e^{h(i-1)}}{e^{h(i-1)} - 1}$$

3.3 INTEGRATION

All integrations are done using the 11-point Newton-Cotes method. The grid is divided into 11-point segments and area of each segment is calculated using

$$\int_{x_1}^{x_{11}} f(x) dx = \frac{5}{299376} h [16067(f_1 + f_{11}) + 106300(f_2 + f_{10}) - 48525(f_3 + f_9) + 272400(f_4 + f_8) - 260550(f_5 + f_7) + 427368f_6]$$

where h is the distance between two consecutive points.

3.4 WIGNER-3J

I am using Sovkov (2022) to calculate the Wigner-3j symbol. It is freely available to download at Matlab File Exchange.

3.5 SCF PROCEDURE

The first guess for the density matrix is generally taken to be $P = 0$. This corresponds to neglecting the electron electron interaction and is therefore a logical guess to make. This also means that there is no need to calculate the two electron operator during the first iteration.

The difference between consecutive density matrices is calculated as

$$\delta = \left[K^{-2} \sum_{\mu} \sum_{\nu} \left[P_{\mu\nu}^{(i)} - P_{\mu\nu}^{(i-1)} \right]^2 \right]^{1/2}$$

where $K = 2$.

It is generally seen according to Szabo and Ostlund (1996) that a value of $\delta = 10^{-4}$ will usually give an error in the energy of less than 10^{-6} Hartrees.

If the maximum number of iterations are exceeded without convergence, the code stops. At the end of the code, I only try to calculate the total energy as given by equation 1.12 to no avail however, as discussed in the next chapter.

The complete Matlab code is attached in Appendix A.

CHAPTER 4

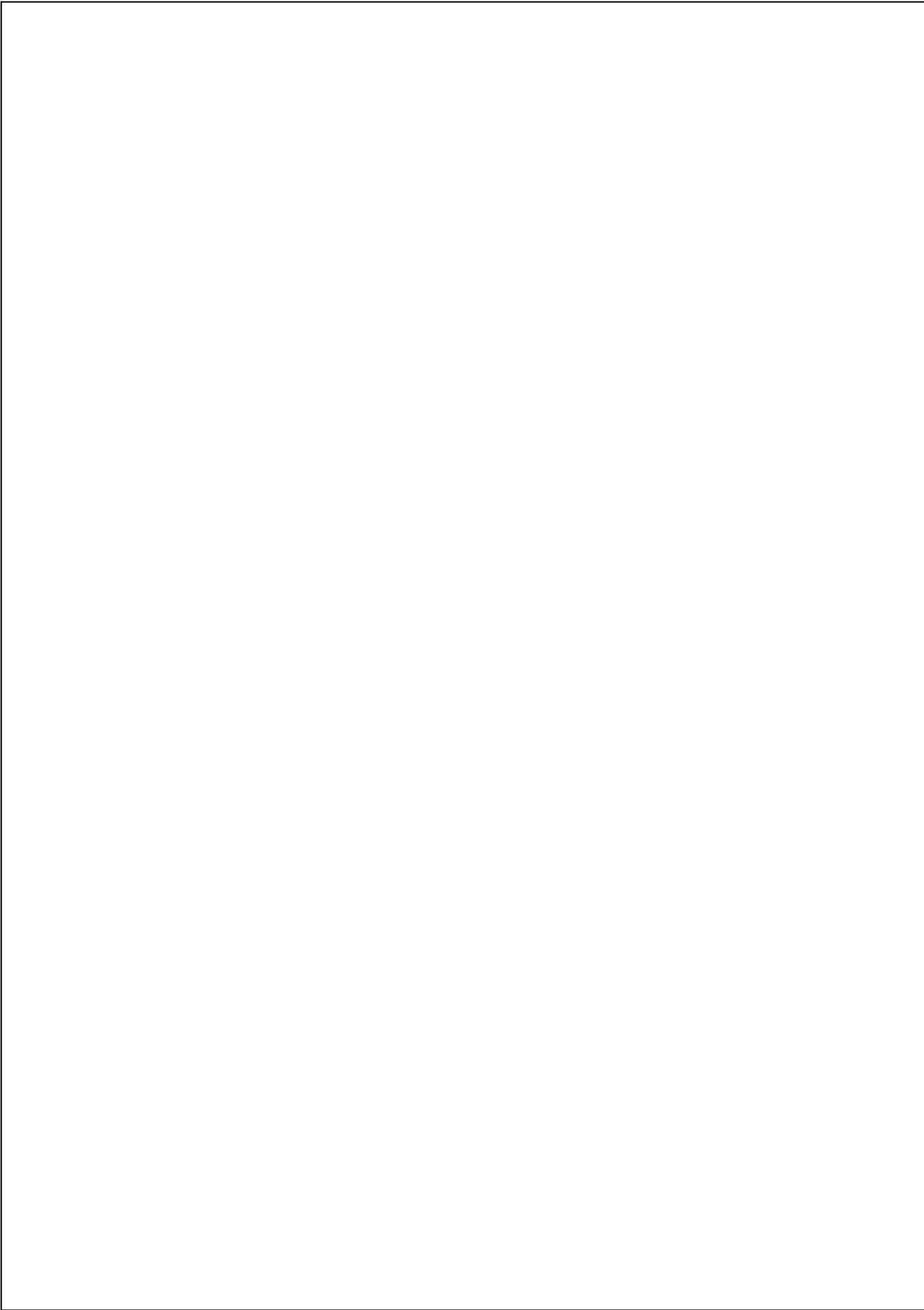
FAILURE AND SUGGESTIONS

I have been unable to get the SCF Procedure to converge. Therefore, I didn't add any more features to the code as planned earlier.

A second problem is that calculation of the double integrals takes too long. Some ways of approximation the inner integral at the cost of accuracy should be added as in Nataraj (2021a).

Some suggestions for anyone who builds upon my work are as follows:

1. Some working code should be used to generate a solution very close to convergence. This should then be used as an initial guess to check the code.
2. If that works, some advanced methods of accelerating convergence ,for example in Schlegel (1991), may be looked at.
3. If the speed of calculating double integrals is increased, atoms with high atomic number should be used. In this case, our approximate solutions are closer to the exact solution as the approximation of an average potential due to all the electrons is more valid.



APPENDIX A

CODE

A.1 MAIN

```
% Input Values
%
% (a) atom : symbol of atom in two capital letters
%
% (b) nsym: no. of symmetry to be used
%
% (c) nbas(i) : no. of basis for each symmetry
%
% (d) nocorb(i) : no. of occupied orbitals for each symmetry
%
% (e) alpha and beta : values for generating basis
%
% (f) maxit : max. no. of iterations it should check for
↳ convergence
%
% (g) npower : tolerance parameter for  $10^{(-npower)}$ 
%
% (h) amass : mass number
%
% (i) z : atomic number

%-----
% the output files are:
↳
%
↳
% scfout.out: contains all information of orbital energies
↳
% wfn.dat : binary file containing df wave functions
↳
%
↳
%-----

% this is the tiny number to check density consistency in each
↳ iteration
global tiny
```



```
tiny = 1.0e-12;
```

```
readingp();  
setgrd();  
setbasis();  
setmatrix();  
scfiter();
```

A.2 READ INPUT

```
function readingp
```

```
% This subroutine reads input from scfinp.dat
```

```
global atom stdout stdin iwfn nsym nbas nocorb alpha0 beta maxit
```

```
↳ npower ...
```

```
orbj kap amass z nbasis nocc mbasis crit h n rnt rrms rho
```

```
stdout = fopen('scfout.out','w');
```

```
stdin = fopen('scfinp.dat','r');
```

```
iwfn = fopen('wfn.dat','w');
```

```
% read atom
```

```
atom = fgetl(stdin);
```

```
% read number of symmetries
```

```
nsym = str2double(fgetl(stdin));
```

```
% read number of basis for each symmetry in the form of space
```

```
↳ separated values
```

```
nbas = str2num(fgetl(stdin));
```

```
% read number of occupied orbitals for each symmetry in the form
```

```
↳ of space separated values
```

```
nocorb = str2num(fgetl(stdin));
```

```
% total number of basis
```

```
nbasis=sum(nbas);
```

```
mbasis=2*nbasis;
```

```
% read constants to generate exponents
```

```
alpha0 = str2double(fgetl(stdin));
```

```
beta = str2double(fgetl(stdin));
```

```
% read maximum number of iterations
```

```
maxit = str2double(fgetl(stdin));
```

```
% read tolerance
```



```

rpor(1) = 0;

fprintf(stdout,'stepsize=%f total grids= %d\n',h,n);
fprintf(stdout,'maximum radius r(n) = %f\n',r(n));

end

```

A.4 FACTORIAL

```

%c ^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^
%c function idbf
%c ^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^
%c      calculates factorial
%c-----
function fac = idbf(x,i)
k = 1;
for m = x
    if(m<-1)
        fprintf(stdout,'factorial problem: m<-1 %d',m);
        return

    else

        if(m==0 || m==-1)

            if(m==0)
                tmp=1;
            end

            if(m==-1)
                if(i==2)
                    tmp=1;
                else
                    fprintf('factorial problem: m<0 %d',m);
                    return
                end
            end

        else

            tmp=1;

            for j=m:-i:1
                tmp=j*tmp;
            end

```

end

end

fac(k) = tmp;

k = k+1;

end

end

A.5 SET BASIS

function setbasis

% This subroutine calculates the GTOs

global stdout nsym nbas nocorb alpha1 beta1 orbj kap r nbasis gl

↪ gs dgl ...

dg1 dg2 kappe orbje kappc orbjc iqe iqc lorba lorbb nskipe

↪ nskipc alpha

lorba=[0 1 1 2 2 3 3 4 4 5 5 6 6 7 7];

lorbb=[1 0 2 1 3 2 4 3 5 4 6 5 7 6 8];

nk = lorba+1;

nskipc = [0 cumsum(nbas)];

for isym=1:nsym

ii = nskipc(isym);

nn = nbas(isym);

if (nn~=0)

kappe(ii+1:ii+nn)=kap(isym);

orbje(ii+1:ii+nn)=orbj(isym);

nke(ii+1:ii+nn)=nk(isym);

iqe(ii+1:ii+nn) = (-1)^(isym+1);

alpha(ii+1:ii+nn) = alpha1.*(beta1.^(0:(nbas(isym)-1)));

end

end

nskipc = [0 cumsum(nocorb)];

for isym=1:nsym

ii = nskipc(isym);

nn=nocorb(isym);

if(nn~=0)

kappc(ii+1:ii+nn)=kap(isym);

orbjc(ii+1:ii+nn)=orbj(isym);

iqc(ii+1:ii+nn) = (-1)^(isym+1);

end

end

```

fprintf(stdout,' total number of basis function= %d',nbasis);
fprintf(stdout,'symmetry  no. of occ orbits  nskipc');

for isym=1:nsym
    fprintf(stdout,'%d          %d
    ↪ %d',isym,nocorb(isym),nskipc(isym));
end

fprintf(stdout,'symmetry  no. of basis function  nskie');
for isym=1:nsym
    fprintf(stdout,'%d          %d
    ↪ %d',isym,nbas(isym),nskie(isym));
end

ifact=idbf(2.*nke-1,2);
power=(2.*nke+1)./2;
cnl=sqrt((2.^(2.*nke+1.5)).*(alpha.^power)./(ifact.*sqrt(pi)));
fact1=4.*alpha.*((nke+kappe).^2)./(2.*nke-1);
fact2=(2.*nke+1).*alpha;
fact3=-4.*alpha.*(nke+kappe);
cns=sqrt(1./(fact1+fact2+fact3));

expon= exp(-(alpha.').*r.*r);

gl=(cnl.').*expon.*(r.^(nke.')). %9
gs=(cns.').*gl.*((nke. '+kappe.')./r - 2.*(alpha.').*r);
gs(:,1)=0; %9
dgl=gl.*((nke. '+kappe.')./r - 2.*(alpha.').*r);
dgl(:,1)=0; %9
dg1=((nke.')./r) - (2.*(alpha.').*r);
dg1(:,1)=0; %9
dg2=-(((nke. '+kappe.')./r)/(r.^2))+2.*(alpha.'))./...
((nke. '+kappe.')./r-2.*(alpha.').*r);
dg2(:,1)=0;

end

```

A.6 INTEGRAL

```

function res = valint(fx)
%C  ^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^
%C   this is the integration routine using 11-point Newton-Cotes
%C  ^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^
global h n

```



```

nskipec nskipc ...
df_two orbjc vec mbasis gl gs orbje rp

Jll(mbasis,mbasis)=0;
Jss(mbasis,mbasis)=0;
Kll(mbasis,mbasis)=0;
Kss(mbasis,mbasis)=0;
Kls(mbasis,mbasis)=0;
Ksl(mbasis,mbasis)=0;

for isym=1:nsym
    for ip=1:nbas(isym)

        jp=ip+nskipec(isym);
        kp=ip+2*nskipec(isym);
        indexp=ip+nbas(isym)+2*nskipec(isym);
        j1 = orbje(jp);

        for iq=1:nbas(isym)

            jq=iq+nskipec(isym);
            kq=iq+2*nskipec(isym);
            indexq=iq+nbas(isym)+2*nskipec(isym);
            j2 = orbje(jq);

            for jsym=1:nsym
                for ik=1:nocorb(jsym)

                    jk=ik+nskipc(jsym);
                    kk=ik+2*nskipec(jsym);

                    Nk = 2*orbjc(jk)+1;

                    for ir=1:nbas(jsym)

                        jr=ir+nskipec(jsym);
                        kr=ir+2*nskipec(jsym);
                        indexr=ir+nbas(jsym)+2*nskipec(jsym);

                        for is=1:nbas(jsym)

                            js=is+nskipec(jsym);
                            ks=is+2*nskipec(jsym);
                            indexs=is+nbas(jsym)+2*nskipec(jsym);

                            Dll = Nk*vec(kr,kk)*vec(ks,kk);

```

```

Dss =
→ Nk*vec(indexr,kk)*vec(indexs,kk);
    Dls = Nk*vec(kr,kk)*vec(indexs,kk);
    Dsl = Nk*vec(indexr,kk)*vec(ks,kk);

Jl1l1 =
→ valint(gl(jp,:).*gl(jq,:).*valint2(0,gl(jr,:),gl(js,:)).*rp);
    Jl1ss =
→ valint(gl(jp,:).*gl(jq,:).*valint2(0,gs(jr,:),gs(js,:)).*rp);
    Js1ss =
→ valint(gs(jp,:).*gs(jq,:).*valint2(0,gs(jr,:),gs(js,:)).*rp);
    Js1sl =
→ valint(gs(jp,:).*gs(jq,:).*valint2(0,gl(jr,:),gl(js,:)).*rp);

→ J1l(kp,kq)=J1l(kp,kq)+D1l*Jl1l1+Dss*Jl1ss;
→ Jss(indexp,indexq)=Jss(indexp,indexq)+Dss*Js1ss+D1l*Js1sl;

    for v=abs(j1-j2):(j1+j2)

        factor =
→ Wigner3j(j1,v,j2,0.5,0,-0.5)^2;
        %Vladimir Sovkov (2022). Wigner
→ 3j-6j-9j ...
→ %https://www.mathworks.com/matlabcentral/fileexchange/74069-wigner-3j-6j-9j

    K1l1l =
→ valint(gl(jp,:).*gl(jr,:).*valint2(v,gl(jq,:),gl(js,:)).*rp);
    Ks1ss =
→ valint(gs(jp,:).*gs(jr,:).*valint2(v,gs(jq,:),gs(js,:)).*rp);
    K1sls =
→ valint(gl(jp,:).*gl(jr,:).*valint2(v,gs(jq,:),gs(js,:)).*rp);
    Ks1sl =
→ valint(gs(jp,:).*gs(jr,:).*valint2(v,gl(jq,:),gl(js,:)).*rp);

→ K1l(kp,kq)=K1l(kp,kq)+factor*D1l*K1l1l;
→ Kss(indexp,indexq)=Kss(indexp,indexq)+factor*Dss*Ks1ss;
→ K1s(kp,indexq)=K1s(kp,indexq)+factor*D1s*K1sls;
→ Ksl(indexp,kq)=Ksl(indexp,kq)+factor*Dsl*Ks1sl;

```



```

        dfpotiter();
    end
    for isym=1:nsym
        ndim=nbas(isym);
        ndim2=2*ndim;
        skip = 2*nskipe(isym);
        stemp = S(1+skip:ndim2+skip,1+skip:ndim2+skip);

        drs = stemp;

        [drs,temp] = eig(drs);
        [sa,ind] = sort(diag(temp),'descend');
        drs = drs(:,ind);

→ %C-----
        %C         canonical transformation

→ %C-----

        if (min(abs(sa))>tiny)
            can = drs./sqrt(abs(sa'))
        else
            fprintf('there is diagonalisation problem
→ %f\n\n',min(abs(sa)));
            return
        end

        if(iter~=1)
            a=df_single(1+skip:ndim2+skip,1+skip:ndim2+skip)+...
              df_two(1+skip:ndim2+skip,1+skip:ndim2+skip)
        else
            a=df_single(1+skip:ndim2+skip,1+skip:ndim2+skip)
        end

        df_mat = can'*a*can

        [df_mat,temp] = eig(df_mat)
        [eng,ind] = sort(diag(temp),'ascend')
        df_mat = df_mat(:,ind)

        drs = df_mat

        eigv = can*drs

        oe(1:ndim2,isym)=eng

```

```

        pold(1+skip:ndim2+skip,1+skip:ndim2+skip) =
↪ p1(1+skip:ndim2+skip,1+skip:ndim2+skip);

        nn=nocorb(isym);
        if(nn~=0)
            p1(1+skip:ndim2+skip,1+skip:ndim2+skip) =
↪ (2*orbj(isym)+1)*eigv(:,1:nn)*eigv(:,1:nn)'
            end

        vec(1+skip:ndim2+skip,1+skip:ndim2+skip)=eigv

    end
    delta=sum(sum((p1-pold).^2))

    delta=sqrt(delta/4.0)

    fprintf(stdout,'%3d  %20.7f\n',iter,delta);
    fprintf('%3d  %20.7f\n',iter,delta);
    if(delta<crit)
        break
    end
end
if (iter>=maxit)
    fprintf(stdout,'\n\n scf fails to converges at cycle
↪ %4d\n',iter);
    return
end

en = 0.5*sum(sum(p1.*(2*df_single+df_two)))

fprintf(stdout,'\n\nscf converges at cycle, %4d\n',iter);
fprintf(stdout,'\n\nscf electronic energy=, %25.15f\n',en);

fprintf(stdout,'\n\norbital energies (+ve and -ve)\n');

for isym=1:nsym
    for ibas=1:nbas(jsym)
        fprintf(stdout,['%2d %s %25.15f
↪ %25.15f\n',ibas,nh_i(isym), ...
            oe(ibas,isym),oe(ibas+nbas(jsym),isym)]);
        end
    end
end
end

```

A.11 SAMPLE INPUT

RB

11

8 6 6 4 4 3 3 2 2 1 1

4 3 3 1 1 0 0 0 0 0 0

0.00625

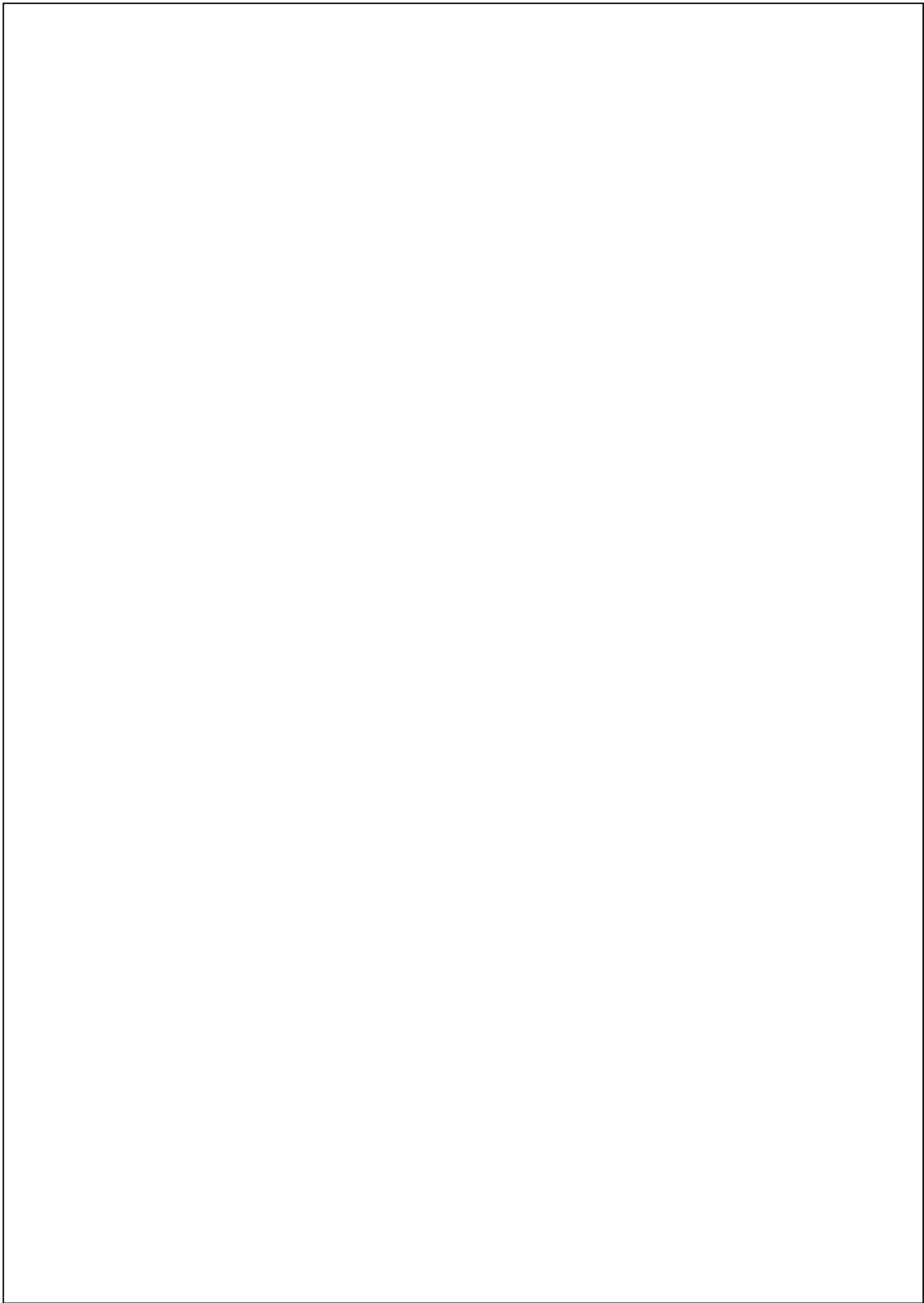
2.63

25

4

85.4678

37



REFERENCES

1. Clementi, E. (1991). Modern techniques in computational chemistry: Motecc-91.
2. Levine, Z. H. and J. W. Wilkins (1991). An energy-minimizing mesh for the schrödinger equation. *Journal of Computational Physics*, **83**, 361–372. ISSN 0021-9991. URL <https://www.sciencedirect.com/science/article/pii/0021999189901241>.
3. Nataraj, H. S. (2021a). Fortran code df_scf.f90.
4. Nataraj, H. S. (2021b). Unit-1 many electron atoms. PHN-626 Advanced Atomic and Molecular Physics, IIT Roorkee.
5. Schlegel, J., H.B. and McDouall (1991). Do you have scf stability and convergence problems? *Computational Advances in Organic Chemistry: Molecular Structure and Reactivity*, **330**. URL https://link.springer.com/chapter/10.1007/978-94-011-3262-6_2.
6. Sovkov, V. (2022). Wigner 3j-6j-9j. URL <https://www.mathworks.com/matlabcentral/fileexchange/74069-wigner-3j-6j-9j>.
7. Szabo, A. and N. S. Ostlund, *Modern quantum chemistry: Introduction to advanced electronic structure theory*. Dover Publications, inc., 1996. ISBN 9780486691862.

dissertation file

ORIGINALITY REPORT

14%

SIMILARITY INDEX

9%

INTERNET SOURCES

9%

PUBLICATIONS

6%

STUDENT PAPERS

PRIMARY SOURCES

- | | | |
|---|--|----|
| 1 | Submitted to Indian Institute of Technology, Madras
Student Paper | 2% |
| 2 | Ajaya K. Mohanty. "A Dirac-Fock self-consistent field method for closed-shell molecules including Breit interaction", International Journal of Quantum Chemistry, 05/20/1992
Publication | 1% |
| 3 | gim.unex.es
Internet Source | 1% |
| 4 | Pedro Antonio Soares de Alcântara. "On symbol correspondences for spin and quark systems", Universidade de Sao Paulo, Agencia USP de Gestao da Informacao Academica (AGUIA), 2022
Publication | 1% |
| 5 | www.mathworks.com
Internet Source | 1% |
| 6 | Submitted to Facultad Latinoamericana de Ciencias Sociales (FLACSO) - Sede Ecuador | 1% |

7

cfile25.uf.tistory.com

Internet Source

1 %

8

Hans Shih-Han Wang, Cory Cornelius, Brandon Edwards, Jason Martin. "Toward Few-step Adversarial Training from a Frequency Perspective", Proceedings of the 1st ACM Workshop on Security and Privacy on Artificial Intelligence, 2020

Publication

<1 %

9

Rezaei, G.. "Nonlinear optical properties of a hydrogenic impurity in an ellipsoidal finite potential quantum dot", Current Applied Physics, 201103

Publication

<1 %

10

fismed.ciemat.es

Internet Source

<1 %

11

www.osti.gov

Internet Source

<1 %

12

Nan Wang, Zhen Qin, Xuanhui Wang, Hongning Wang. "Non-Clicks Mean Irrelevant? Propensity Ratio Scoring As a Correction", Proceedings of the 14th ACM International Conference on Web Search and Data Mining, 2021

Publication

<1 %

13

Internet Source

<1 %

14

Submitted to Indian Institute of Technology
Guwahati

Student Paper

<1 %

15

deepblue.lib.umich.edu

Internet Source

<1 %

16

www.ee.iitm.ac.in

Internet Source

<1 %

17

Submitted to Pennsylvania State System of
Higher Education

Student Paper

<1 %

18

Submitted to Indian Institute of Technology,
Kanpur

Student Paper

<1 %

19

Submitted to The University of Manchester

Student Paper

<1 %

20

Fei Song, Zhengyang Ai, Haowei Zhang, Ilsun
You, Shiyong Li. "Smart Collaborative
Balancing for Dependable Network
Components in Cyber-Physical Systems", IEEE
Transactions on Industrial Informatics, 2020

Publication

<1 %

21

Submitted to Australian National University

Student Paper

<1 %

22 Luis Serrano-Andrés, Juan José Serrano-Pérez. "Chapter 14 Calculation of Excited States: Molecular Photophysics and Photochemistry on Display", Springer Science and Business Media LLC, 2012 $<1\%$

Publication

23 Submitted to KTH - The Royal Institute of Technology $<1\%$

Student Paper

24 Mukhopadhyay, Atashi Basu. "Theoretical Investigation of Static and Dynamic Properties of Zeolite ZSM-5 Based Amorphous Material", Kölner UniversitätsPublikationsServer, 2011. $<1\%$

Publication

25 web.archive.org $<1\%$

Internet Source

26 Jakob Sternby. "Frame Deformation Energy Matching of On-Line Handwritten Characters", Lecture Notes in Computer Science, 2005 $<1\%$

Publication

27 Jingtao Yao, Chew Lim Tan. "A case study on using neural networks to perform technical forecasting of forex", Neurocomputing, 2000 $<1\%$

Publication

28 Svetlana Kotochigova, Zachary H. Levine, Eric L. Shirley, M. D. Stiles, Charles W. Clark. $<1\%$

"Local-density-functional calculations of the energy of atoms", Physical Review A, 1997

Publication

29

arxiv.org

Internet Source

<1 %

30

epdf.pub

Internet Source

<1 %

31

epljournal.edpsciences.org

Internet Source

<1 %

32

researchbank.rmit.edu.au

Internet Source

<1 %

33

www.ideals.illinois.edu

Internet Source

<1 %

Exclude quotes Off

Exclude matches < 10 words

Exclude bibliography Off