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

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Topic

To solve the Dirac Equation for many electron atoms using Dirac Hartree Fock Self Consistent Field method

Dirac Hartree Fock Theory

N-electron Dirac Hamiltonian

- We are interested in finding a set of spin orbitals such that the single determinant formed from these spin orbitals is the best approximation to the ground state of an N-electron system.

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

$$\hat{H}_D(i) = c\vec{\alpha}_i \cdot \vec{p}_i + c^2(\beta_i - 1) + V_{nuc}(r_i),$$

- And the two electron part, consisting of Coulomb repulsion and Breit Interaction (which I am not considering for now): $H_{12} = \sum_{\substack{ij \\ i<j}} \frac{1}{r_{ij}} + \sum_{\substack{ij \\ i<j}} B_{ij}.$

Clementi, E., Modern Techniques in Computational Chemistry: MOTECC-91, *Chapter 4.*

Hartree-Fock Equations

- According to the variational principle, the 'best' spin orbitals are those which minimize the electronic energy

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

$$= \sum_a \langle a|h|a \rangle + \frac{1}{2} \sum_{ab} [aa|bb] - [ab|ba]$$

- The resulting equation is the Hartree Fock Integro-differential equation

$$\left[h(1) + \sum_{b \neq a} \mathcal{J}_b(1) - \sum_{b \neq a} \mathcal{K}_b(1) \right] \chi_a(1) = \varepsilon_a \chi_a(1)$$

where, h = one electron operator

$$\mathcal{J}_b(1)\chi_a(1) = \left[\int dx_2 \, \chi_b^*(2) r_{12}^{-1} \chi_b(2) \right] \chi_a(1)$$

    J = direct coulomb operator

    K = exchange coulomb operator

$$\mathcal{K}_b(1)\chi_a(1) = \left[\int dx_2 \, \chi_b^*(2) r_{12}^{-1} \chi_a(2) \right] \chi_b(1)$$

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

Hartree-Fock Equations

- Considering, $[\mathscr{J}_a(1) - \mathscr{K}_a(1)]\chi_a(1) = 0$

- We can add this to the previous equation and define the fock operator as

$$f(1) = h(1) + \sum_b \mathscr{J}_b(1) - \mathscr{K}_b(1)$$

- So that the Hartree Fock equation becomes $f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle$

- Keep in mind that we are not solving the exact electronic Schrodinger equation $\mathscr{H}|\Phi_0\rangle = \mathscr{E}_0|\Phi_0\rangle$ but rather we have used the variational principle to find an approximation.

- Therefore, the sum of orbital energies we get as a result is not the total energy. The orbital energies are actually negative of the ionisation potentials required to remove the corresponding electrons (Koopmans' theorem).

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

Restricted Closed shell Hartree-Fock: Roothaan Equations

- Only even number of electrons such that all spatial orbitals are doubly occupied.

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

$$f(1)\psi_j(1) = \varepsilon_j \psi_j(1)$$

$$f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle$$

$$f(1) = h(1) + \sum \mathscr{J}_b(1) - \mathscr{K}_b(1)$$

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

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

Integrating over spin $\longrightarrow$

$$J_a(1) = \int d\mathbf{r}_2 \, \psi_a^*(2) r_{12}^{-1} \psi_a(2)$$

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

$$K_a(1)\psi_i(1) = \left[\int d\mathbf{r}_2 \, \psi_a^*(2) r_{12}^{-1} \psi_i(2)\right]\psi_a(1)$$

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

Basis

- We introduce a set of known basis functions and write our unknown spatial orbitals as a linear combination of these spin orbitals.

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu$$

- Substituting this into the Roothaan equations, we get $\sum F_{\mu v} C_{vi} = \varepsilon_i \sum_v S_{\mu v} C_{vi}$

Where, F is the fock matrix

$$F_{\mu v} = \int d\mathbf{r}_1 \, \phi_\mu^*(1) f(1) \phi_v(1)$$

S is the overlap matrix

$$S_{\mu v} = \int d\mathbf{r}_1 \, \phi_\mu^*(1) \phi_v(1)$$

- This is more compactly written as a single matrix equation $\mathbf{FC} = \mathbf{SC\varepsilon}$

Where C is a matrix of the expansion coefficients, e is a diagonal matrix of the

orbital energies.

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

Density Matrix

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

- Therefore, the total charge density

$$\rho(\mathbf{r}) = 2 \sum_a^{N/2} |\psi_a(\mathbf{r})|^2 \, , \quad \int d\mathbf{r} \, \rho(\mathbf{r}) = 2 \sum_a^{N/2} \int d\mathbf{r} \, |\psi_a(\mathbf{r})|^2 = 2 \sum_a^{N/2} 1 = N$$

- Inserting the basis set function into the expression for charge density, we get

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

where, $\quad P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^*$ This is called the density matrix.

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

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

Orthogonalisation of basis

- The basis functions are normalized but not orthogonal, giving rise to the overlap matrix S leading to a pseudo eigen value problem.

- If we can orthogonalize the basis functions, S will be an identity matrix. This puts Roothaan equations into the form of the usual matrix eigenvalue problem.

- We need to find a transformation matrix X such that $\phi'_\mu = \sum_\nu X_{\nu\mu} \phi_\nu$ form an orthogonal set, i.e., $\int d\mathbf{r}\, \phi'^*_\mu(\mathbf{r})\phi'_\nu(\mathbf{r}) = \delta_{\mu\nu} \longrightarrow \mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1}$

- Canonical Orthogonalisation:

$$\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2}$$, where $\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s}$,where s is a diagonal eigenvalue matrix.

- That is, the columns of the unitary matrix U are divided by the square root of the corresponding eigenvalue.

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

Orthogonalisation of basis

$$FC = SC\varepsilon$$

- Consider a new coefficient matrix $\quad C = XC'$

$$FXC' = SXC'\varepsilon$$
$$(X^{\dagger}FX)C' = (X^{\dagger}SX)C'\varepsilon$$

- Define a new matrix

$$F' = X^{\dagger}FX$$

$$F'C' = C'\varepsilon$$

- This equation now can be solved as a usual eigen value problem given F. Given C', C can be obtained using the above relations

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

SCF Procedure

1. Specify the atom and basis set.

2. Calculate the overlap matrix S. Diagonalise to get transformation matrix X.

3. Guess the Coeffient Matrix C and density matrix P.

4. Calculate F, F'.

5. Diagonalise F' to obtain C'.

6. Calculate C.

7. Form new density matrix P.

8. Check if the procedure has converged by comparing the new density matrix with the previous. If not, return to step 4.

9. If there is convergence, use the resultant solution C, P, F to calculate various quantities of interest.

Code - Theory

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 and Q are the large and small component of the radial wave function, while χ is the spin angular part.

- κ defines the orbital symmetry is given by: $\kappa = -2(j - l)(j + \tfrac{1}{2}),$

Symmetry	$s_{\frac{1}{2}}$	$p_{\frac{1}{2}}$	$p_{\frac{3}{2}}$	$d_{\frac{3}{2}}$	$d_{\frac{5}{2}}$	$f_{\frac{5}{2}}$	$f_{\frac{7}{2}}$	$g_{\frac{7}{2}}$	$g_{\frac{9}{2}}$
n_κ	1	2	2	3	3	4	4	5	5
κ	-1	+1	-2	+2	-3	+3	-4	+4	-5

Clementi, E., Modern Techniques in Computational Chemistry: MOTECC-91, *Chapter 4*.

Basis – Gaussian Type Orbitals (GTOs)

- The radial functions are expanded in terms of the basis sets as:

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

$$Q_{n\kappa}(r) = \sum_{p} C_{\kappa p}^{S} \; g_{\kappa p}^{S}(r),$$

- For GTOs: $g_{\kappa i}^{L}(r) = C_{N_{\kappa i}}^{L} \; r^{n_\kappa} \; e^{-\alpha_i r^2}, g_{\kappa i}^{S}(r) = C_{N_{\kappa i}}^{S} \; \left(\dfrac{d}{dr} + \dfrac{\kappa}{r}\right) \; g_{\kappa i}^{L}(r).$

- We have constrained the small component using the kinetic balance condition to prevent variational collapse.

Basis – Gaussian Type Orbitals (GTOs)

- The normalisation factors are given by

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

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

- The exponents are generated according to

$$\alpha_i = \alpha_0 \, \beta^{i-1}, \quad i = 1, 2, \dots N$$

where α_0 and β are input parameters.

Clementi, E., Modern Techniques in Computational Chemistry: MOTECC-91, *Chapter 4*.

Matrices

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

$$F_\kappa C_\kappa = \varepsilon_\kappa S_\kappa C_\kappa$$

$$C_\kappa = \begin{bmatrix} C_\kappa^L \\ C_\kappa^S \end{bmatrix} \qquad S_\kappa = \begin{bmatrix} S_\kappa^{LL} & 0 \\ 0 & S_\kappa^{SS} \end{bmatrix}$$

- The Fock has two contributions

One electron operator $\qquad F_\kappa = h_\kappa + g_\kappa \qquad$ Coulomb repulsion term

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

Clementi, E., Modern Techniques in Computational Chemistry:
MOTECC-91, *Chapter 4*.

Integrals

$$V_{\kappa ij}^{TT} = \int_0^\infty g_{\kappa i}^T(r) \; V_{nuc}(r) \; g_{\kappa j}^T(r) \; (r)dr$$

For a point nucleus, $V_{nuc}(r) = -\dfrac{Z}{r}$

$$\Pi_{\kappa ij}^{SL} = \int_0^\infty dr \, g_{\kappa i}^S(r) \left[\frac{d}{dr} + \frac{\kappa}{r} \right] g_{\kappa j}^L(r)$$

$$S_{\kappa ij}^{TT} = \int_0^\infty g_{\kappa i}^T(r) \; g_{\kappa j}^T \; (r)dr$$

Π^{LS} and Π^{SL} are matrix adjoints of each other.

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

$$T\overline{T} = LS/SL$$

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

$$T, T' = L/S$$

$$N_\kappa = 2j + 1$$

$$K_{\kappa pq}^{TT'} = \sum_v \sum_{\kappa' rs} [\overline{b}_v^c(jj')] \; D_{\kappa' rs}^{TT'} \; K_{\kappa pq, \, \kappa' rs}^{vTT', \, TT'}$$

$$|j - j'| \leq v \leq j + j' \quad \overline{b}_v^c = \begin{bmatrix} j & v & j' \\ \tfrac{1}{2} & 0 & -\tfrac{1}{2} \end{bmatrix}^2$$

Clementi, E., Modern Techniques in Computational Chemistry: MOTECC-91, *Chapter 4*.

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Integrals

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

$$U_\nu(r_1,\, r_2) = r_1^\nu / r_2^{\nu+1}, \quad \text{if} \quad r_1 < r_2$$
$$r_2^\nu / r_1^{\nu+1}, \quad \text{if} \quad r_1 > r_2$$

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

Clementi, E., Modern Techniques in Computational Chemistry:
MOTECC-91, *Chapter 4.*

Code

Input parameters

- Atomic number, atomic mass
- Number of symmetries, number of basis and occupied orbitals for each symmetry
- α_0 and β for the GTOs.
- Maximum number of iterations, critical value to establish convergence.

Check all these parameters for being consistent with each other.

Grid

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

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

$$h = 0.03, \quad a = \frac{e^{-65/16}}{Z}$$

- For calculating integrals later, we also store the following:

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

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

Setting Up

- Calculate the various g^L and g^S as a function of r.

- Calculate the overlap matrix and the one electron part of the Fock Matrix by calculating the various integrations using 10-point Newton Cotes' Method.

SCF Procedure

- Neglect electron-electron interaction in the first iteration, eq. to P=0
- Calculate coulomb repulsion part of Fock matrix if iteration>1.
- Diagonalise S to obtain X.
- Calculate F'.
- Diagonalise F' to obtain C'.
- Calculate C.
- Calculate the density matrix. Calculate the norm of the difference between this and the old density matrix. If it is less than the critical value, end the procedure. Otherwise return to step 2 if iter<maxiter.
- If iter>=maxiter, equations didn't converge.

Calculating total energy

- Total Energy is calculated using the following relation:

$$E_0 = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\nu\mu}(H_{\mu\nu}^{core} + F_{\mu\nu})$$

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

Problems

- Unable to get the SCF procedure to converge.

Future Objectives

- Check the code for errors which might lead to divergence.
- Try eliminating basis for which eigenvalues of the overlap matrix are too small.
- Add other features like different types of basis, Breit interaction, finite nuclei, isotope shift, correlation energy using post mean field methods and open shell calculations

References

- Nataraj, H. S., Notes, Unit-1 Many electron atoms, PHN-626 Advanced Atomic and Molecular Physics (2021), IIT Roorkee.

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

- Clementi, E., Modern Techniques in Computational Chemistry: MOTECC-91, *Chapter 4.*

- Nataraj, H. S.,DF SCF.F90 Fortran Code.

Thank You.