Computational Quantum Physics

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Abstract. *Study of the informative content of the atoms from He to Ne*

1. Introduction

In this project we are aiming to study the information entropy and other informative quantities from the elements He to Ne and their relation to atomic number Z. Specifically we will calculate the wavefunctions of these elements and by calculating the densities in position and momentum space we will evaluate Shannon entropy and related measures. We will then plot these functions to understand their behavior and then we will perform regression to S-Z in order to examine further their relation.

2. Mathematical Background

2.1. Roothaan-Hartree-Fock Wave Functions

The Roothaan-Hartree-Fock (RHF) method is a formulation of the Hartree-Fock approach for atoms and molecules using a finite basis set expansion. Instead of solving the Hartree-Fock which are difficult and only solved numerically, RHF expresses the orbitals as linear combinations of known basis functions which are the Slater type orbitals (STOs).The expansion is of the form:

$$R_{nl}(r) = \sum_j C_{jnl} S_{jl}(r) \tag{2.1}$$

Here, $S_{jl}(r)$ are the basis functions (STOs), and C_{jnl} are the coefficients to be determined.The STOs are normalized and have the form:

$$S_{jl}(r) = N_{jl} r^{njl-1} e^{-Zjlr} \tag{2.2}$$

where N_{jl} is the normalization constant and equals to:

$$N_{jl} = \frac{(2Z_{jl})^{njl+1/2}}{\sqrt{2n_{jl}!}} \tag{2.3}$$

where n_{jl} is the principal quantum number, Z_{jl} the orbital exponent and l the azimuthal quantum number. In equations 1.1, 1.2, 1.3, n_{jl} is the principal quantum number, Z_{jl} is the orbital exponent, and l is the azimuthal quantum number. The wave functions in position space $\varphi_i(r)$ and k-space $\tilde{\varphi}_i(k)$ are written as:

$$\varphi_i(r) = \varphi_{nlm}(r) = R_{nl}(r)Y_{lm}(\Omega_R) \tag{2.4}$$

$$\tilde{\varphi}_i(k) = \tilde{\varphi}_{nlm}(k) = \tilde{R}_{nl}(k)Y_{lm}(\Omega_R) \tag{2.5}$$

However, we only need the radial components ($R_{nl}(r)$ and $\tilde{R}_{nl}(k)$) for this project.

It is important to note that the STOs and thus the radials we use are the normalized ones meaning they comply to :

$$\int_0^\infty R_{nl}(r)r^2dr = 1 \quad \text{and} \quad \int_0^\infty \tilde{R}_{nl}(k)k^2dk = 1 \tag{2.6}$$

Based on these (1.1) we can also calculate the electron density distributions in both spaces. For systems of spherical symmetry these equations are:

$$\rho(r) = \frac{1}{4\pi Z}\sum_i A_i|R_{nl}(r)|^2 \quad \text{and} \quad \eta(k) = \frac{1}{4\pi Z}\sum_i A_i|\tilde{R}_{nl}(k)|^2 \tag{2.7}$$

2.2. Shannon Entropy and related measures

Shannon or information entropy refers to the average level of uncertainty (information loss) in the outcome of a variable in a system. The general equation is:

$$S = -\int_{x_{min}}^{x_{max}} p(x)lnp((x)) \geq 0 \tag{2.9}$$

Where p(x) is the probability density. So we can define the two information entropies (in both spaces) accordingly :

$$S_r = -4\pi\int_0^\infty \rho(r)ln\rho(r)r^2dr \quad S_k = -4\pi\int_0^\infty \eta(k)ln\eta(k)k^2dk \tag{2.10}$$

And the total entropy is $S_{tot} = S_r + S_k$. We can also define the maximum entropy as:

$$S_{max} = 3(1 + ln(\pi)) + \frac{3}{2}ln(\frac{4}{9}\langle r^2\rangle\langle k^2\rangle) \tag{2.11}$$

The rest of the measures are Onisescu information energy **O** which is a dimensionless measure of the information concentration in the system and the Landsbergh's order parameter Ω which is a more perceptible measure of the order of the system. The quantities are described by the following equations (2.12) and (2.13):

$$O = \frac{1}{E_rE_k} \tag{1.12}$$

Where:

$$E_r = \int_0^\infty 4\pi r^2 \rho^2(r)\, dr \quad \text{(position space)} \tag{2.12a}$$

$$E_k = \int_0^\infty 4\pi k^2 n^2(k)\, dk \quad \text{(momentum space)} \tag{2.12b}$$

And also:

$$\Omega = 1 - \frac{S}{S_{\max}} \tag{15}$$

$\Omega \to 1$ indicates perfect order whereas $\Omega \to 0$ translates to complete disorder.

3. Computational Implementation and Workflow

In this section we describe the computational approach used to realize the theoretical framework previously discussed. The implementation consists of a modular Python code that executes the further computations using basis functions in both position and momentum space. We used Python 3.12.2 from Jupyter Lab on Anaconda and run it on Apple M1 chip (MacBook Air, 8-core CPU).

3.1. Code Structure

The implementation is organized into two main components:

- `wf_basis.py`: A module that defines a library of analytical basis functions in position and momentum space.
- `final_main.ipynb`: A Jupyter notebook that contains the full computational workflow, the wavefunction evaluation, and result analysis.

3.2. Basis Functions

The basis functions are the STOs we discussed further and characterized by radial dependencies of the form $r^n e^{-zr}$ in position space, and their corresponding analytical Fourier transforms in momentum space. These functions are defined for various principal quantum numbers and angular momenta, such as $1s$, $2s$, $3p$, $3d$, etc. Of course we used only some of them since we study only the atoms from He to Ne.

3.3. Main Code

The computation begins by importing a CSV file (`df.csv`) that contains expansion coefficients and parameters for Slater-type orbitals (STOs), assigned for each element Z and each orbital (`1s`, `2s`, `2p`). A dictionary `ELEC_CONFIG` provides the number of electrons occupying each type of orbital for every atomic number.

The function `build_orbital_func()` is a nested function that dynamically creates callable orbital functions from the data, after defining the space (position (r) or momentum (k) using STOs defined in the `wf_basis.py` module. These functions represent the total wavefunction for each orbital as a linear combination of STOs multiplied by the coefficients extracted from the dataset.

Later for a given element Z, the script constructs:

- $P(r)$: The electron density in real space.
- $N(k)$: The electron density in momentum space.

Using these, the informational quantities $S_r, S_k, S, S_{max}, \Omega, O$ are computed.

Hence for each element from He to Ne ($Z = 2 \ldots 10$), these quantities are computed and stored in a list. This list is then converted into a Pandas DataFrame for display and further analysis. The final table has the form:

```
['Z', 'Element', 'Sr', 'Sk', 'S', 'Smax', 'Ω', 'O']
```

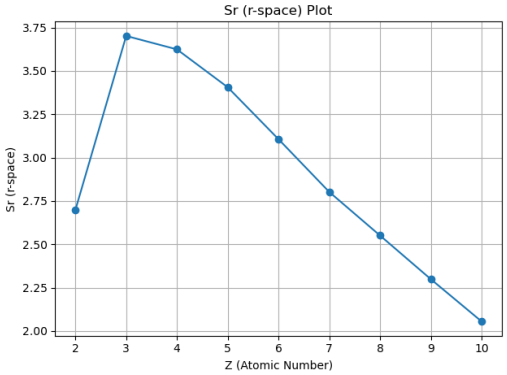
Then we plotted each of these quantities with Z in order to understand each relation with the atomic number. The last part of the file performs a linear regression to the given data for all the 54 elements and their entropy to define the exponential relation this quantity has with the atomic number. We considered an exponential relation on Z-S. We got the logarithm of it and ended with a linear relation. We performed linear regression to the data after logarithmizing Z data and returned the values of this line to our exponential relation we initialy defined. Then we plotted it into our data.

4. Results

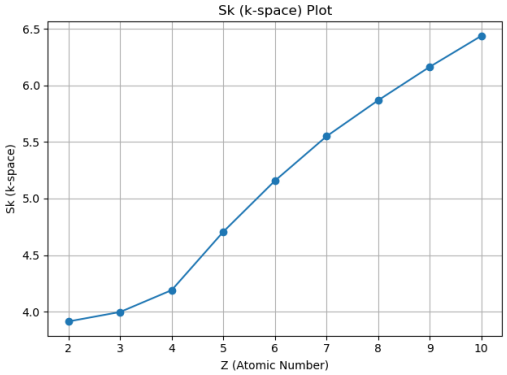
4.1. Final Data

	Z	Element	Sr	Sk	S	Smax	Omega	O
0	2	He	2.698511	3.913418	6.611929	7.049299	0.062045	100.361326
1	3	Li	3.701437	3.996817	7.698254	10.357839	0.256770	9.157127
2	4	Be	3.623859	4.190185	7.814044	10.395028	0.248290	8.454339
3	5	B	3.405445	4.705898	8.111344	10.373844	0.218097	15.965316
4	6	C	3.106025	5.156572	8.262597	10.262419	0.194868	25.712130
5	7	N	2.801688	5.549331	8.351019	10.151972	0.177399	37.431982
6	8	O	2.550539	5.867346	8.417885	10.111271	0.167475	48.483769
7	9	F	2.298827	6.163317	8.462144	10.053278	0.158270	61.145004
8	10	Ne	2.055138	6.437058	8.492196	9.990766	0.149995	75.244712

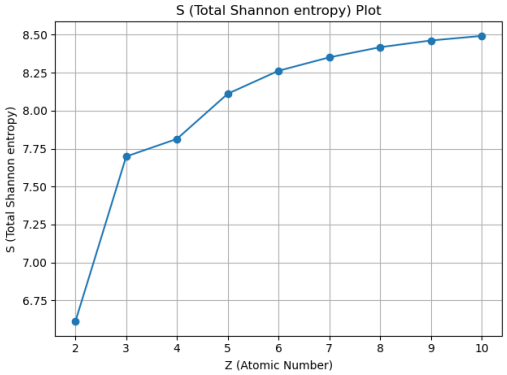
4.2. Plots



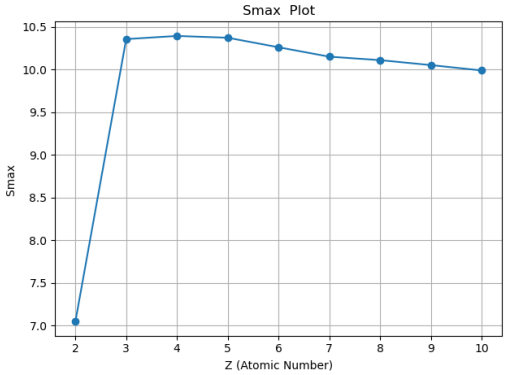
(a) Entropy in r space plot



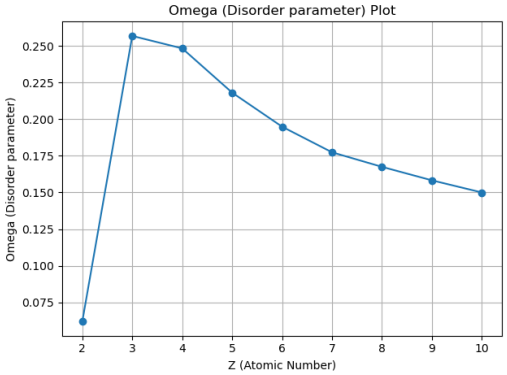
(b) Entropy in momentum space plot



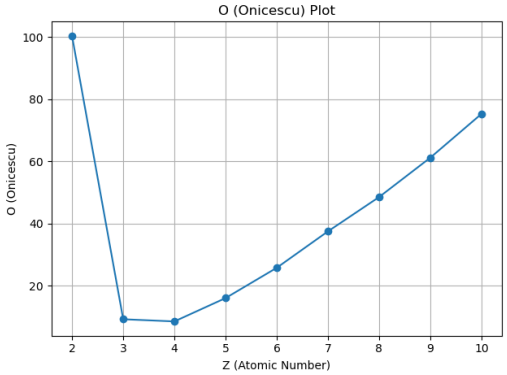
(c) Total Entropy



(d) Maximum Entropy



(e) Landsberg's entropy (Ω)



(f) Onisescu Information Energy (O)

Figure 1. Entropy and Information Measures

4.3. Regression

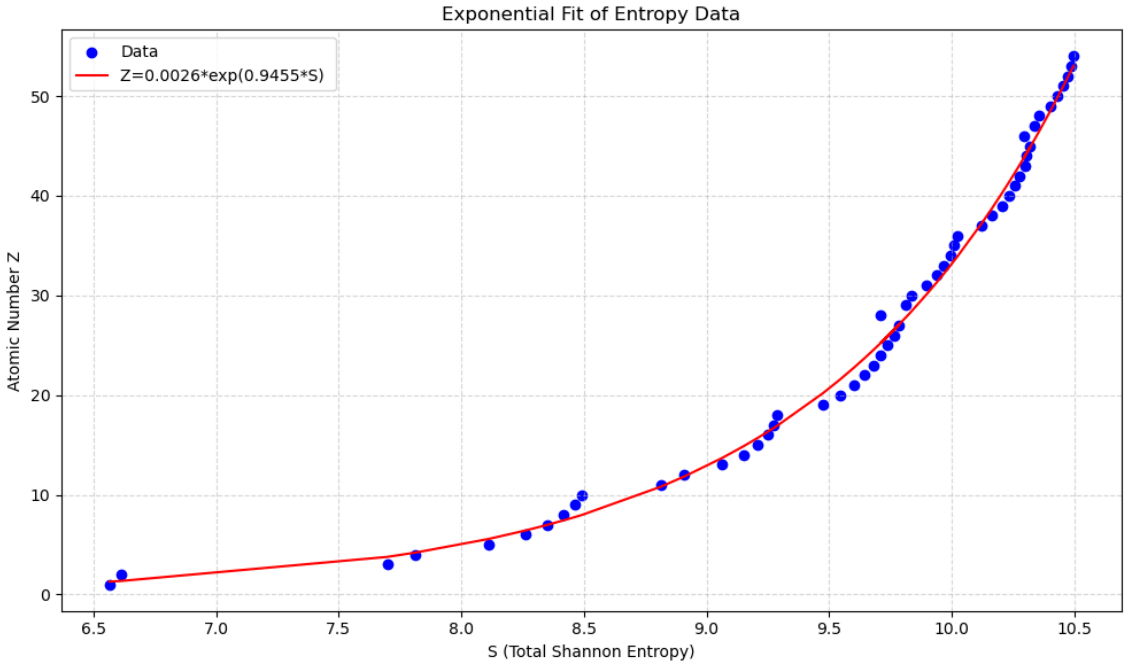


Figure 2. Exponential relation of entropy-atomic number

5. Discussion

- Observing the entropy plots we can clearly see that as for the entropy in r space that it peaks at Lithium and drops as the elements are becoming heavier where in momentum space we have the completely opposite, with the total entropy to steadily increasing as Z increases.
- As for Omega we see that higher Z atoms exhibit more ordered electron distributions whereas lighter atoms like Helium have higher disorder.For Onisescu we see that heavy atoms have more delocalized electron densities meaning they are reducing the information energy.
- As for regression we see that considering more atoms to our system we can confirm the exponential relation of these to quantities as it performed in the data for all the 54 elements.

References

[1] Carlos F. Bunge, José A. Barrientos, and Annik Vivier Bunge. *Roothaan-Hartree-Fock ground-state atomic wave functions: Slater-type orbital expansions and expectation values for* $z = 2 - 54$. 1993.

[2] K. Ch. Chatzisavvas, Ch. C. Moustakidis, and C. P. Panos. *Information entropy, information distances, and complexity in atoms*. The Journal of Chemical Physics, 2005.