

Modelling the energy levels of atoms using the Hartree-Fock method on a radial finite difference grid.

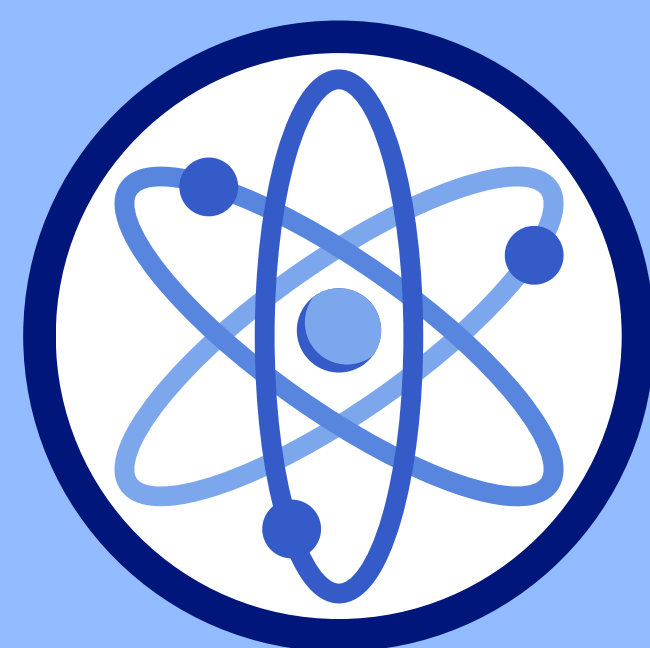
1. Introduction

The atom is a complex many-body system. While the Hydrogen atom can be solved analytically, larger systems from Helium onwards require numerical approaches. Multi-electron atoms present a significant computational challenge because electron-electron repulsion makes the Schrödinger equation analytically unsolvable. This project implements the Hartree-Fock method to numerically approximate the energy levels of light atoms (Li, Be, B, and C).

$$\hat{H} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

Authors:
Ben Greensmith

Supervisor:
Prof. Morten Førre



2. Theory

The model utilises the many-body Hamiltonian on a radial grid, reducing the 3D problem to 1D via the central field approximation. It enforces the Pauli exclusion principle through Slater Determinants and the variational principle. We try to minimise our total energy.

$$\mathcal{L}\{\{\chi_a\}\} = E_0\{\{\chi_a\}\} - \sum_{a=1}^N \sum_{b=1}^N \epsilon_{ba} \left(\int dx_1 \chi_a^*(1) \chi_b(1) - \delta_{ab} \right)$$

Then we derive the Fock equation, changing the core-Hamiltonian, Coulomb (J), and Exchange (K) operators into matrices.

$$J_b(1)\chi_a(1) = \left[\int dx_2 \chi_b^*(2) \frac{1}{r_{12}} \chi_b(2) \right] \chi_a(1)$$

$$K_b(1)\chi_a(1) = \left[\int dx_2 \chi_b^*(2) \frac{1}{r_{12}} \chi_a(2) \right] \chi_b(1)$$

3. Method

A 1D radial finite difference grid was constructed to discretise wavefunctions into matrices. Each term in the Hamiltonian has its own matrix representation. We employed a Self-Consistent Field (SCF) iterative loop using Restricted (RHF) and Unrestricted (UHF) methods to solve the total fock matrix. The solutions are the energy levels and new wavefunctions we need. Once we reach convergence, we can calculate the final energy of the system.

$$F = T + V + J - K$$

$$FC = CE$$

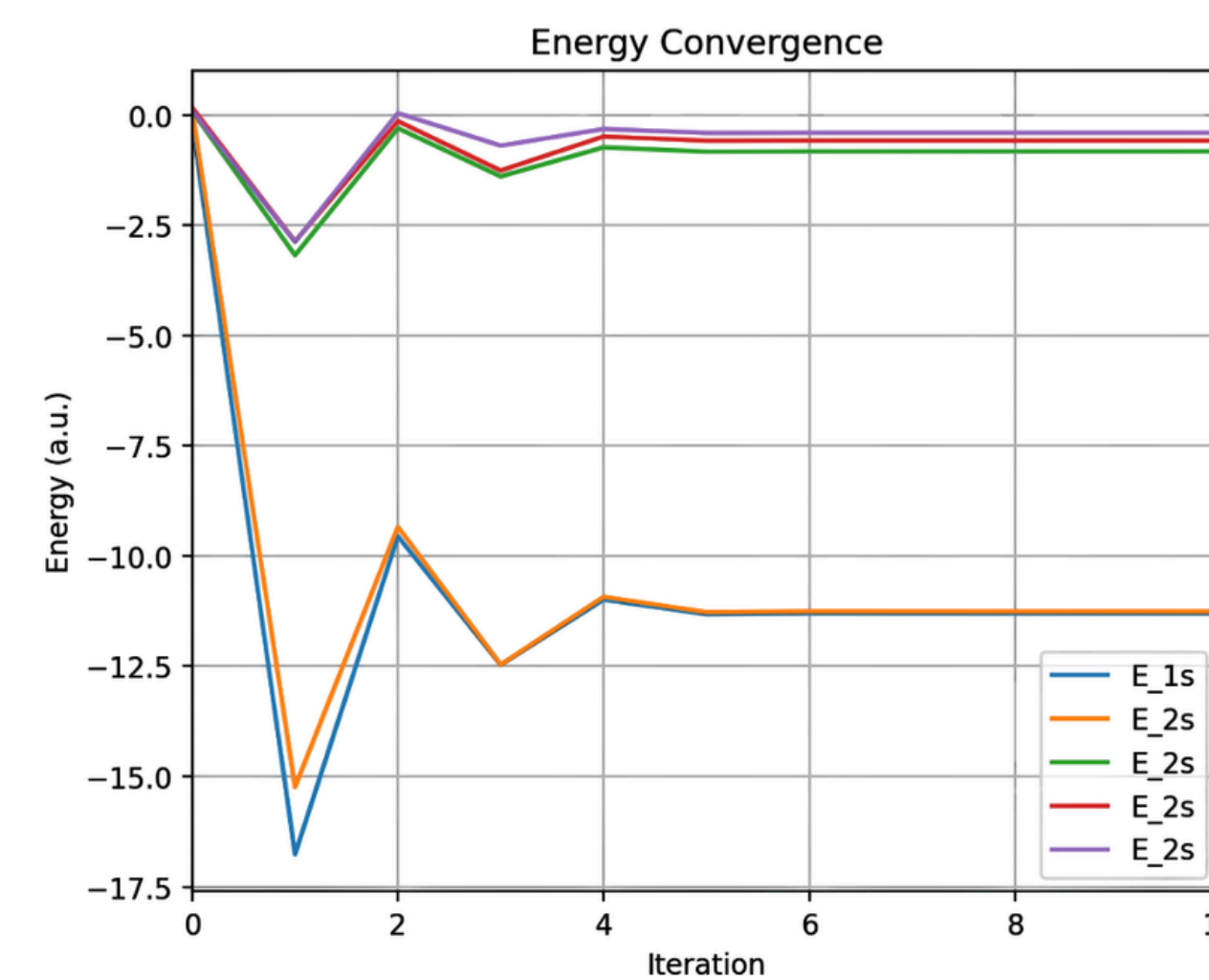
4. Results

- The model successfully converged for all atoms in the study.
- The results agree with literature values.
- As we increase the size of the atom, we deviate slightly from the literature value.

Atom	Elec config	E_{total}	$E_{reference}$	$\Delta_{reference}$	E_{exact}
Li	$1s^2 2s^1$	-7.4285	-7.4332	-0.0047	-7.4786
Be (Rhf)	$1s^2 2s^2$	-14.5673	-14.5752	-0.0079	-14.6693
Be (Uhf)	$1s^2 2s^2$	-14.5673	-14.5752	-0.0079	-14.6693
B	$1s^2 2s^2 2p^1$	-24.4857	-24.5351	-0.0494	-24.6591
C	$1s^2 2s^2 2p^2$	-37.5734	-37.7022	-0.1288	-37.8574
C $p_y \downarrow$	$1s^2 2s^2 2p^2$	-37.8075	-37.7022	-	-37.8574

- Individual orbital energies also validate our method, agreeing with literature values.
- The results also agree with Koopmans' theorem.

Atom	Elec config	$1s \uparrow$	$1s \downarrow$	$2s \uparrow$	$2s \downarrow$	$2p_x \uparrow$	$2p_y \uparrow$
Li	$1s^2 2s^1$	-2.4837	-2.4656	-0.1961	-	-	-
Li ref	$1s^2 2s^1$	-2.5233	-2.4764	-0.1963	-	-	-
Be (Rhf)	$1s^2 2s^2$	-4.7292	-4.7292	-0.3088	-0.3088	-	-
Be ref	$1s^2 2s^2$	-4.7327	-4.7327	-0.3093	-0.3093	-	-
B	$1s^2 2s^2 2p^1$	-7.6769	-7.6619	-0.5414	-0.4436	-0.3102	-
B ref	$1s^2 2s^2 2p^1$	-7.7663	-7.6493	-0.5694	-0.4431	-0.3091	-
C	$1s^2 2s^2 2p^2$	-11.3049	-11.2610	-0.8280	-0.5867	-0.4071	-0.4071
C ref	$1s^2 2s^2 2p^2$	-11.3934	-11.3130	-0.7816	-0.6273	-0.4333	-0.4333



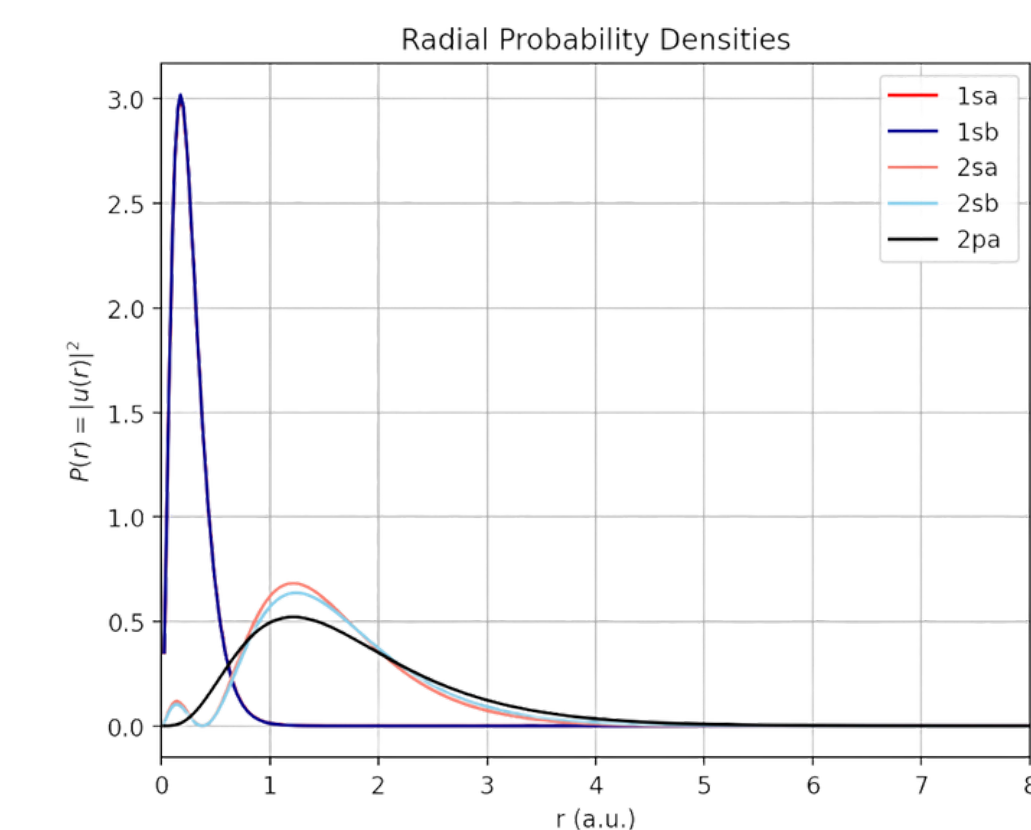
UNIVERSITY OF BERGEN
Faculty of Science and Technology



P299.6

5. Radial position

- The Radial position of the electrons can be plotted as it is equal to the square of the modulus.
- We can see effects of the larger nucleus and the exchange principle.



6. Conclusion

- The Hartree-Fock method on a discrete radial grid provides a robust and accurate framework for modeling atomic systems.
- This implementation effectively bridges the gap between theoretical quantum formalism and practical numerical simulation for future students.
- To improve upon the model the code could be upgraded from a radial grid to a logarithmic one.

