

Dissertation Stage-II (PHN-600B) End-Term Presentation

Supervisor – Dr H S Nataraj

Laksh Arora

20615013

Topic

Solving the Dirac Hamiltonian for Many
Electron Atoms using Dirac Hartree Fock
Self Consistent Field Method in MATLAB

Dirac Hartree Fock Theory

A summary of Szabo and Ostlund (1996) and Nataraj (2021*b*).

Dirac Hamiltonian

The total Dirac-Breit Hamiltonian for a many electron system has two terms, a one 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 we 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,

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

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,

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

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

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

Hartree-Fock Equations

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,

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

Hartree-Fock Equations

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,

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

Hartree-Fock Equations

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

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

Interpretation of Solutions

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

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

$$E_0 \neq \sum_a \epsilon_a$$

Interpretation of Solutions

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

$$\begin{aligned}IP &= {}^{N-1}E_a - {}^NE_0 \\&= \sum_{c \neq a} \langle c|h|c \rangle + \frac{1}{2} \sum_{c \neq a} \sum_{b \neq a} \langle cb||cb \rangle - \sum_c \langle c|h|c \rangle - \frac{1}{2} \sum_c \sum_b \langle cb||cb \rangle \\&= -\langle a|h|a \rangle - \frac{1}{2} \sum_c \langle ca||ca \rangle - \frac{1}{2} \sum_b \langle ab||ab \rangle \\&= -\langle a|h|a \rangle - \sum_b \langle ab||ab \rangle \\&= -\epsilon_a\end{aligned}$$

Interpretation of Solutions

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,

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

Restricted Closed shell Hartree-Fock

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:

Restricted Closed shell Hartree-Fock

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

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

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

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

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

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

$$f(1) \sum_{\nu} C_{\nu i} \phi_\nu(1) = \epsilon_i \sum_{\nu} C_{\nu i} \phi_\nu(1)$$

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

$$\sum_{\nu} C_{\nu i} \int dr_1 \phi_\mu^*(1) f(1) \phi_\nu(1) = \epsilon_i \sum_{\nu} C_{\nu i} \int dr_1 \phi_\mu^*(1) \phi_\nu(1) \quad (1.8)$$

Basis: Roothan Equations

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

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i},$$

Szabo, A., & Ostlund, N. S. (1996). Modern quantum chemistry:
Introduction to advanced electronic structure theory.

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

Basis: Roothan Equations

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 $C_{\mu i}$.

and ϵ is a diagonal matrix of orbital energies ϵ_i ,

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

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

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

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

Charge Density

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.

Orthogonalisation of basis: Solving the Roothan Eqs.

If the basis were orthogonal, S would be an identity matrix and the Roothan equations 1.9 would become, $FC = SC\epsilon$

$$FC = C\epsilon$$

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.

Orthogonalisation of basis: Solving the Roothan Eqs.

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.

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

or,

$$X^\dagger S X = \mathbb{1} \tag{1.10}$$

Orthogonalisation of basis: Solving the Roothan Eqs.

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.

Orthogonalisation of basis: Solving the Roothan Eqs.

Now, considering

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

becomes

$$FC = SC\epsilon$$

$$FXC' = SXC'\epsilon$$

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

$$(X^\dagger FX)C' = (X^\dagger SX)C'\epsilon$$

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

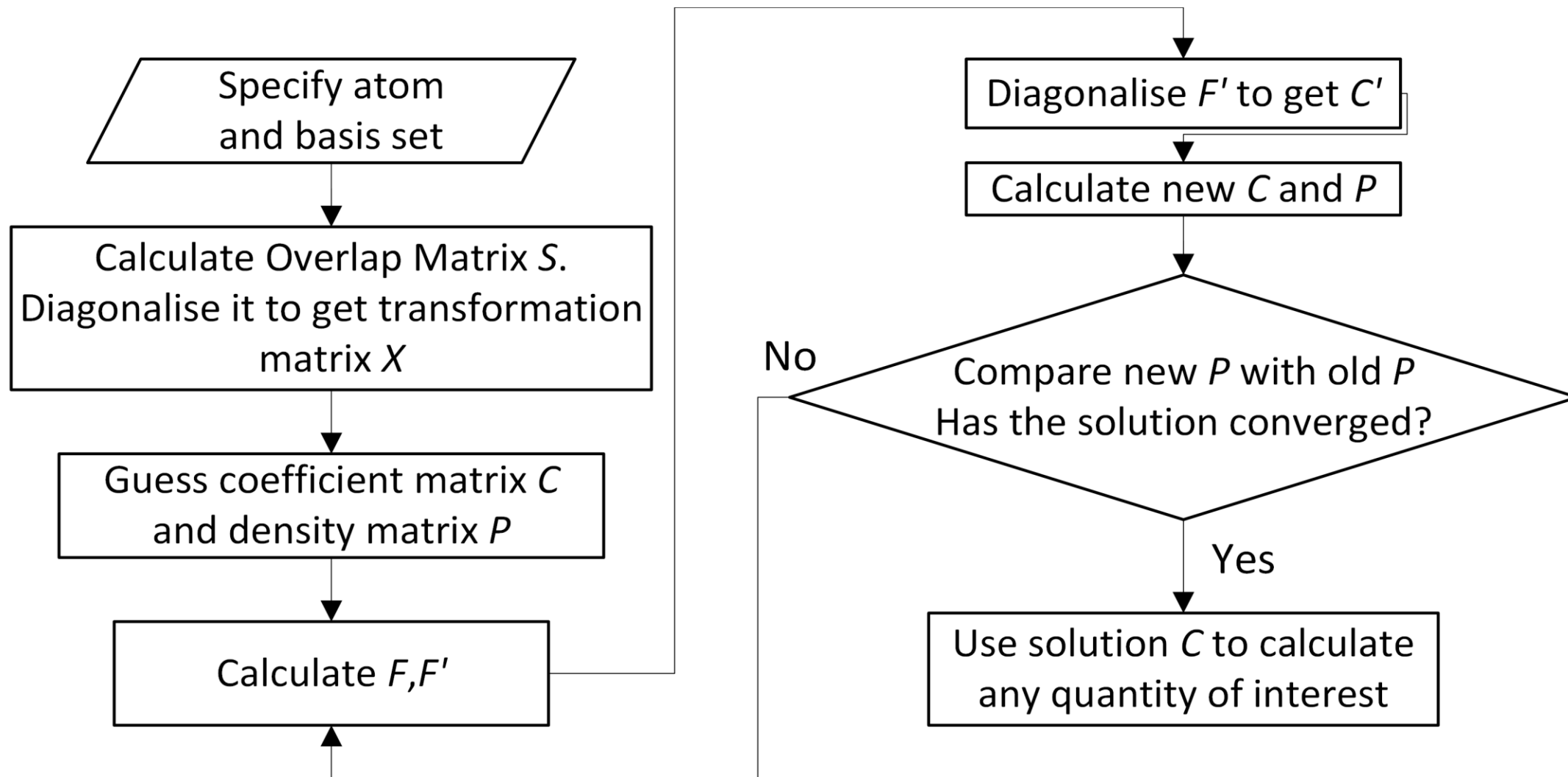
$$F'C' = C'\epsilon$$

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.

SCF 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.



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,

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

Gaussian Basis Set Expressions

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 angular state is characterised by the quantum number κ given by

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

Basis

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:

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

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

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

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

Basis

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.

Relativistic Roothan 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

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

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

Relativistic Roothan Equations

Let the fock operator be $F_K = h_K + g_K$, where

$$h_K = \begin{bmatrix} V_K^{LL} & c\Pi_K^{LS} \\ c\Pi_K^{SL} & V_K^{SS} - 2c^2 S_K^{SS} \end{bmatrix}$$

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

$$g_K = \begin{bmatrix} J_K^{LL} - K_K^{LL} & -K_K^{LS} \\ -K_K^{SL} & J_K^{SS} - K_K^{SS} \end{bmatrix}$$

is the two electron operator.

Relativistic Roothan Equations

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

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

Relativistic Roothan Equations

The two electron matrix has the elements,

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

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

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

The density matrices are defined as,

$$D_{\kappa pq}^{TT'} = N_{\kappa} C_{\kappa p}^T C_{\kappa q}^{T'}$$

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

Relativistic Roothan Equations

ν is in the range

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

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

$$\bar{b}_\nu^c(j j') = \left[\begin{array}{ccc} j_p & \nu & j_q \\ 1/2 & 0 & -1/2 \end{array} \right]^2$$

where

$$\left[\begin{array}{ccc} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{array} \right]$$

is the Wigner-3j symbol.

Relativistic Roothan Equations

The Coulomb integrals are given by,

$$J_{\kappa p q, \kappa' r s}^{\nu T T', T' T'} = \int_0^\infty \int_0^\infty g_{\kappa p}^T(r_1) g_{\kappa q}^T(r_1) U_\nu(r_1, r_2) g_{\kappa' r}^{T'}(r_2) g_{\kappa' s}^{T'}(r_2) dr_1 dr_2$$

$$K_{\kappa p q, \kappa' r s}^{\nu T T', T T'} = \int_0^\infty \int_0^\infty g_{\kappa p}^T(r_1) g_{\kappa' r}^T(r_1) U_\nu(r_1, r_2) g_{\kappa q}^{T'}(r_2) g_{\kappa' s}^{T'}(r_2) dr_1 dr_2$$

where,

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

Code - Considerations

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.

Grid

We choose a grid which is 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 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).

Integration and the Wigner-3j symbol

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.

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

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.

Failure and Suggestions

Failures

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 approximating the inner integral at the cost of accuracy should be added as in Nataraj (2021*a*).

Suggestions

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 controlling and 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.

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