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MSc Computational Physics

**Scaling of Quantum Information Measures
in Atomic Systems from $Z = 2$ to $Z = 10$**

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1 Introduction

This project focuses on the study of information entropy in atomic systems, specifically how it scales with the atomic number Z . We examine atoms from Helium ($Z = 2$) to Neon ($Z = 10$), computing their ground-state wavefunctions.

From these wavefunctions, we derive the electronic probability densities in both position space $\rho(r)$ and momentum space $n(k)$, and compute information-theoretic measures such as Shannon entropy and Onicescu energy to quantify the system's complexity.

We also analyze the radial probability distributions to investigate how the spatial localization of electrons evolves across atoms with increasing atomic number.

2 Theoretical Background

2.1 Roothaan-Hartree-Fock Wavefunctions

To compute the electronic probability densities of atoms, we employ the Roothaan-Hartree-Fock (RHF) method, a widely used self-consistent field (SCF) approach for approximating the ground-state wavefunctions of many-electron systems. This method solves the non-relativistic Schrödinger equation under the mean-field approximation, where electron-electron interactions are incorporated via averaged potentials.

In RHF theory, the atomic orbitals are expanded as linear combinations of Slater-type orbitals (STOs), forming the basis set used to construct the radial part of the wavefunctions. Specifically, each radial wavefunction $R_{nl}(r)$ is written as a sum over primitive STOs $S_{jl}(r)$:

$$R_{nl}(r) = \sum_j C_{jnl} S_{jl}(r) \quad (1)$$

Each $S_{jl}(r)$ is a Slater-type function of the form:

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

where n_{jl} is the principal quantum number of the primitive function, Z_{jl} is an effective orbital exponent, and N_{jl} is a normalization constant given by:

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

The total single-electron wavefunction for a hydrogenic-like orbital is then formed by combining the radial function with spherical harmonics $Y_{lm}(\Omega)$:

$$\phi_i(\vec{r}) = R_{nl}(r)Y_{lm}(\Omega_r) \quad (4)$$

$$\tilde{\phi}_i(\vec{k}) = \tilde{R}_{nl}(k)Y_{lm}(\Omega_k) \quad (5)$$

where \vec{r} and \vec{k} denote position and momentum coordinates, respectively. The wavefunctions in momentum space $\tilde{\phi}_i(\vec{k})$ are obtained via the Fourier transform of the spatial orbitals.

2.2 Shannon Entropy in Quantum Systems

Shannon entropy is a fundamental concept from information theory, representing the degree of uncertainty or randomness in a probability distribution. In quantum systems, it provides a quantitative measure of the spread of the electronic density either in real space or in momentum space, offering insight into the delocalization of the wavefunction.

The Shannon entropy in position space is defined as:

$$S_r = - \int \rho(\vec{r}) \ln \rho(\vec{r}) d^3r = -4\pi \int_0^\infty \rho(r) \ln \rho(r) r^2 dr \quad (6)$$

Similarly, in momentum space:

$$S_k = - \int n(\vec{k}) \ln n(\vec{k}) d^3k = -4\pi \int_0^\infty n(k) \ln n(k) k^2 dk \quad (7)$$

Here, $\rho(r)$ and $n(k)$ are the normalized probability densities in position and momentum space, respectively, derived from the squared moduli of the corresponding wavefunctions:

$$\rho(r) = |\phi(\vec{r})|^2 \quad (8)$$

$$n(k) = |\tilde{\phi}(\vec{k})|^2 \quad (9)$$

The total Shannon entropy of the system is given by the sum of the two contributions:

$$S_{\text{total}} = S_r + S_k \quad (10)$$

This total entropy is often interpreted as a global measure of uncertainty in both coordinate and momentum representations. According to the entropic uncertainty principle, the total entropy satisfies the bound:

$$S_{\text{total}} \geq 3(1 + \ln \pi) \approx 6.434 \quad (\text{in atomic units}) \quad (11)$$

A tighter, system-dependent upper bound for the entropy is given by:

$$S_{\text{max}} = 3(1 + \ln \pi) + \frac{3}{2} \ln \left(\frac{4}{9} r^2 k^2 \right) \quad (12)$$

where r^2 and k^2 are the second moments (mean square radius and mean square momentum) of the corresponding densities. This expression captures how the spatial and momentum extensions of the system limit its maximal informational content.

Using this maximum entropy, we can define the **order parameter** Ω , which quantifies the degree of organization (or departure from maximal disorder) in the system:

$$\Omega = 1 - \frac{S_{\text{total}}}{S_{\text{max}}} \quad (13)$$

Values of Ω close to 1 indicate a highly ordered, structured state, while values near 0 suggest maximal entropy or disorder.

In addition to entropy-based measures, we also compute the **Onicescu information energy**, defined as:

$$E_r = \int \rho^2(r) d^3r, \quad E_k = \int n^2(k) d^3k \quad (14)$$

These quantities reflect the concentration or localization of the probability distributions. Unlike Shannon entropy, which increases with delocalization, Onicescu energy decreases. As a combined measure of structural complexity, we define the **Onicescu complexity**:

$$O = \frac{1}{E_r E_k} \quad (15)$$

Higher values of O suggest a more complex and delocalized electron cloud, whereas lower values correspond to more localized and less complex configurations.

In this project, we compute S_r , S_k , S_{total} , Ω , and O for atoms with atomic number $Z = 2$ to $Z = 10$, using analytical RHF wavefunctions, and analyze how these quantities evolve as the atomic size increases.

3 Computational Implementation

The project was implemented in Python using Jupyter Notebooks. To construct the required dataset, an initial script utilized the `pytesseract` OCR engine to extract the Slater-type orbital expansion coefficients from the publication *Roothaan-Hartree-Fock Ground-State Atomic Wave-Functions – Slater-Type Orbital Expansions and Expectation Values for Z=2–54*. The extracted orbital parameters for the elements He through Ne were stored in a structured `.csv` file for further processing.

Additionally, data from the article *Information entropy, information distances, and complexity in atoms* were extracted via OCR in a similar manner. These included values of S_r , S_k , S , S_{\max} , Ω , and O , and were stored in a separate `.csv` file for later comparison with our own computed results.

The main computational script performs the following tasks:

- Constructs the wavefunctions in both position and momentum space.
- Computes the corresponding probability densities $\rho(r)$ and $n(k)$.
- Normalizes the densities in both spaces.
- Calculates Shannon entropies S_r and S_k , their sum S , the maximum entropy S_{\max} , the order parameter Ω , and the Onicescu complexity O .
- Stores all computed quantities for each atom into a Python dictionary.

A separate script was developed to visualize the dependence of the total entropy S on the atomic number Z , and to fit an approximate exponential relationship between them.

The entire implementation was modular and data-driven, enabling straightforward extension to heavier atoms if required.

4 Results

Using the computed RHF wavefunctions and the derived probability densities for elements from He ($Z = 2$) to Ne ($Z = 10$), we calculated the relevant information-theoretic quantities and visualized their behavior as functions of atomic number Z .

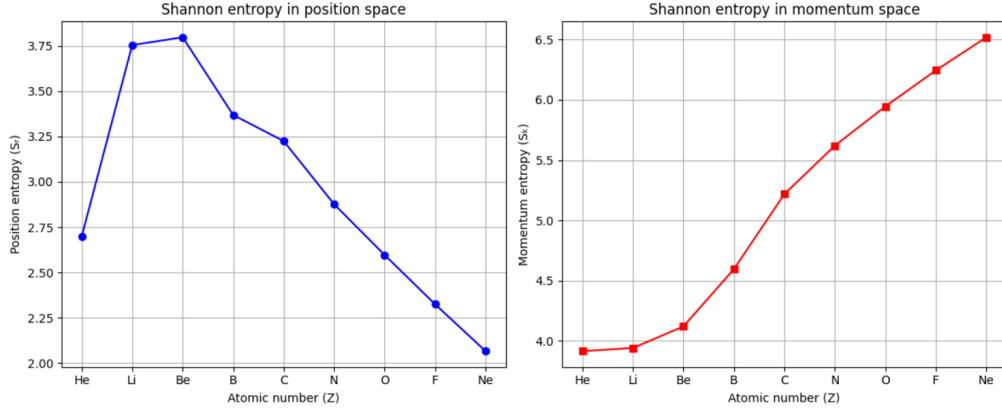


Figure 1: Position-space entropy S_r and momentum-space entropy S_k as a function of atomic number Z .

As expected, the position-space entropy S_r decreases with increasing Z , indicating stronger spatial localization of the electronic cloud in heavier atoms. Conversely, S_k increases, reflecting greater delocalization in momentum space. This behavior is consistent with the entropic uncertainty principle.

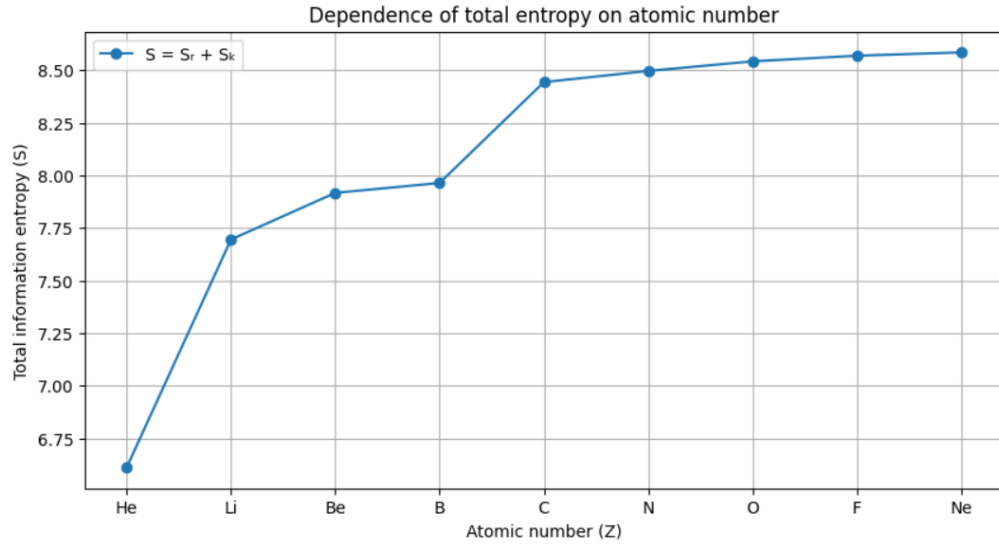


Figure 2: Total Shannon entropy $S = S_r + S_k$ versus atomic number Z .

The total entropy S exhibits a slowly increasing trend with Z , suggesting a net increase in overall uncertainty (information content) as atomic complexity grows.

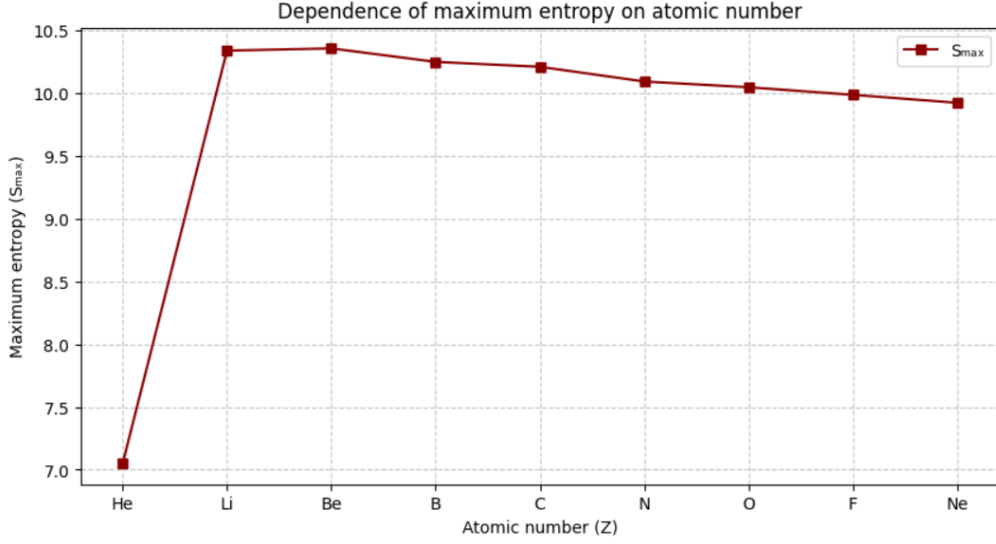


Figure 3: Maximum entropy S_{\max} based on spatial and momentum spreads.

The computed S_{\max} also increases with Z , consistent with the broadening of the electron density distributions in both spaces.

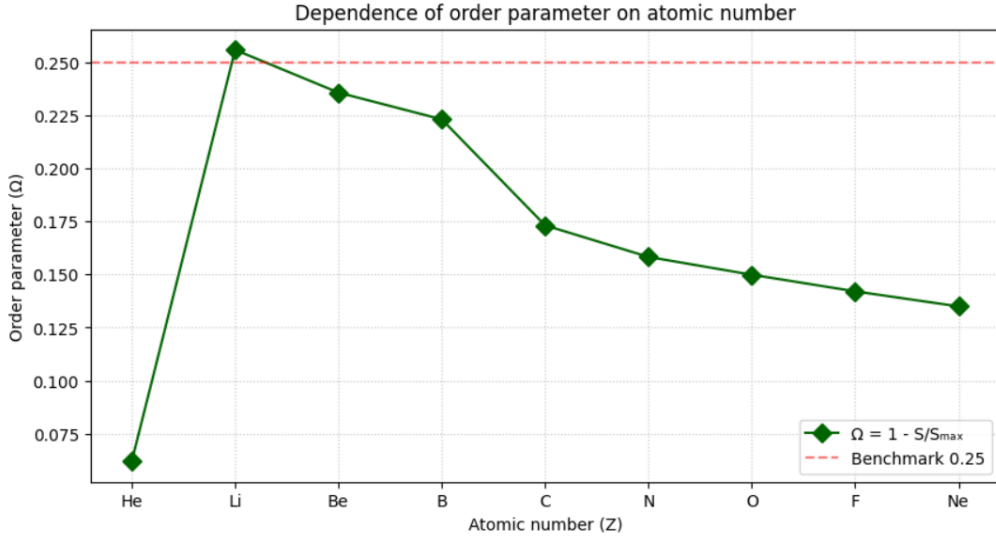


Figure 4: Order parameter $\Omega = 1 - S/S_{\max}$ as a function of Z .

The order parameter Ω shows a decreasing trend, indicating that atoms become relatively less ordered (in the information-theoretic sense) as their atomic number increases.

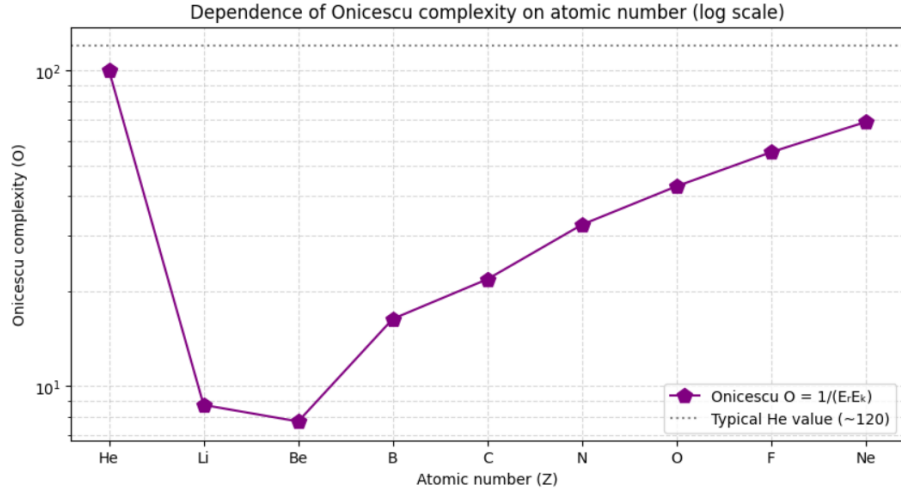


Figure 5: Onicescu complexity $O = 1/(E_r E_k)$ across atomic number Z .

Onicescu complexity grows significantly with Z , reflecting the higher structural complexity and delocalization of electron clouds in heavier atoms.

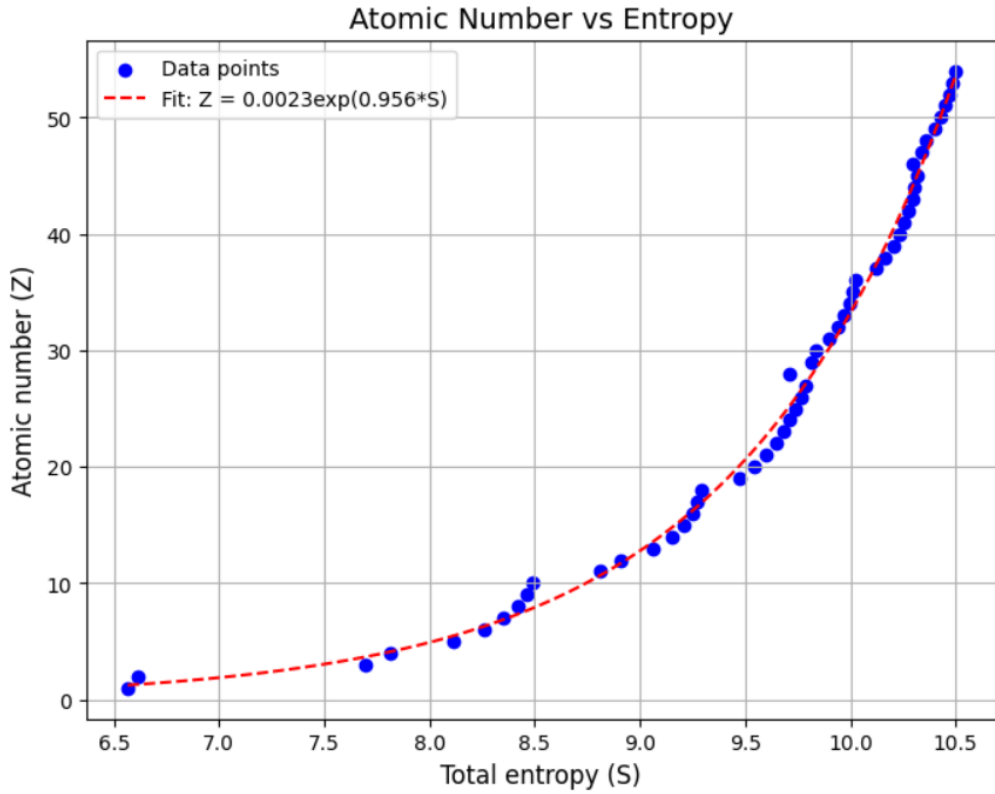


Figure 6: Exponential regression of total entropy S versus atomic number Z .

Finally, a regression model was fitted to approximate the functional dependence of atomic number Z on total entropy S . The fit suggests an approximately exponential relationship of the form:

$$Z(S) \approx 0.0023 \cdot e^{0.956 \cdot S}$$

This expression highlights the observed trend that higher information entropy correlates with larger atomic number. The result reinforces the utility of entropy-based measures in capturing the systematic increase in complexity across atomic systems.