Aristotle University Of Thessaloniki

Physics Department

# Computational Quantum Mechanics Project

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**Abstract**

The purpose of this project is to investigate the information loss in the quantum mechanical description of atoms with atomic numbers $2 \leq Z \leq 10$. The approach used to achieve this is calculating the Shannon information entropy in both position space ($S_r$) and momentum space ($S_k$). First, the wave function of each atom in position space and momentum space is defined using the Roothaan-Hartree-Fock wave functions. Having these, the electron density and subsequently the Shannon information entropy are determined in both spaces ($\rho(r)$, $\eta(k)$ & $S_r$, $S_k$) for each atom. Finally, the validity and accuracy of the results yielded by this process are assessed by comparing them to those presented in the reference study given.

# Contents

# Chapter 1

# Theoretical and Mathematical Background

This chapter presents the essential background for understanding this project. More specifically, the RHF wave functions are introduced and discussed briefly and then the needed information concerning the Shannon information entropy is given.

## 1.1 Roothaan-Hartree-Fock Wave Functions

The Hartree-Fock equations describe the non-relativistic Schrödinger equation for the motion of electrons in an atom. They are complex functions solvable only numerically. Thus, the RHF method is utilized to provide approximate analytical solutions to the HF equations, which are easier to implement in computational programs. More specifically, the Roothaan-Hartree-Fock (RHF) wave functions approximate the radial atomic part of the HF wave functions, $R_{nl}(r)$, expressed as a superposition of primitive radial functions $S_{jl}(r)$:

$$R_{nl}(r) = \sum_j C_{jnl} S_{jl}(r) \tag{1.1}$$

$S_{jl}$ are normalized Slater-Type Orbitals (STOs):

$$S_{jl}(r) = N_{jl} r^{n_{jl}-1} e^{-Z_{jl} r} \tag{1.2}$$

with the normalization constant $N_{jl}$ given by:

$$N_{jl} = \frac{(2Z_{jl})^{n_{jl}+\frac{1}{2}}}{\sqrt{(2n_{jl})!}} \tag{1.3}$$

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:

$$\varphi_i(r) = \varphi_{nlm}(r) = R_{nl}(r)Y_{lm}(\Omega_R) \tag{1.4}$$

$$\tilde{\varphi}_i(k) = \tilde{\varphi}_{nlm}(k) = \tilde{R}_{nl}(k)Y_{lm}(\Omega_R) \tag{1.5}$$

However, as mentioned, only the radial components ($R_{nl}(r)$ and $\tilde{R}_{nl}(k)$) are of interest. These components are computed with the help of Python code using equations 1.1, 1.2, 1.3 and the position and k-space STOs given to us a reference.

It is important to note that $R_{nl}(r)$ and $\tilde{R}_{nl}(k)$ need to be normalized in a way such that:

$$\int_0^\infty R_{nl}(r)r^2dr = 1 \quad \text{and} \quad \int_0^\infty \tilde{R}_{nl}(k)k^2dk = 1 \tag{1.6}$$

These integrals are also computed in our Python program.

The wave functions in position and k-space are respectively defined as:

$$\Psi(r) = \frac{1}{2\pi\sqrt{Z}} \sum_i \sqrt{A_i} \times R_{nl}(r) \tag{1.7}$$

$$\tilde{\Psi}(k) = \frac{1}{2\pi\sqrt{Z}} \sum_i \sqrt{A_i} \times \tilde{R}_{nl}(k) \tag{1.8}$$

Based on these, The electron densities in position space ($\rho(r)$) and k-space ($\eta(k)$) can be written as:

$$\rho(r) = \frac{1}{4\pi Z} \sum_i A_i \times |R_{nl}(r)|^2 \tag{1.9}$$

$$\eta(k) = \frac{1}{4\pi Z} \sum_i A_i \times |\tilde{R}_{nl}(k)|^2 \tag{1.10}$$

These two last equations ( 1.9, 1.10) are used in our code to determine the density of states (DOS). Normalization should also be ensured here such that:

$$4\pi \int_0^\infty \rho(r)r^2dr = 1 \quad \text{and} \quad 4\pi \int_0^\infty \eta(k)k^2dk = 1 \tag{1.11}$$

## 1.2 Shannon Information Entropy

The concept of Shannon entropy (or information entropy) was introduced by Claude Shannon. It refers to the average level of uncertainty (information loss) inherent to a variable's possible outcomes. For a system, it is given by the following equation:

$$S = -\int_{x_{\min}}^{x_{\max}} p(x)\ln(p(x))\,dx \geq 0 \tag{1.12}$$

where $p(x)$ is the probability density. According to 1.12, if there is no randomness in the system there is no loss of information, so $S = 0$. Analogously, for maximum information loss, $S = ln(2)$.

Using 1.9 and 1.10 the Shannon entropy in position and k-space can be computed with the use of spherical coordinates:

$$S_r = -4\pi\int_0^{\infty} \rho(r)\ln(\rho(r))r^2\,dr \tag{1.13}$$

$$S_k = -4\pi\int_0^{\infty} \eta(k)\ln(\eta(k))k^2\,dk \tag{1.14}$$

Finally, the total information entropy of each atom is determined by:

$$S = S_r + S_k \tag{1.15}$$

In our code, equations 1.13, 1.14 and 1.15 are used to calculate the amount of information loss for each atom's wave function definition. Since 1.9 and 1.10 invlove the atom's atomic number Z, the entropies computes are also functions of Z.

# Chapter 2

# Computational Implementation Results

Having set the theoretical and mathematical background, the next step is computational implementation. This is achieved through the use of a Python code we developed. First, for each element from Z=2 to Z=10, the numerical results for the integrals of 1.6 and 1.11 as well as the information entropy values given by 1.13, 1.14, 1.15. Having obtained these values, the relation of the Shannon entropy and the atomic number Z is studied and presented through figures created with the help of our code.

## 2.1 Results for each element

### 2.1.1 Z=2 (He)

Since Z=2 (number of electrons), Helium's orbital configuration is $1s^2$ (n=1, l=0). Based on that, the appropriate STOs are calculated by our program using 1.1. 1.2, 1.3. After $R_{1s}$ (for position space) and $K_{1s}$ (for k-space) are determined, the integrals of 1.6 are calculated to confirm normalization:

$$I_{R_{1s}} = 1.0000016264426703 \tag{2.1}$$

$$I_{K_{1s}} = 1.0000016264426548 \tag{2.2}$$

The density of states for position space and k-space are derived with the use of 1.9 and 1.10:

$$\rho_{\mathrm{He}}(r) = \frac{1}{4\pi} \times R_{1s}^{\mathrm{He}}(r)^2 \tag{2.3}$$

$$\eta_{\mathrm{He}}(k) = \frac{1}{4\pi} \times K_{1s}^{\mathrm{He}}(k)^2 \tag{2.4}$$

The integrals given by 1.11 are calculated as well to check for DOS normalization:

$$I_\rho = 1.000001626442671 \tag{2.5}$$

$$I_\eta = 1.000001626442657 \tag{2.6}$$

By plugging equations 2.3 and 2.4 into the equations for Shannon entropy (1.13, 1.14, 1.15), the program yields the following results:

$$S_r = 2.698510983702253 \tag{2.7}$$

$$S_k = 3.913418756309648 \tag{2.8}$$

$$S = 6.611929740011901 \tag{2.9}$$

The following table showcases the numerical results for all the quantities computed by our code.

| He (Z=2) | |
|---|---|
| Quantity | Value |
| I_R1s | 1.000001626 |
| I_R2s | 0 |
| I_R2p | 0 |
| Ip | 1.000001626 |
| Sr | 2.698510984 |
| I_K1s | 1.000001626 |
| I_K2s | 0 |
| I_K2p | 0 |
| In | 1.000001626 |
| Sk | 3.913418756 |
| S | 6.61192974 |

Figure 2.1: Results for He

As shown in the table,

$$I_{R_{1s}} \simeq 1 \quad \text{and} \quad I_{K_{1s}} \simeq 1 \tag{2.10}$$

$$I_\rho \simeq 1 \quad \text{and} \quad I_\eta \simeq 1 \tag{2.11}$$

which means that the normalization conditions set by 1.6 and 1.11 are met, confirming the validity of the method employed and the fact that our code is working as expected.

Finally, DOS in position space and momentum space are graphed against r and k respectively.

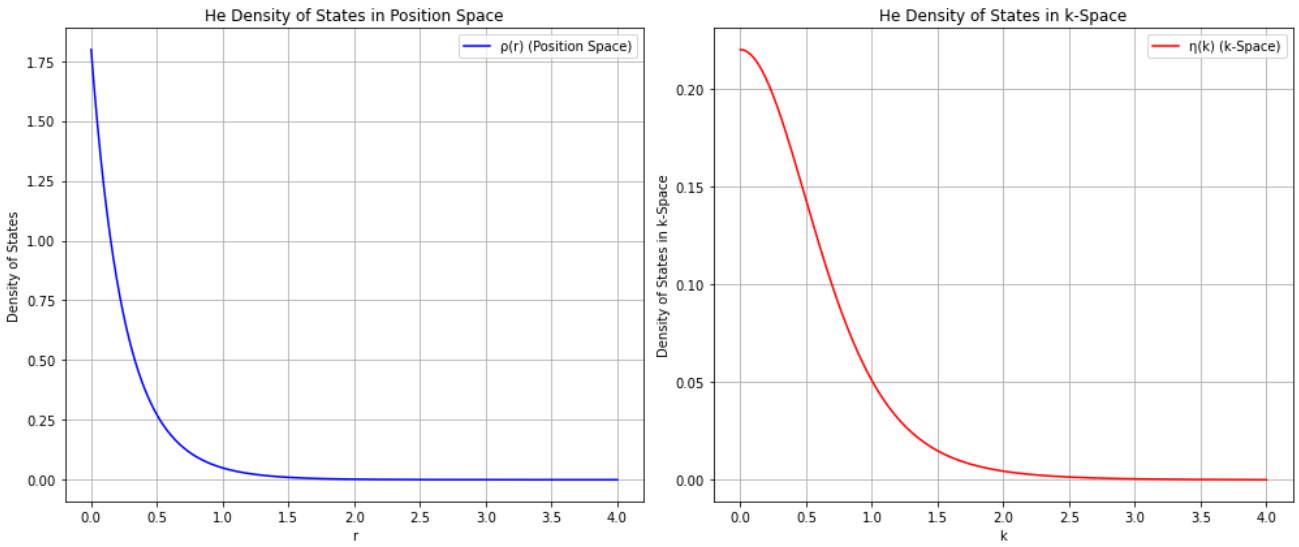


Figure 2.2: He DOS in position space (left) and in k-space (right)

The same process is followed for the rest of the elements. For the sake of brevity, only the numerical results and figures produced by the code will be presented for elements with atomic numbers 2 through 10.

### 2.1.2 Z=3 (Li)

Numerical results for Lithium ($1s^2 2s^1$) are presented in the following table.

| Li | |
|---|---|
| **Quantity** | **Value** |
| I_R1s | 0.99999962 |
| I_R2s | 0.99999975 |
| I_R2p | 0 |
| Ip | 0.999999664 |
| Sr | 3.70143692 |
| I_K1s | 0.99999962 |
| I_K2s | 0.99999975 |
| I_K2p | 0 |
| In | 0.999999664 |
| Sk | 3.996819022 |
| S | 7.698255942 |

Figure 2.3: Results for Li

Shannon entropy results:

$$S_r = 3.701436920386733 \tag{2.12}$$

$$S_k = 3.996819021607306 \tag{2.13}$$

$$S = 7.69825594199404 \tag{2.14}$$

Normalization conditions are met, as:

$$I_{R_{1s}} \simeq 1 \quad , I_{R_{2s}} \simeq 1 \quad \text{and} \quad I_{K_{1s}} \simeq 1, \quad I_{K_{2s}} \simeq 1 \tag{2.15}$$

$$I_\rho \simeq 1 \quad \text{and} \quad I_\eta \simeq 1 \tag{2.16}$$

indicating once again that the process followed is valid and the rest of the numerical results are to be trusted as accurate.

The DOS graphs in position space with respect to r and in momentum space with respect to k are shown below.

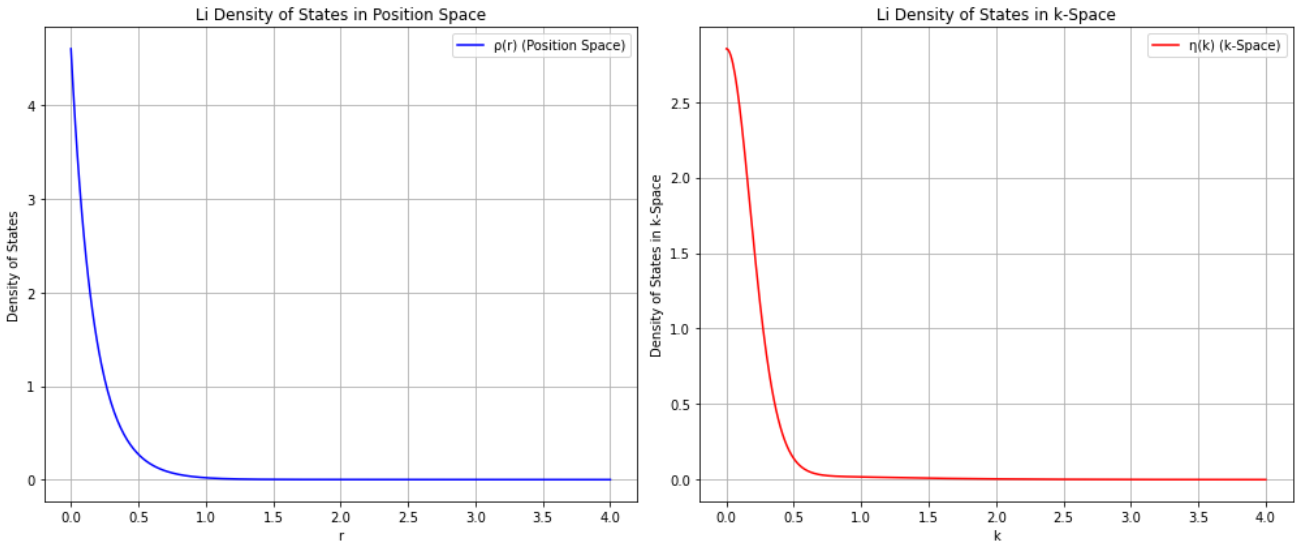


Figure 2.4: Li DOS in position space (left) and in k-space (right)

### 2.1.3 Z=4 (Be)

Numerical results for Berilium with orbital configuration $1s^2 2s^2$ are presented in the following table.

| Be | |
|---|---|
| Quantities | Value |
| I_R1s | 0.999999614 |
| I_R2s | 1.000001122 |
| I_R2p | 0 |
| Ip | 1.000000368 |
| Sr | 3.623859023 |
| I_K1s | 0.999999614 |
| I_K2s | 1.000001122 |
| I_K2p | 0 |
| In | 1.000000368 |
| Sk | 4.190187548 |
| S | 7.81404657 |

Figure 2.5: Results for Be

Shannon entropy results:

$$S_r = 3.623859022670154 \tag{2.17}$$

$$S_k = 4.190187547827826 \tag{2.18}$$

$$S = 7.81404657049798 \tag{2.19}$$

Normalization conditions are met with:

$$I_{R_{1s}} \simeq 1 \quad , I_{R_{2s}} \simeq 1 \quad \text{and} \quad I_{K_{1s}} \simeq 1, \quad I_{K_{2s}} \simeq 1 \tag{2.20}$$

$$I_\rho \simeq 1 \quad \text{and} \quad I_\eta \simeq 1 \tag{2.21}$$

DOS graphs in position space and momentum space:

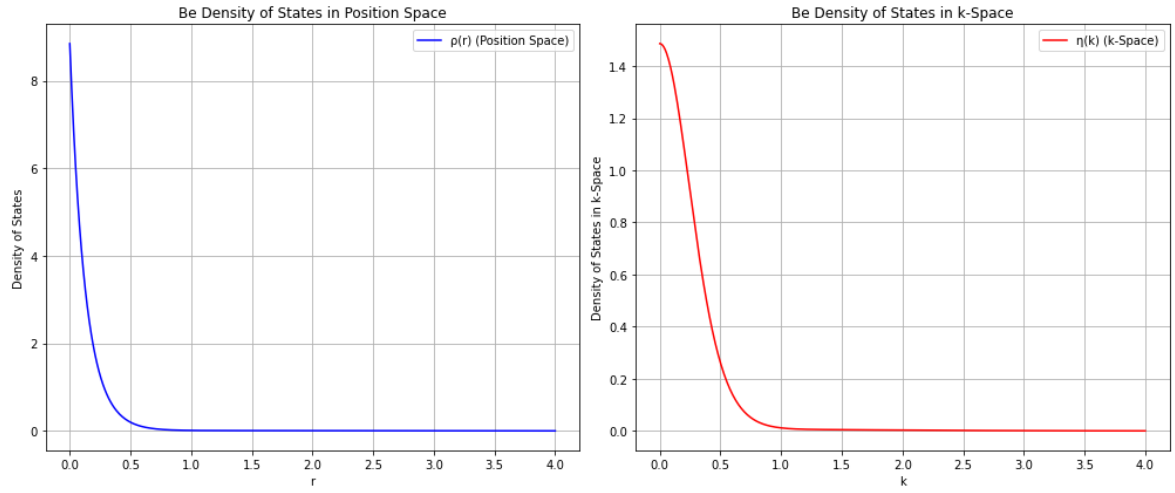


Figure 2.6: Be DOS in position space (left) and in k-space (right)

### 2.1.4 Z=5 (B)

Numerical results for Boron with orbital configuration $1s^2 2s^2 2p^1$ are presented in the following table.

| B | |
|---|---|
| Quantity | Value |
| I_R1s | 1.00000036 |
| I_R2s | 1.000000111 |
| I_R2p | 1.000000781 |
| Ip | 1.000000345 |
| Sr | 3.405445227 |
| I_K1s | 1.00000036 |
| I_K2s | 1.000000111 |
| I_K2p | 1.000000781 |
| In | 1.000000345 |
| Sk | 4.70590177 |
| S | 8.111346997 |

Figure 2.7: Results for B

Shannon entropy results:

$$S_r = 3.4054452271411555 \tag{2.22}$$

$$S_k = 4.705901770023134 \tag{2.23}$$

$$S = 8.11134699716429 \tag{2.24}$$

Normalization conditions are met, as:

$$I_{R_{1s}} \simeq 1 \quad , I_{R_{2s}} \simeq 1 \quad , I_{R_{2p}} \simeq 1 \quad \text{and} \quad I_{K_{1s}} \simeq 1, \quad I_{K_{2s}} \simeq 1, \quad I_{K_{2p}} \simeq 1 \tag{2.25}$$

$$I_\rho \simeq 1 \quad \text{and} \quad I_\eta \simeq 1 \tag{2.26}$$

DOS graphs in position space and momentum space:

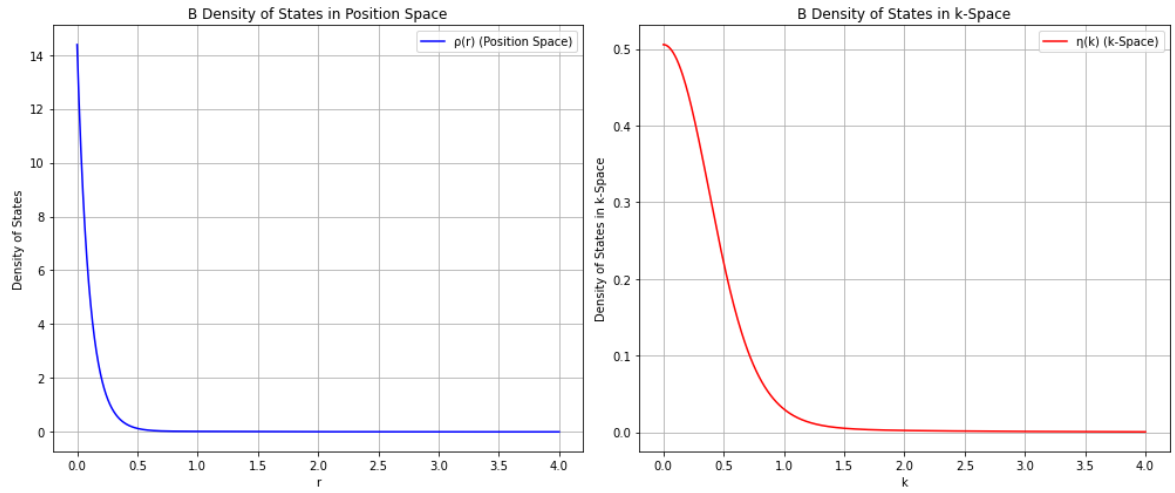


Figure 2.8: B DOS in position space (left) and in k-space (right)

### 2.1.5 Z=6 (C)

Numerical results for Carbon with orbital configuration $1s^2 2s^2 2p^2$ are presented in the following table.

| C | |
|---|---|
| **Quantity** | **Value** |
| I_R1s | 1.000000226 |
| I_R2s | 0.999998506 |
| I_R2p | 0.999999749 |
| Ip | 0.999999494 |
| Sr | 3.106024954 |
| I_K1s | 1.000000226 |
| I_K2s | 0.999998506 |
| I_K2p | 0.999999749 |
| In | 0.999999494 |
| Sk | 5.156576254 |
| S | 8.262601208 |

Figure 2.9: Results for C

Shannon entropy results:

$$S_r = 3.1060249537958877 \tag{2.27}$$

$$S_k = 5.156576254092469 \tag{2.28}$$

$$S = 8.262601207888357 \tag{2.29}$$

Normalization conditions are met, as:

$$I_{R_{1s}} \simeq 1 \quad , I_{R_{2s}} \simeq 1 \quad , I_{R_{2p}} \simeq 1 \quad \text{and} \quad I_{K_{1s}} \simeq 1, \quad I_{K_{2s}} \simeq 1, \quad I_{K_{2p}} \simeq 1 \tag{2.30}$$

$$I_{\rho} \simeq 1 \quad \text{and} \quad I_{\eta} \simeq 1 \tag{2.31}$$

DOS graphs in position space and momentum space:

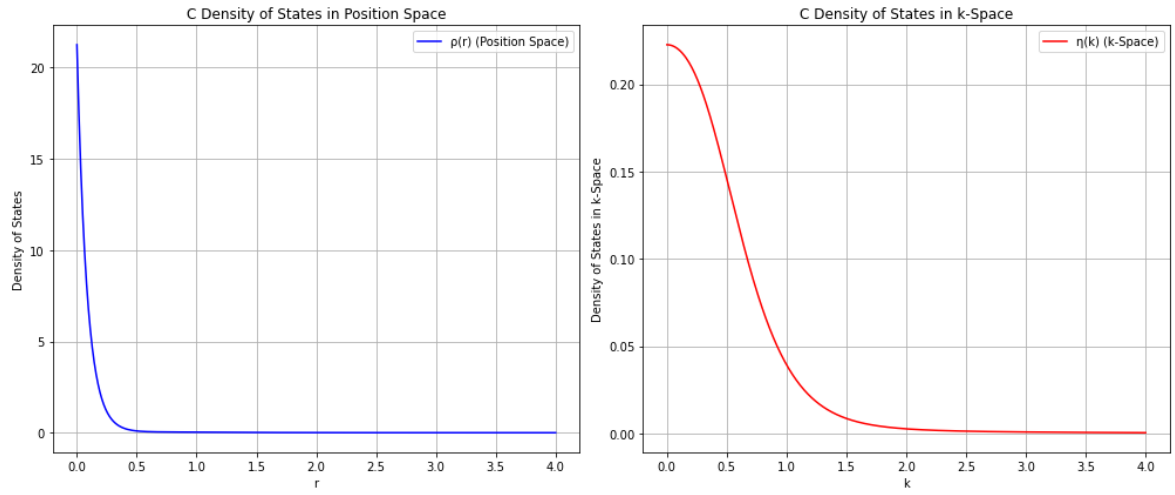


Figure 2.10: C DOS in position space (left) and in k-space (right)

### 2.1.6 Z=7 (N)

Numerical results for Nitrogen with orbital configuration $1s^2 2s^2 2p^3$ are presented in the following table.

| N | |
|---|---|
| **Quantity** | **Value** |
| **I_R1s** | 0.999999205 |
| **I_R2s** | 0.999999139 |
| **I_R2p** | 0.999999891 |
| **Ip** | 0.99999948 |
| **Sr** | 2.801688154 |
| **I_K1s** | 0.999999205 |
| **I_K2s** | 0.999999139 |
| **I_K2p** | 0.999999891 |
| **In** | 0.99999948 |
| **Sk** | 5.549337131 |
| **S** | 8.351025285 |

Figure 2.11: Results for N

Shannon entropy results:

$$S_r = 2.8016881540456646 \tag{2.32}$$

$$S_k = 5.549337130976648 \tag{2.33}$$

$$S = 8.351025285022313 \tag{2.34}$$

Normalization conditions are met, as:

$$I_{R_{1s}} \simeq 1 \quad , I_{R_{2s}} \simeq 1 \quad , I_{R_{2p}} \simeq 1 \quad \text{and} \quad I_{K_{1s}} \simeq 1, \quad I_{K_{2s}} \simeq 1, \quad I_{K_{2p}} \simeq 1 \tag{2.35}$$

$$I_\rho \simeq 1 \quad \text{and} \quad I_\eta \simeq 1 \tag{2.36}$$

DOS graphs in position space and momentum space:

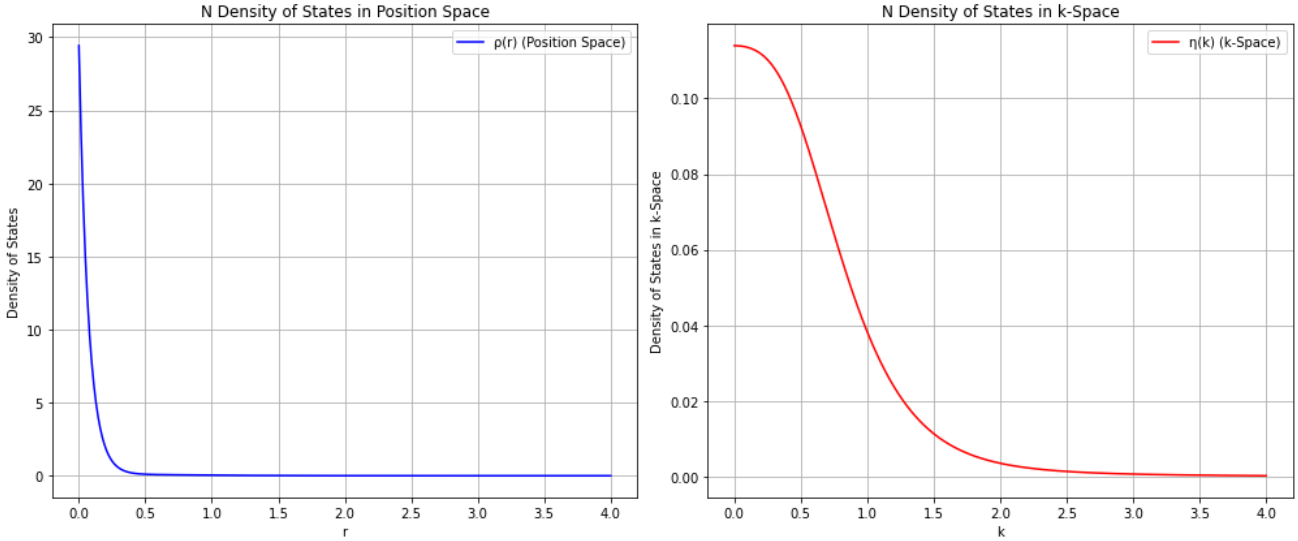


Figure 2.12: N DOS in position space (left) and in k-space (right)

### 2.1.7 Z=8 (O)

Numerical results for Oxygen with orbital configuration $1s^2 2s^2 2p^4$ are presented in the following table.

| O | |
|---|---|
| Quantity | Value |
| I_R1s | 1.000000549 |
| I_R2s | 0.999999495 |
| I_R2p | 0.999999764 |
| Ip | 0.999999893 |
| Sr | 2.550538734 |
| I_K1s | 1.000000549 |
| I_K2s | 0.999999495 |
| I_K2p | 0.999999764 |
| In | 0.999999893 |
| Sk | 5.867353572 |
| S | 8.417892306 |

Figure 2.13: Results for O

Shannon entropy results:

$$S_r = 2.550538733960005 \tag{2.37}$$

$$S_k = 5.867353571616235 \tag{2.38}$$

$$S = 8.41789230557624 \tag{2.39}$$

Normalization conditions are met, as:

$$I_{R_{1s}} \simeq 1 \quad , I_{R_{2s}} \simeq 1 \quad , I_{R_{2p}} \simeq 1 \quad \text{and} \quad I_{K_{1s}} \simeq 1, \quad I_{K_{2s}} \simeq 1, \quad I_{K_{2p}} \simeq 1 \tag{2.40}$$

$$I_\rho \simeq 1 \quad \text{and} \quad I_\eta \simeq 1 \tag{2.41}$$

DOS graphs in position space and momentum space:

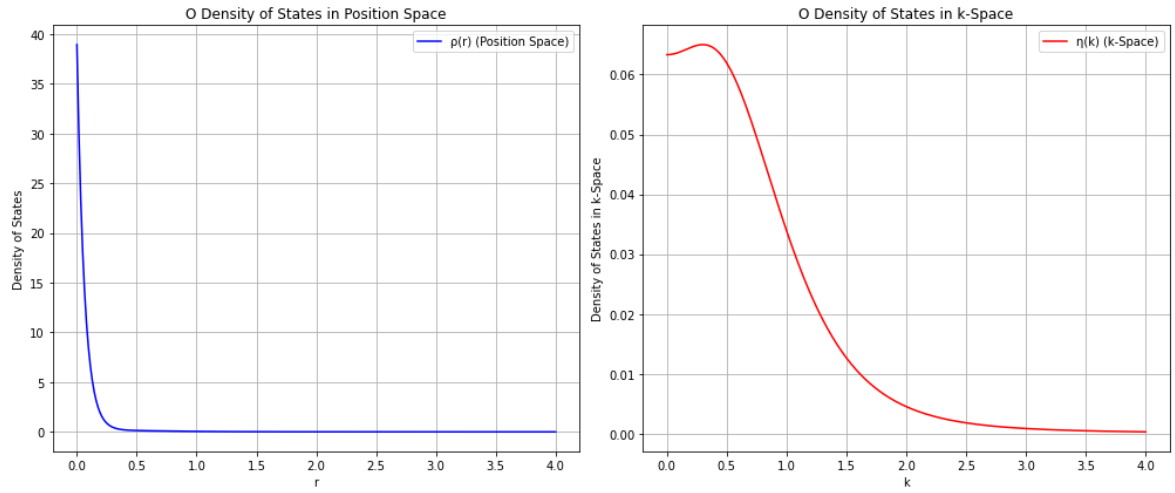


Figure 2.14: O DOS in position space (left) and in k-space (right)

### 2.1.8 Z=9 (F)

Numerical results for Fluorine with orbital configuration $1s^2 2s^2 2p^5$ are presented in the following table.

| F | |
|---|---|
| Quantity | Value |
| I_R1s | 1.000000289 |
| I_R2s | 1.000000281 |
| I_R2p | 0.999999134 |
| Ip | 0.999999646 |
| Sr | 2.298826999 |
| I_K1s | 1.000000289 |
| I_K2s | 1.000000281 |
| I_K2p | 0.999999134 |
| In | 0.999999646 |
| Sk | 6.16332515 |
| S | 8.462152149 |

Figure 2.15: Results for F

Shannon entropy results:

$$S_r = 2.2988269994389445 \tag{2.42}$$

$$S_k = 6.16332514982518 \tag{2.43}$$

$$S = 8.462152149264124 \tag{2.44}$$

Normalization conditions are met, as:

$$I_{R_{1s}} \simeq 1 \quad , I_{R_{2s}} \simeq 1 \quad , I_{R_{2p}} \simeq 1 \quad \text{and} \quad I_{K_{1s}} \simeq 1, \quad I_{K_{2s}} \simeq 1, \quad I_{K_{2p}} \simeq 1 \tag{2.45}$$

$$I_\rho \simeq 1 \quad \text{and} \quad I_\eta \simeq 1 \tag{2.46}$$

DOS graphs in position space and momentum space:

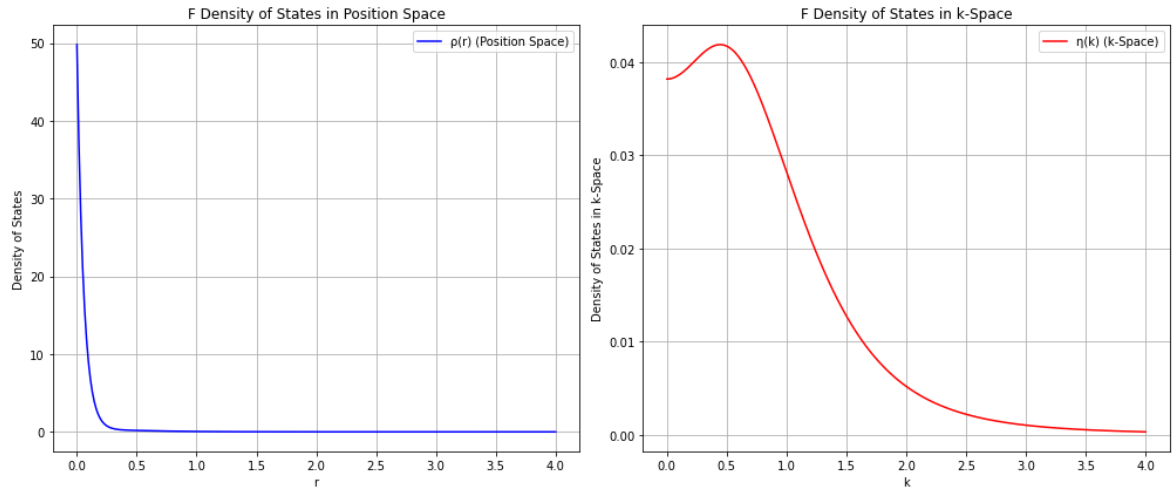


Figure 2.16: F DOS in position space (left) and in k-space (right)

### 2.1.9 Z=10 (Ne)

Numerical results for Neon with orbital configuration $1s^2 2s^2 2p^6$ are presented in the following table.

| Ne | |
|---|---|
| **Quantity** | **Value** |
| I_R1s | 1.000001634 |
| I_R2s | 0.999999813 |
| I_R2p | 1.000000692 |
| Ip | 1.000000704 |
| Sr | 2.055137743 |
| I_K1s | 1.000001634 |
| I_K2s | 0.999999813 |
| I_K2p | 1.000000692 |
| In | 1.000000704 |
| Sk | 6.437068485 |
| S | 8.492206228 |

Figure 2.17: Results for Ne

Shannon entropy results:

$$S_r = 2.055137743241695 \tag{2.47}$$

$$S_k = 6.437068484732485 \tag{2.48}$$

$$S = 8.49220622797418 \tag{2.49}$$

Normalization conditions are met, as:

$$I_{R_{1s}} \simeq 1 \quad , I_{R_{2s}} \simeq 1 \quad , I_{R_{2p}} \simeq 1 \quad \text{and} \quad I_{K_{1s}} \simeq 1, \quad I_{K_{2s}} \simeq 1, \quad I_{K_{2p}} \simeq 1 \tag{2.50}$$

$$I_{\rho} \simeq 1 \quad \text{and} \quad I_{\eta} \simeq 1 \tag{2.51}$$

DOS graphs in position space and momentum space:

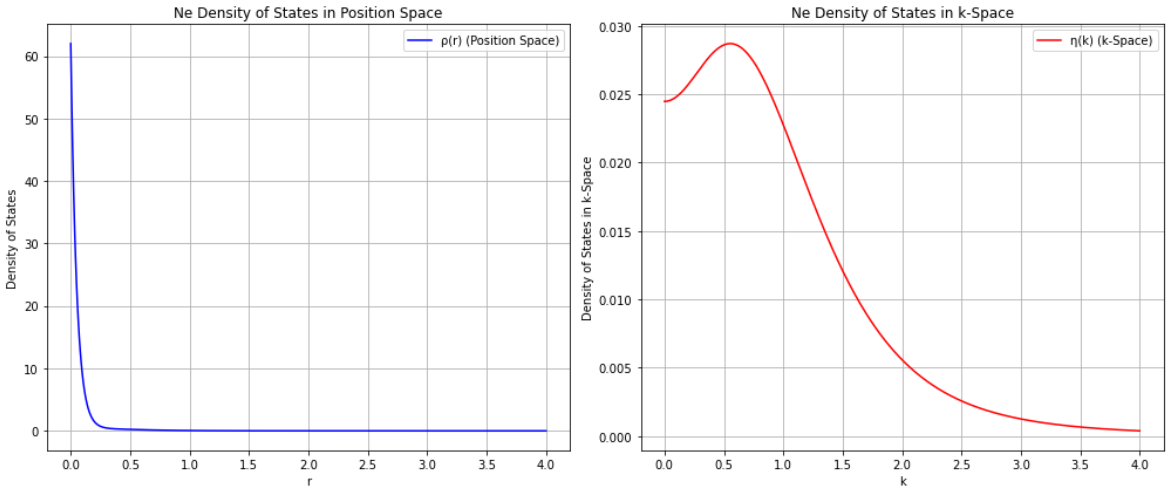


Figure 2.18: Ne DOS in position space (left) and in k-space (right)

## 2.2 Shannon Entropy

The numerical results for Shannon entropy in position space, k-space and in total for each atom (from Z=2 through Z=10) computed in the previous section are showcased in the table below. It is reminded that these are calculated numerically by our Python code using equations 1.13 and 1.14 for entropy in position space and momentum space respectively, while S is given by the sum of the two (1.15)

A graph containing the plots for information entropy in position space ($S_r$), in momentum space ($S_k$) and total information entropy ($S$) is also presented.

| Shannon Entropy | | | |
|---|---|---|---|
| Z | S_r | S_k | S |
| 2 | 2.698511 | 3.913419 | 6.61193 |
| 3 | 3.701437 | 3.996819 | 7.698256 |
| 4 | 3.623859 | 4.190188 | 7.814047 |
| 5 | 3.405445 | 4.705902 | 8.111347 |
| 6 | 3.106025 | 5.156576 | 8.262601 |
| 7 | 2.801688 | 5.549337 | 8.351025 |
| 8 | 2.550539 | 5.867354 | 8.417892 |
| 9 | 2.298827 | 6.163325 | 8.462152 |
| 10 | 2.055138 | 6.437068 | 8.492206 |

Figure 2.19: Shannon entropy values in position space ($S_r$), k-space ($S_k$) and total Shannon entropy ($S$) for elements with atomic numbers $2 \leq Z \leq 10$.

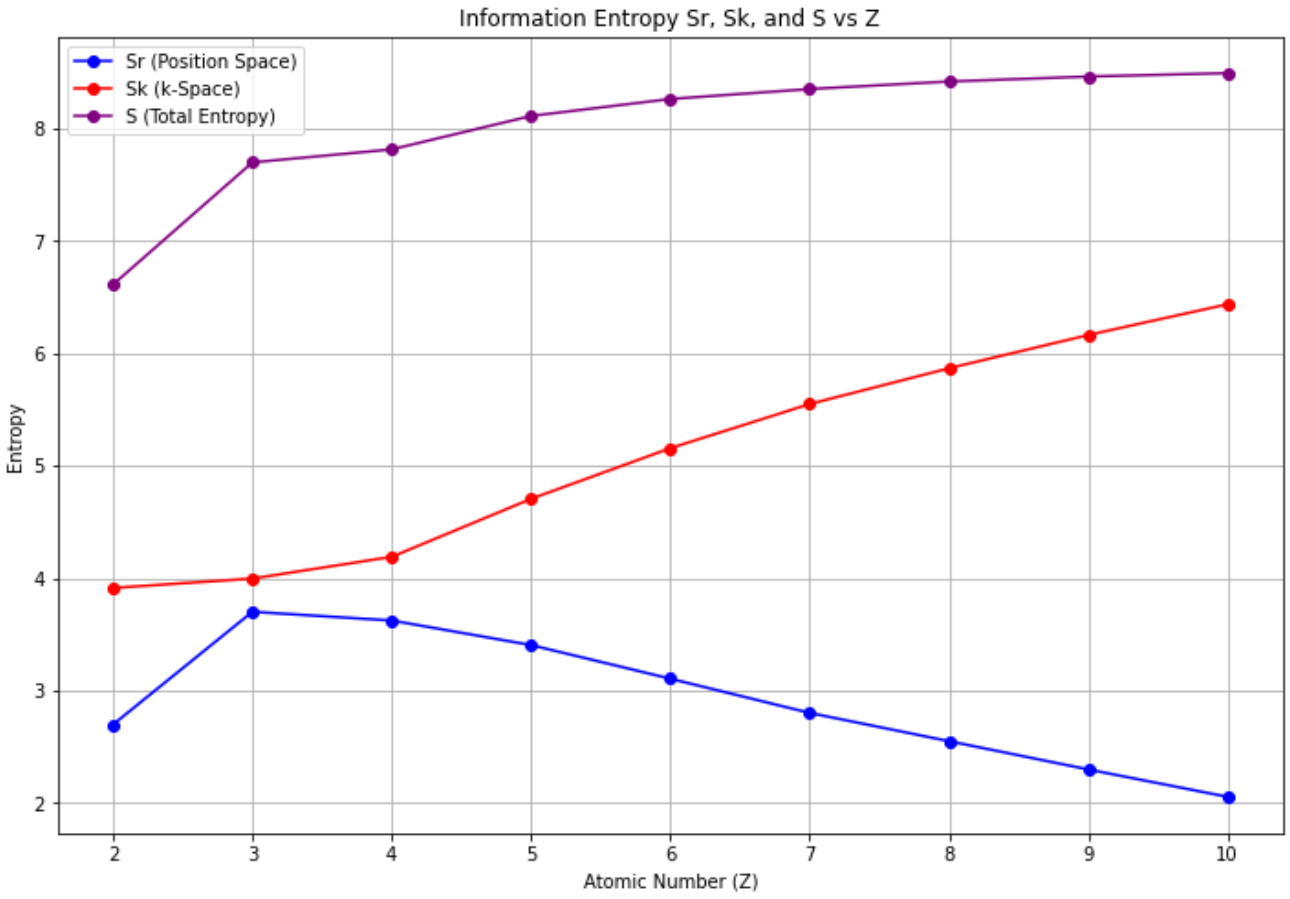


Figure 2.20: Graph of Shannon entropy in position space (blue), k-space (red) and total Shannon entropy (purple) against atomic number Z for $2 \leq Z \leq 10$.

It is evident by table 2.19, and visualized in the Shannon entropy graph (2.20) that:

- $S_r$ decreases with the increase of Z (with an exception of increase when going from Z=2 to Z=3).
- $S_k$ increases with the increase of Z.
- Total Shannon entropy $S$ increases with the increase of Z.

# Chapter 3

# Conclusions

- The validation of the method and code used in this study is strongly supported by the **consistent satisfaction of the normalization conditions** set by equations 1.6 and 1.11 for every element studied. This consistency indicates that the computed DOS, Shannon entropy, and other quantities are correct as well.

- Further validity confirmation is offered by comparing the values of table 2.19 for the Shannon entropy in position space ($S_r$), momentum space ($S_k$) and the total Shannon entropy ($S$) to the ones of the reference paper given to us, "Information entropy, information distances, and complexity in atoms". Our **results are almost a perfect match, with relative error less than 0.0005% for all quantities**.

- Studying the plots of DOS in position space ($\rho(r)$) and k-space ($\eta(k)$) offers interesting isnights. **DOS $\boldsymbol{\rho(r)}$ decreases as r increases and tends to 0 at an increasing rate (for smaller and smaller values of r) as atomic number Z increases**. In k-space, **$\boldsymbol{\eta(k)}$ also decreases with the increase of k, but as Z values get larger the rate at which it tends to 0 decreases (happens at larger and larger values of k)**.

- Similar behavior is observed in the Shannon entropy plots (2.20). Shannon entropy in position space **$\boldsymbol{S_r}$ decreases with Z increasing** (with the exception of increase when going from Z=2 to Z=3), while Shannon entropy in k-space **$\boldsymbol{S_k}$ increases with the increase of Z**. The **total Shannon entropy $\boldsymbol{S}$ increases as the atomic number increases**. This is because the increase of $S_k$ is more significant than the decrease of $S_r$.

The last two points lead to the following conclusion: The **increase of Z leads to decrease of information loss in position space and increase of information loss in momentum space**. Such a result is expected taking into consideration Heisenberg's uncertainty principle (the more precisely the position is known the more uncertain the momentum is and vice versa) However, **in total, information loss (uncertainty of the system) increases the increase of Z**, as the rates of information loss decrease and increase are not proportional.