Computational Quantum Physics

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[*]Project 1: 2025

ABSTRACT

This project investigates information and theoretical measures, specifically Shannon entropy, Onicescu information energy, Kullback-Leibler relative entropy, Jensen-Shannon divergence, and the quantum mechanical description of atoms within the range of Z [2, 10]. With Roothaan-Hartree-Fock (RHF) wave functions for position space and momentum space, the calculations achieve the Shannon entropy in both position space (S_r) and momentum space (S_k). With these acquired, the electron density and the Shannon information entropy are in both $\rho(r), \eta(k) \& S_r, S_k$ for each atom.

1 Introduction

1.1 Roothaan-Hartree-Fock Wave Functions

The RHF method[1] is applied in order to calculate the analytical self-consistent-field of atomic wave function, in other words it describes a non relativistic Schrödinger for the motion of electrons. The radial atomic part of HF wavefunctions, $R_{nl}(r)$ are expressed as a superposition of primitive radial functions $R_{jl}(r)$:

$$R_{nl}(r) = \sum_j C_{knl} S_{jl}(r) \tag{1}$$

S_{jl} is taken as a Slater-type orbital set,

$$S_{jl}(r) = N_{jl} r^{n_{jl}-1} e^{-Z_{jl}r} \tag{2}$$

the normalization factor N_{jl} is given by

$$N_{jl} = (2Z_{jl})^{(n_{jl}+1/2)}/[(2n_{jl})!]^{1/2} \tag{3}$$

From the equations, n_{jl} is the principal quantum number, Z_{jl} is the orbital exponent, and l is the azimuthal quantum number. The wavefunctions $\tilde{\phi}_i(k)$ and $\phi_i(r)$ used for k-space and position space respectively:

$$\phi_i(r) = \phi_{nlm}(r) = R_{nl}(r)Y_{lm}(\Omega_R) \tag{4}$$

$$\tilde{\phi}_i(k) = \tilde{\phi}_{nlm}(k) = \tilde{R}_{nl}(k)Y_{lm}(\Omega_R) \tag{5}$$

1.2 Shannon Entropy

Shannon entropy, also known as information entropy, is a measure of uncertainty or unpredictability in a set of possible outcomes. It is defined as the average amount of information produced by a stochastic source of data. The entropy of a distribution represents the anticipated amount of information contained in an event sampled from that distribution.

The formula for Shannon entropy is represented as:

$$\begin{cases} S_r = -\int \rho(r)\ln\rho(r)dr = -4\pi\int_0^\infty \rho(r)\ln\rho(r)r^2 dr \\ S_k = -\int n(k)\ln n(k)dk = -4\pi\int_0^\infty n(k)\ln n(k)k^2 dk \end{cases} \tag{6}$$

The total entropy is calculated by the values of (6):

$$S_{total} = S_r + S_k \tag{7}$$

2 Computational approach

The project implemented using Python to compute the entropies, electron density distribution and momentum density distribution. The first step was to create a library in python, which does all the computational work. The library starts by defining the functions of $S(r)$ and $S(k)$ orbitals, with the variables Z, r and Z, k respectively. To compute the functions $R_{nl}(r)$ and $K_{nl}(k)$, the coefficients and factors of $S(r)$ and $S(k)$ orbital functions are extracted from RHF paper[2] .

The function that computes wavefunction takes the s, p coefficient orbitals and the atomic number Z for arguments. The $R_{nl}(r)$ and $K_{nl}(k)$ are computed by adding each orbital S multiplied by its respective factor with the corresponding variables. To ensure that the correct calculations were made, each function is squared, multiplied by r^2 or k^2 and integrated from 0 to infinity.

The next step is to compute the wavefunctions $\rho(r)$ and $n(k)$. As we iterate though electrons, the $R_{nl}(r)$ for $\rho(r)$ and $K_{nl}(k)$ for $n(k)$ are added with a factor. The accuracy is verified by integrating the $\rho(r) \cdot r^2$ and $n(k) \cdot k^2$ from 0 to infinity. After the calculations the $\rho(r)$ and $n(k)$ are plotted for r and k values from 0 to 4.

Finally, the function calculates the entropies $\{S_r, S_k, S_{total}, S_{max}\}$. The entropy results are returned with a plot for all entropies against the atomic number Z.

3 Results

3.1 Density Distributions

3.1.1 He(Z=2)

The entropies were calculated:

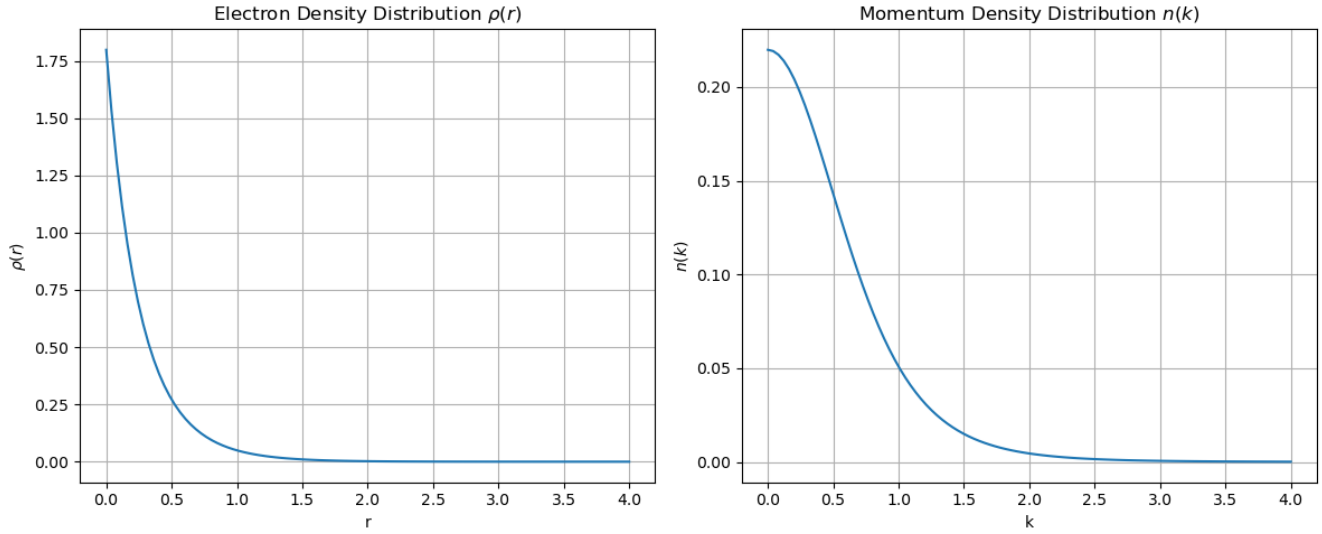S_r: 2.6985, S_k: 3.9134, S: 6.6119, S_{max}: 7.0493

Figure 1. Electron/Momentum Density Distributions of Helium

3.1.2 Li(Z=3)

The entropies were calculated:

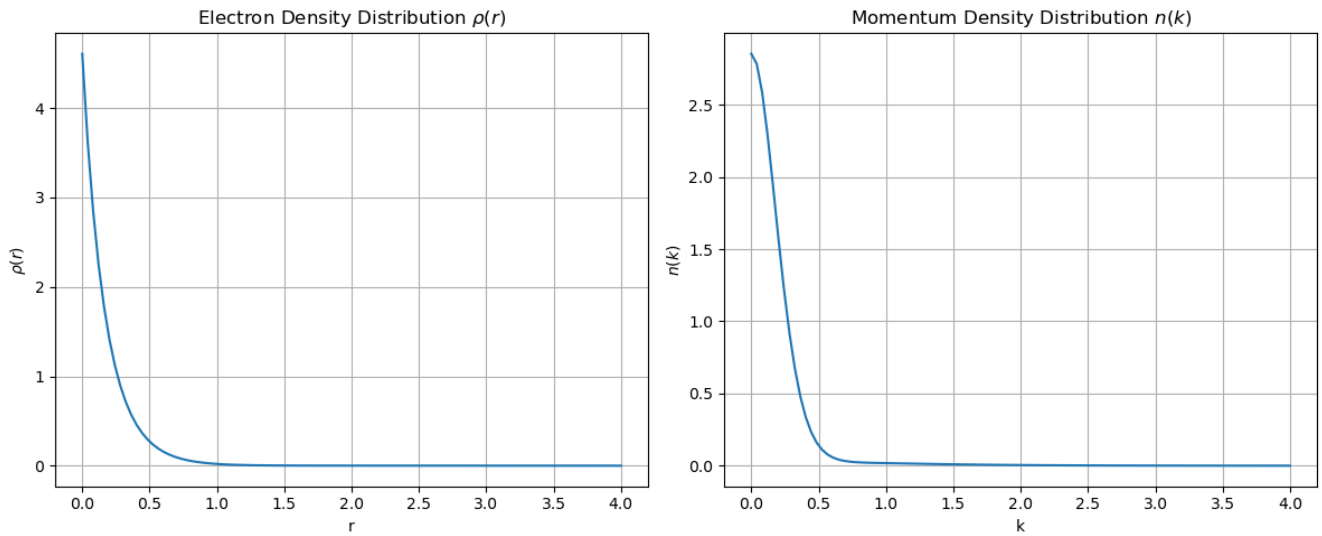S_r: 3.7014, S_k: 3.9968, S: 7.6983, S_{max}: 10.3578

Figure 2. Electron/Momentum Density Distributions of Lithium

3.1.3 Be(Z=4)

The entropies were calculated:

S_r: 3.6239, S_k: 4.1902, S: 7.8140, S_{max}: 10.3950
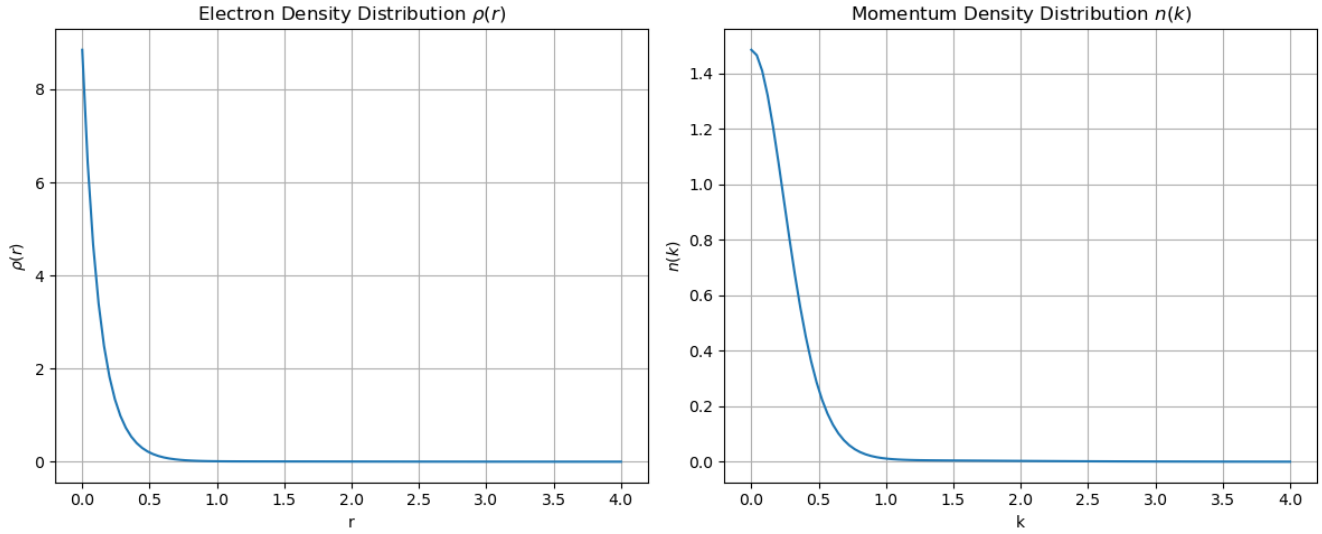

Figure 3. Electron/Momentum Density Distributions of Beryllium

3.1.4 B(Z=5)

The entropies were calculated:

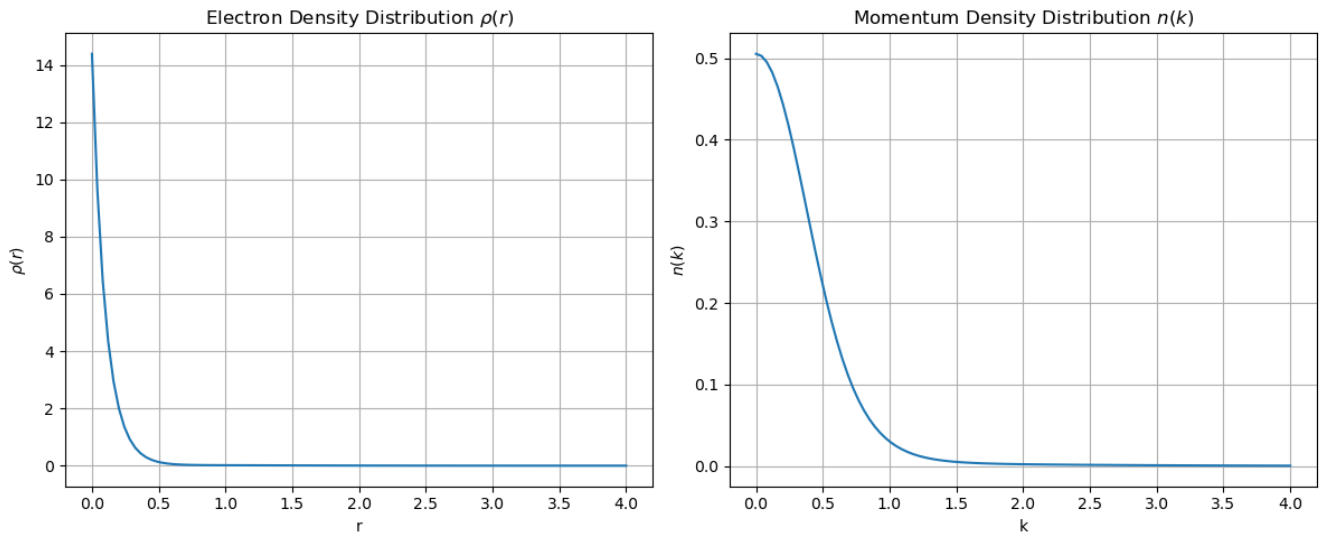S_r: 3.4054, S_k: 4.7059, S: 8.1113, S_{max}: 10.3738

Figure 4. Electron/Momentum Density Distributions of Boron

3.1.5 C(Z=6)

The entropies were calculated:

S_r: 3.1060, S_k: 5.1566, S: 8.2626, S_{max}: 10.2624
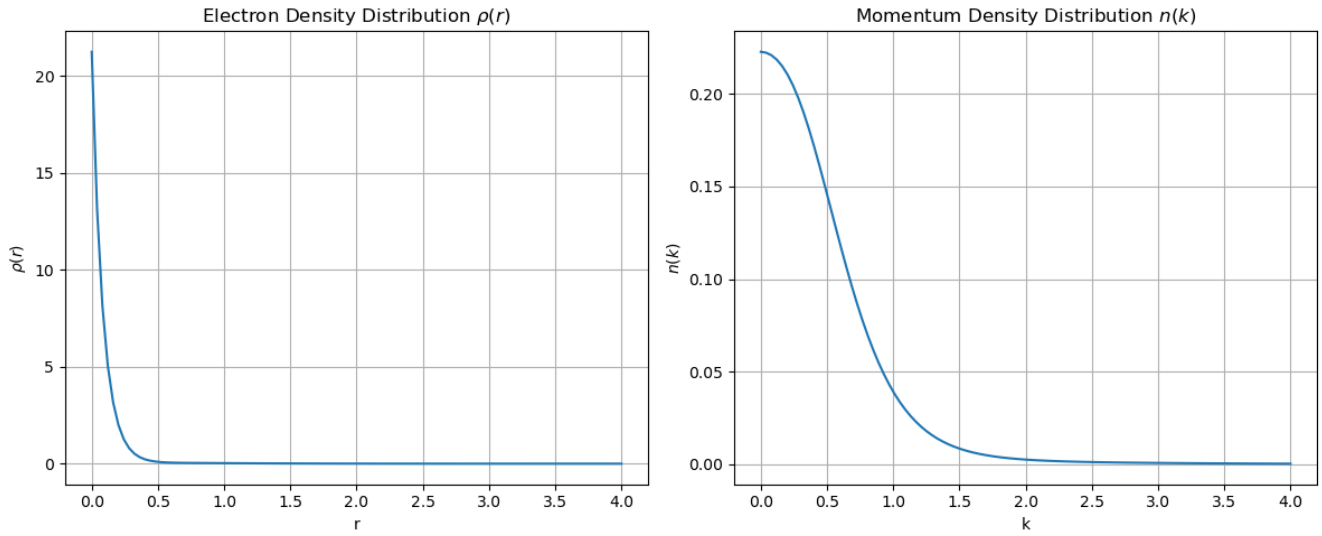

Figure 5. Electron/Momentum Density Distributions of Carbon

3.1.6 N(Z=7)

The entropies were calculated:

S_r: 2.8017, S_k: 5.5493, S: 8.3510, S_{max}: 10.1520
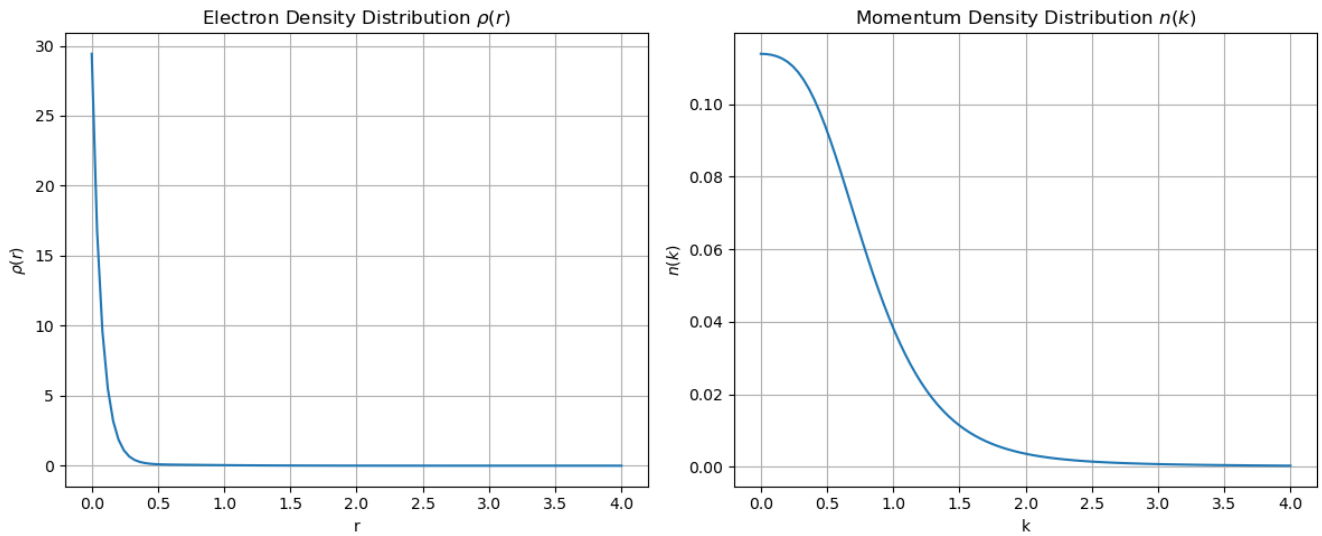

Figure 6. Electron/Momentum Density Distributions of Nitrogen

3.1.7 O(Z=8)

The entropies were calculated:

S_r: 2.5505, S_k: 5.8674, S: 8.4179, S_{max}: 10.1113
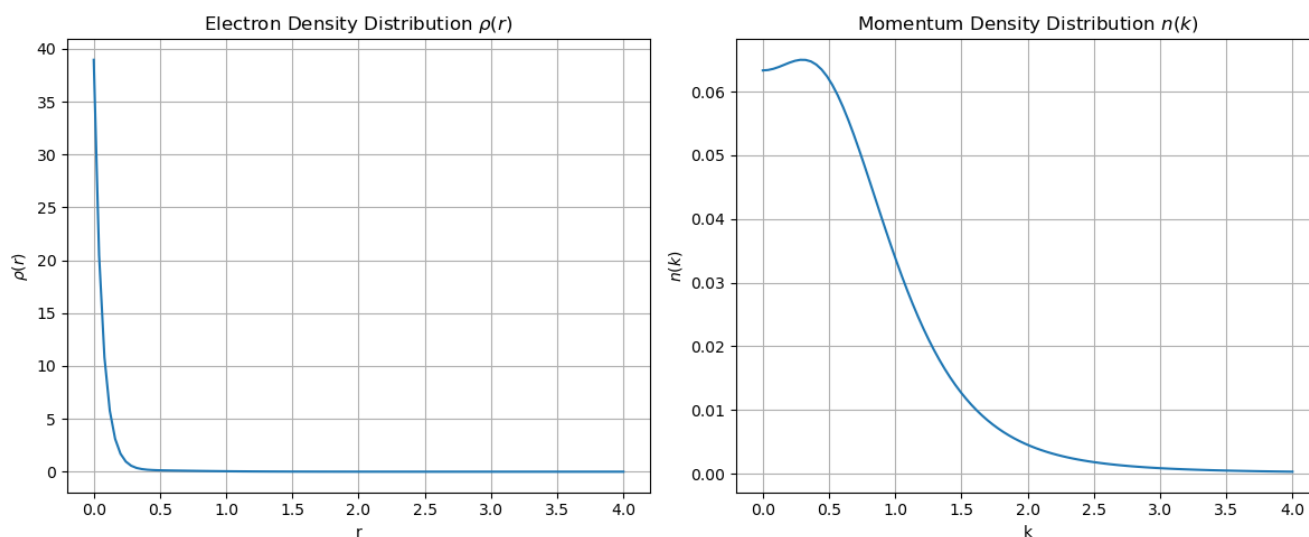

Figure 7. Electron/Momentum Density Distributions of Oxygen

3.1.8 F(Z=9)

The entropies were calculated:

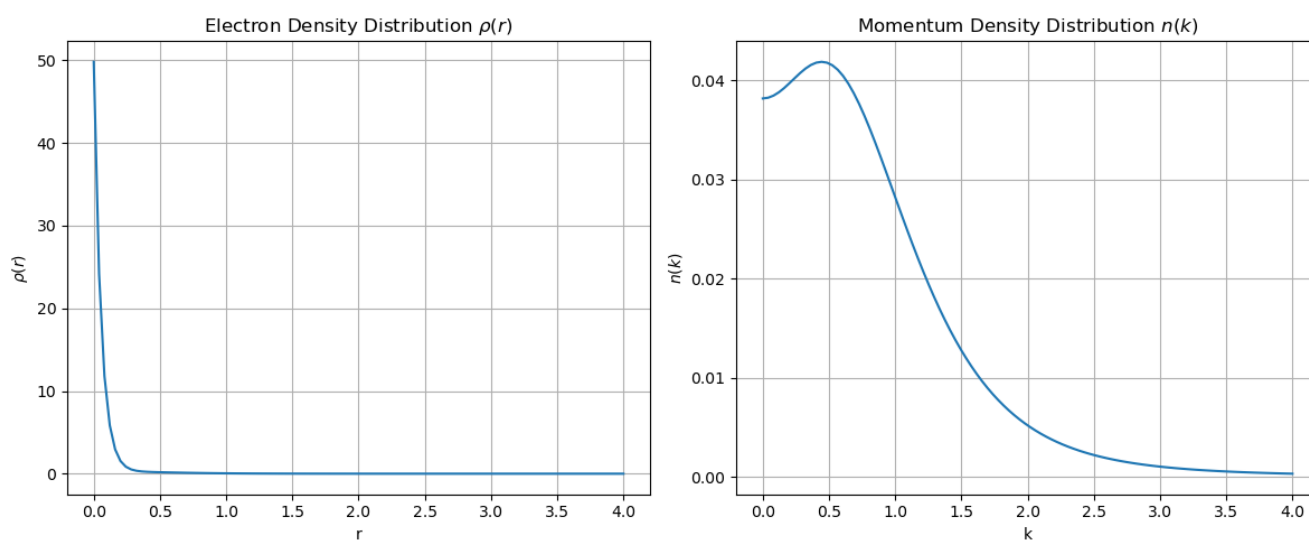S_r: 2.2989, S_k: 6.1629, S: 8.4619, S_{max}: 10.0530

Figure 8. Electron/Momentum Density Distributions of Fluorine

3.1.9 Ne(Z=10)

The entropies were calculated:

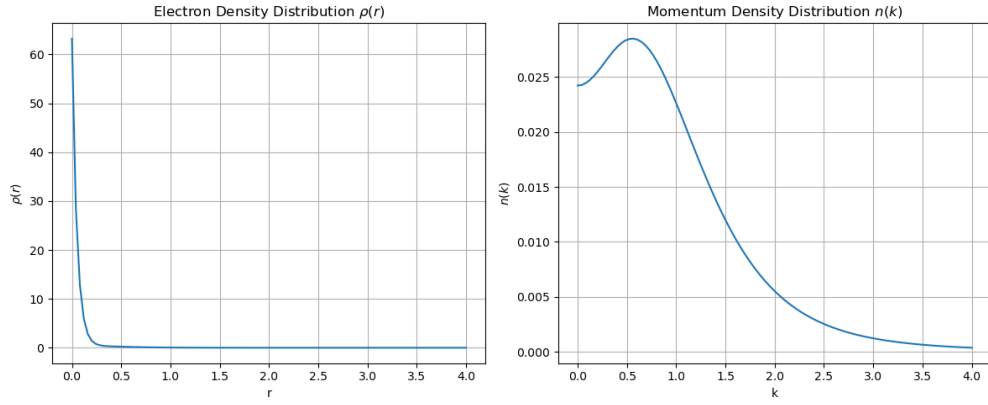S_r: 2.0449, S_k: 6.4649, S: 8.5098, S_{max}: 10.0182

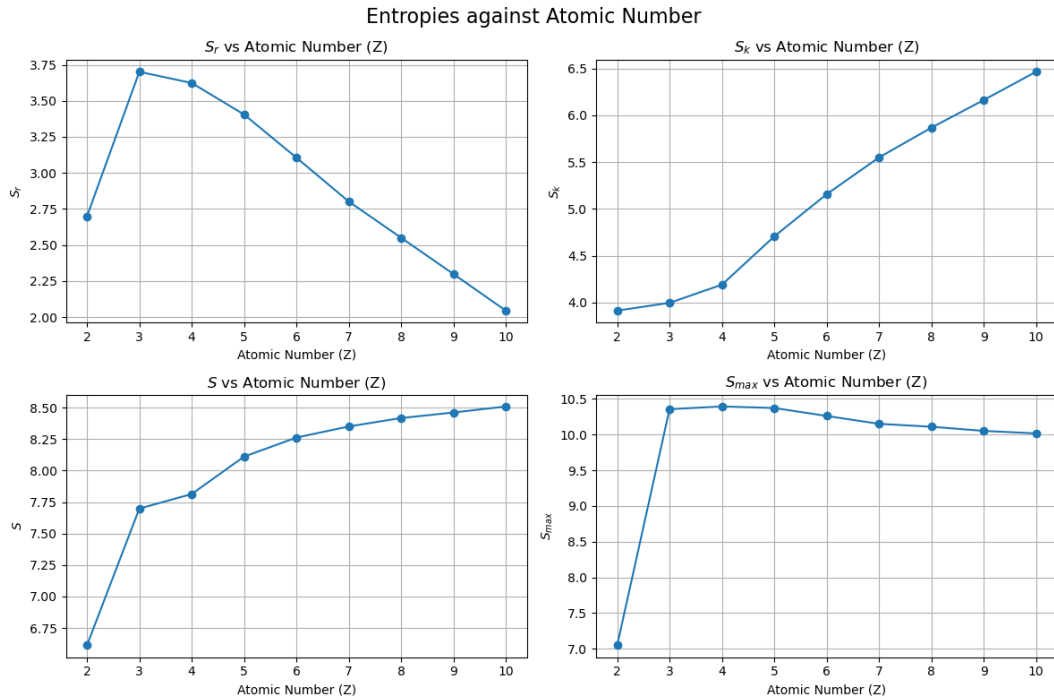**Figure 9.** Electron/Momentum Density Distributions of Neon

3.2 Entropies Plot

Figure 10. Entropies calculation against Atomic Number

3.3 Exponential term of Entropy

Leveraging the entropy values reported in Bunge et al.[2], the Gaussian Process Regression (GPR) is deployed as the machine learning framework. GPR is suited due to its kernel-based architecture, which

enables quantification of prediction uncertainty through local data correlations and efficient training even with limited samples. The model was trained on a small dataset of 54 points, achieving an accuracy $R^2 = 0.99$ and a mean squared error (MSE) of 0.3. The kernel composition included a combination of ConstantKernel, Radial Basis Function (RBF), RationalQuadratic, and WhiteKernel to capture data patterns.
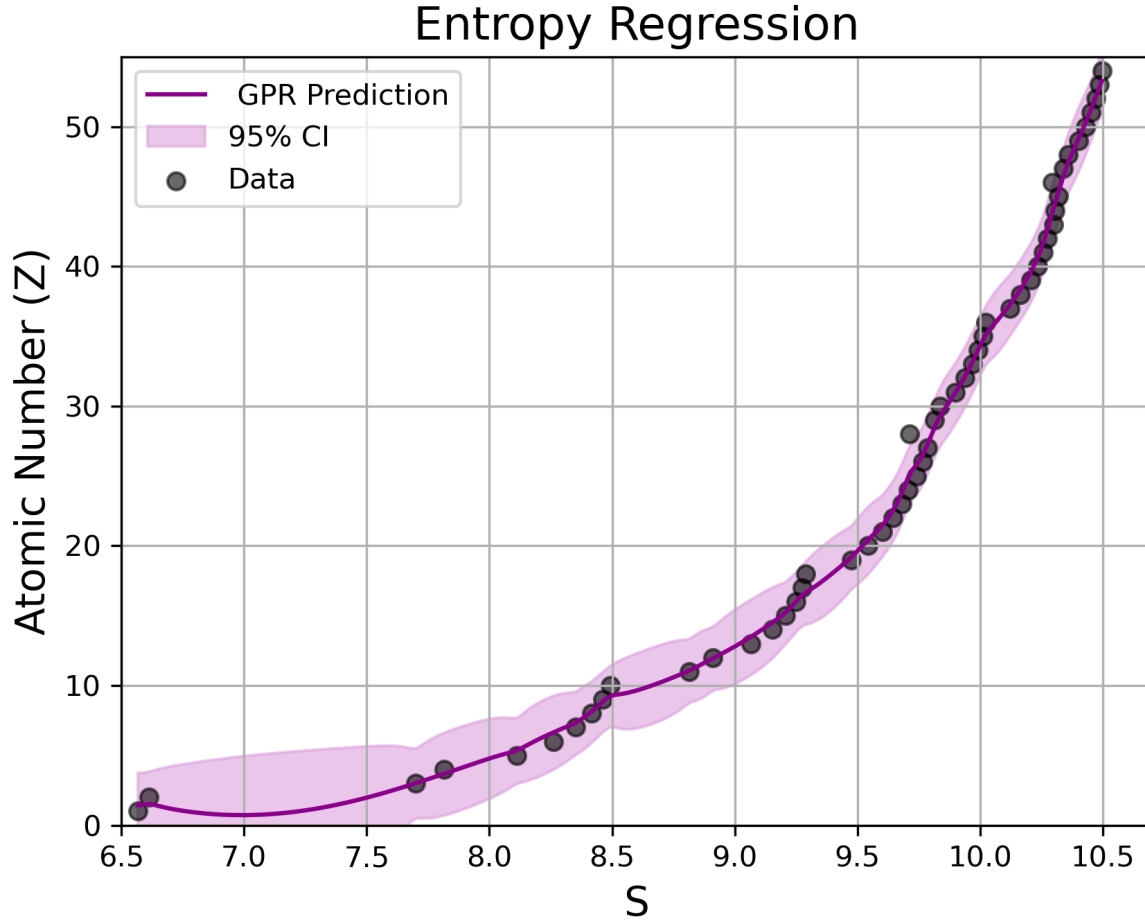

Figure 11. Entropy Regression using Gaussian processes

3.4 Conclusion

3.4.1 Electron and momentum density distributions

The electron density distribution $\rho(r)$ follows an exponential decay as a function of distance r. With increasing atomic number, the decay becomes steeper, and the initial electron density near the nucleus rises. In all cases, the distribution starts at its maximum value at $r = 0$ and sharply declines to zero as r increases. This behavior is consistent with theoretical expectations, as higher nuclear charge leads to stronger electron-nucleus attraction, concentrating more electron density near the nucleus.

The momentum space distribution $n(k)$ displays more complex behavior. For lighter elements, the

distribution decreases nearly exponentially with a subtle oscillatory feature at low momentum values. However, as the atomic number increases, on Nitrogen onward, the peak broadens and becomes more rounded. By Oxygen, a distinct secondary peak emerges, growing more pronounced in heavier elements like Neon. These structural changes reflect shifts in electronic configurations, suggesting that higher atomic numbers introduce additional quantum states with varying momentum distributions.

3.4.2 Information Entropy

The calculated entropy values align closely with those reported[1], demonstrating distinct relationships with atomic number.

- **Position Space Entropy** (S_r): This quantity begins at a moderate value, peaks at lithium (Li, $Z = 3$), and then declines steadily across heavier elements.

- **Momentum Space Entropy** (S_k): In contrast, S_k starts at a lower value and increases with atomic number. After a modest rise for Li ($Z = 3$) and beryllium (Be, $Z = 4$), the trend becomes more pronounced, with consistent incremental increases for subsequent elements.

- **Total Entropy** (S_{total}): The sum $S_{total} = S_r + S_k$ initially rises sharply from helium (He, $Z = 2$) to Li ($Z = 3$), followed by progressively smaller increments. By fluorine (F, $Z = 9$) and neon (Ne, $Z = 10$), the values approach a plateau, suggesting a saturation effect.

- **Maximum Entropy** (S_{max}): S_{max} is lowest for He ($Z = 2$), jumps significantly for Li ($Z = 3$), and stabilizes for Be ($Z = 4$) and boron (B, $Z = 5$). Beyond B ($Z = 5$), it exhibits a gradual decline, though the changes are minimal.

These trends reflect the evolving electronic structure as nuclear charge increases, with S_r and S_k capturing complementary aspects of spatial and momentum localization.

References

1. Chatzisavvas, K. C., Moustakidis, C. C. & Panos, C. P. Information entropy, information distances, and complexity in atoms. *The J. Chem. Phys.* **123**, 174111, DOI: 10.1063/1.2121610 (2005). https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/1.2121610/13576915/174111_1_online.pdf.

2. Bunge, C., Barrientos, J. & Bunge, A. Roothaan-hartree-fock ground-state atomic wave functions: Slater-type orbital expansions and expectation values for z = 2-54. *At. Data Nucl. Data Tables* **53**, 113–162, DOI: https://doi.org/10.1006/adnd.1993.1003 (1993).